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Effective synthesis of propylene carbonate from propylene glycol and carbon dioxide by alkali carbonates

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Alkali carbonates were first used as effective catalysts for the synthesis of propylene carbonate from propylene glycol and carbon dioxide in the presence of acetonitrile. Acetonitrile in the reaction acted as not only the solvent but also the dehydrating reagent to remove the water produced from the reaction. Interestingly, upon ammonium carbonate being introduced into the reaction system, the catalytic selectivity was significantly enhanced.

KEY WORDS: propylene carbonate; alkali carbonates; propylene glycol; carbon dioxide; ammonium carbonate.

1. Introduction

Five-membered cyclic carbonates are commercially important compounds. They are used as electrolytes in lithium batteries, as aprotic polar solvents, and as intermediates for producing polycarbonate and fine chemicals [1–3]. In addition to their biodegradability and high solvency, they have high boiling and flash points, low odor levels and evaporation rate and low toxicities. 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. Especially, the synthesis of DMC from methanol and PC is widely used in the industrial synthetic process and regarded as a process utilizing carbon dioxide as a raw material due to that PC could be effectively synthesized via the cycloaddition of propylene oxide (PO) and carbon dioxide [4–8]. In addition, there are some other methods for the synthesis of DMC via carbon dioxide, which include direct synthesis from carbon dioxide and methanol [9–13] and alcoholysis of urea with methanol [14–16]. It is a perfect route to directly synthesize DMC from carbon dioxide and methanol, but the process has not been yet applied for industrial exploitation due to the quite low productivity. Although alcoholysis of urea is an available approach for the industrial process, the productivity of DMC is likewise far from that of transesterification method. Hence, the transesterification of PC with methanol is still a primary process for producing DMC in industry (see equation (1)) [17–21]. But, propylene glycol (PG) as by-product is inevitably produced in the transesterification process. If PC can be directly synthesized from PG and CO_2 (see equation (2)), the process will become more valuable and promising. In this case, not only PG is recycled but also CO_2 utilized effectively. As a result, DMC can be synthesized from methanol and CO_2 by using PC as a recyclable intermediate.

As a novel route, propylene carbonate was first synthesized from propylene glycol and carbon dioxide via CeO_2-ZrO_2 in the presence of CH_3CN [22,23]. Although the selectivity of propylene carbonate was 100%, the conversion of propylene glycol was very low, which was only about 2%. Recently, dibutyltin oxide or dibutyltin dimethoxide [24] has been used to catalyze the synthesis of propylene carbonate from propylene glycol and carbon dioxide in supercritical conditions using *N*,*N*-dimethylformamide (DMF) as the solvent, but the yield of propylene carbonate was quite low in the same way. Such a low productivity would be attributed to the thermodynamic limitations and hence the removal of H_2O from the reaction system would improve the yield of propylene carbonate [24].

In the present work, alkali carbonates were first used to catalyze the formation of propylene carbonate from propylene glycol and carbon dioxide with relative high yield in the presence of CH_3CN. Differently from the previous reports [22,23], CH_3CN in the reaction acted as not only the solvent but also the dehydrating reagent to remove the water produced from the reaction. At the same time, ammonium carbonate was used as the coupling agent to enhance the selectivity of propylene carbonate.

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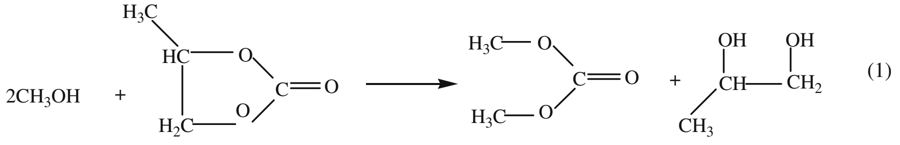
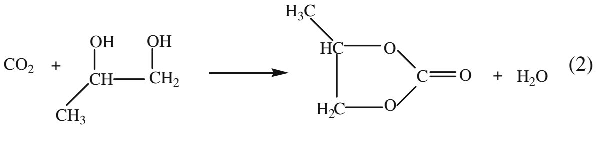


Scheme 1.



Scheme 2.

2. Experimental

2.1. Reagents

Cs_2CO_3, K_2CO_3, Na_2CO_3, $(NH_4)_2CO_3$ were produced by Beijing Chemical Reagent Factory. Propylene glycol and acetiamide 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 provided from Beijing Analytical Instrument Factory.

2.2. Reaction apparatus and operation

The reaction was carried out in a 50 ml stainless-steel autoclave reactor equipped with a magnetic stirrer, in which alkali carbonates (5 mmol) and ammonium carbonate (0.6 g) were added to a solution of propylene glycol (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 magnetically stirred constantly during the reaction. After the reaction, the autoclave was rapidly cooled to ambient temperature in a water bath and the excess of carbon dioxide was vented slowly. 2-propanol was added to the liquid phase as a standard for the quantitative analysis. The products in liquid phase were analyzed by a gas chromatograph (GC-920) equipped with a flame ionization detector and a capillary column (TC-WAX). And the qualitative analysis was further determined by GC–MS (HP G1800A) with a capillary column (HP-5MS).

3. Results and discussion

3.1. Catalytic performance of alkali carbonates in the presence of CH_3CN

The propylene carbonate synthesis from propylene glycol and carbon dioxide was carried out by the alkali carbonates under various reaction conditions (See table 1). Clearly, Without the catalyst, the carboxylation of propylene glycol did not take place whether CH_3CN was present or not (Entries 1 and 2 in table 1). However,

Table 1

Reaction of PG and CO_2 over alkali carbonates under various reaction conditions[a]

Entry	Cat.	Cat. (mmol)	$(NH_4)_2CO_3$ (g)	CH_3CN (ml)	Yield of PC[b] (%)	Selectivity of PC(%)
1	–	–	0	0	0	–
2	–	–	0	10	0	–
3	Cs_2CO_3	5	0	10	15.6	62.5
4	K_2CO_3	5	0	10	12.4	58.5
5	Na_2CO_3	5	0	10	5.8	56.8
6	Cs_2CO_3	5	0.6	10	10.5	100
7	K_2CO_3	5	0.6	10	8.2	100
8	Na_2CO_3	5	0.6	10	3.5	100
9	Cs_2CO_3	2.5	0.6	10	6.5	100
10	Cs_2CO_3	7.5	0.6	10	10.8	100
11	Cs_2CO_3	5	0.4	10	12.6	90.6
12	Cs_2CO_3	5	0.8	10	8	100
13	Cs_2CO_3	5	0.6	0	0	–
14	Cs_2CO_3	5	0.6	5	7.8	100
15	Cs_2CO_3	5	0.6	15	9.5	100

[a] Reaction conditions: PG (100 mmol), CO_2 pressure (10 MPa), 175 °C, 15 h.

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

the considerable amount of propylene carbonate was obtained in the presence of alkali carbonates (Entries 3, 4 and 5 in table 1) and the yield of catalytic production for alkali carbonates was much higher than that of the reported catalysts [22–24]. Considering that CH_3CN was easy to be hydrolyzed in presence of strong base, it was introduced to remove the water produced from the reaction and improve the propylene carbonate synthesis. In addition, to enhance the selectivity of propylene carbonate, ammonium carbonate as the coupling agent was added into the reaction system (Entries 6, 7 and 8 in table 1).

The yield of propylene carbonate appeared to be dependent on the basicity (Entries 6, 7 and 8 in table 1), and the strong basicity was favorable for the reaction due to that the strong basicity could promote the hydrolysis of CH_3CN at the same time. Furthermore, with the amount of alkali carbonates increased, the yield of propylene carbonate was gradually enhanced and reached a certain value at last (Entries 6, 9 and 10 in table 1). Thus, the introduction of CH_3CN appeared very important for the propylene carbonate synthesis from carbon dioxide and propylene glycol via alkali carbonates. In absence of CH_3CN, propylene carbonate was hardly detected (Entry 13 in table 1). In fact, many other reagents were also used as the solvent in our experimental, but they were found not available. The water produced from the reaction could be consumed via the hydrolysis of CH_3CN, and then the production of propylene carbonate could be improved. As a result, CH_3CN acted as not only the solvent but also the dehydrating agent to eliminate the water produced from the reaction. Moreover, CO_2 could be dissolved in CH_3CN, which led to an optimal amount of CH_3CN for the reaction (Entries 13, 14 and 15 in table 1).

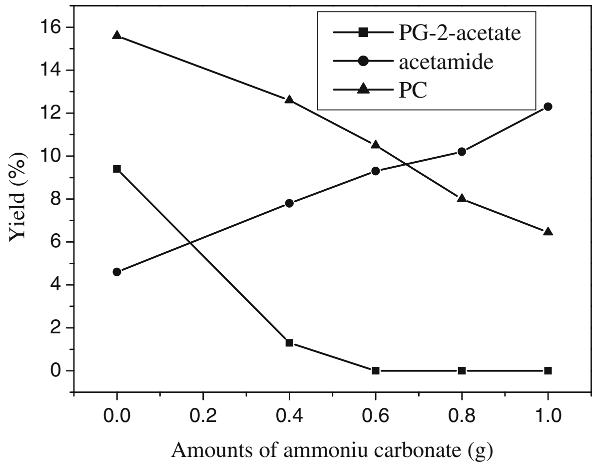


Figure 1. Effect of the amount of ammonium carbonate on the yield of products. Reaction conditions: PG (100 mmol), CH_3CN (10 mL), CO_2 pressure (10 MPa), CS_2CO_3 (5 mmol), 175 °C, 15 h.

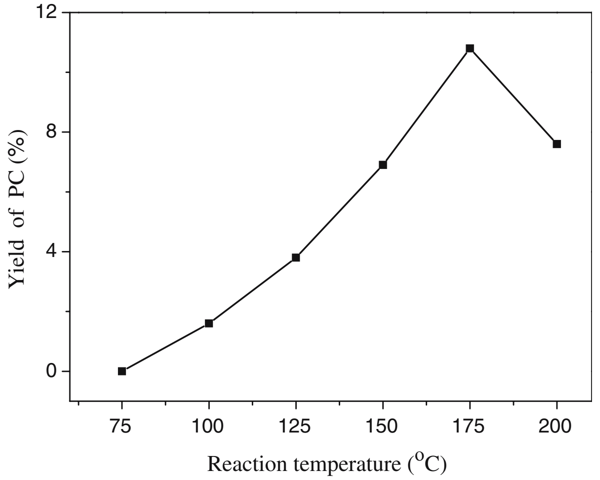
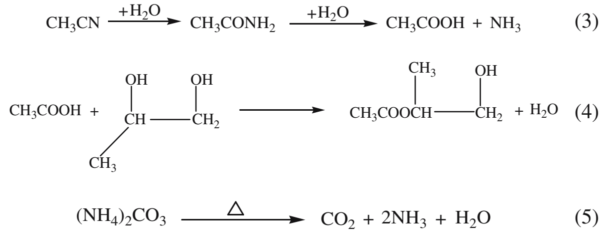


Figure 2. Effect of reaction temperature on the yield of PC. Reaction conditions: PG (100 mmol), CH_3CN (10 ml), CO_2 pressure (10 MPa), CS_2CO_3 (5 mmol), $(NH_4)_2CO_3$ (0.6 g), 15 h.

3.2. *Improvement of the selectivity by ammonium carbonate*

Obviously, the selectivity of propylene carbonate was not very high, although CH_3CN evidently increased the yield of propylene carbonate. The hydrolysis of CH_3CN could generate acetamide and then acetamide reacted with water to form acetic acid and ammonia (see equation (3)). Under the reaction conditions, the produced acetic acid could react with other reagents, such as propylene glycol, to produce propylene glycol-2-acetate (PG-2-acetate) (see equation (4)). In order to enhance the selectivity of propylene carbonate, ammonium carbonate as the coupling agent was added into the reaction system. It was well known that ammonium carbonate was very easy to be decomposed to produce two molecules of NH_3, a molecule of H_2O and a molecule of CO_2 (see equation (5)). As a result, so-produced NH_3 could inhibit the acetamide from the hydrolysis and improved the selectivity of propylene carbonate. As shown in table 1, when ammonium carbonate was added into the reaction system, the selectivity of propylene carbonate was greatly improved (Entry 11 in table 1). With the amount of ammonium carbonate increased, the selectivity of propylene carbonate could reach 100%, although the yield of propylene carbonate was found to decline to a certain extent (Entries 6, 7 and 8 in table 1). However, more ammonium carbonate was disadvantageous to the reaction, which resulted to an obvious drop of the yield of propylene carbonate (Entry 12 in table 1). The detailed variation of propylene carbonate, propylene glycol-2-acetate and acetamide with the amount of ammonium carbonate is shown in figure 1. With the amount of ammonium carbonate increased, the yield of the by-product of propylene glycol-2-acetate decreased or even reached zero, indicating that the reactions took place as equations (3) $\sim$ (5).



Scheme 3.

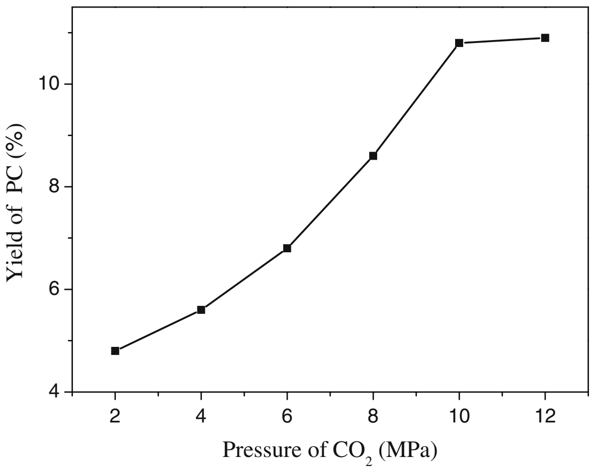


Figure 3. Effect of pressure of CO_2 on the yield of PC. Reaction conditions: PG (100 mmol), CH_3CN (10 ml), CS_2CO_3 (5 mmol), $(NH_4)_2CO_3$ (0.6 g), 175 °C, 15 h.

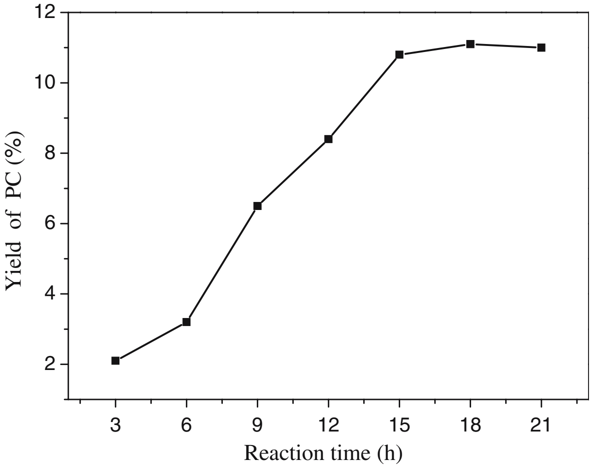


Figure 4. Effect of reaction time on the yield of PC. Reaction conditions: PG (100 mmol), CH_3CN (10 ml), CO_2 pressure (10 MPa), CS_2CO_3 (5 mmol), $(NH_4)_2CO_3$ (0.6 g), 175 °C.

3.3. Effect of reaction conditions

Cs_2CO_3 was chosen as a typical catalyst to investigate the effect of reaction conditions on the yield of propylene carbonate. As shown in figure 2, the yield of propylene carbonate increased with the rise of reaction temperature in the range of 100–175 °C, but the further increase of the temperature caused a sharp decrease in the yield of propylene carbonate, possibly due to the formation of side-products, such as dipropylene glycol, which was produced via the dehydration of propylene glycol [22,23], and the products of propylene carbonate decomposition and polymerization [24]. In fact, some other by-products were detected when the reaction temperature exceeded 200 °C. Considering that propylene carbonate was not detected by GC with the reaction temperature below 75 °C, the suitable reaction temperature should be controlled at about 175 °C.

Figure 3 shows the effect of CO_2 pressure on the propylene carbonate synthesis. The yield of propylene carbonate was nearly proportional to the reaction pressure in the range of 2–10 MPa. As mentioned above, CO_2 could be dissolved in CH_3CN, and the solubility of CO_2 in CH_3CN increased with the pressure of CO_2. As a result, the high concentrations of CO_2 would shift the equilibrium and improved the conversion of propylene glycol. However, the yield of propylene carbonate did not further increase when the CO_2 pressure surpassed 10 MPa. Therefore, the pressure of CO_2 was optimal as 10 MPa.

The effect of reaction time on the yield of PC illustrated that the yield of PC increased with the reaction time (See figure 4). The reaction proceeded rapidly within first 15 h, and then the yield of propylene carbonate increased slightly, indicating that the reaction reached the thermodynamic balance. Furthermore, more by-products could be formed in this case [24]. Thus, 15 h was the optimal reaction time for the reaction of CO_2 with propylene glycol.

4. Conclusion

Propylene carbonate was effectively synthesized via the reaction of propylene glycol with CO_2 catalyzed by alkali carbonate in the presence of CH_3CN. CH_3CN acted as not only the solvent but also the dehydrating reagent to eliminate water produced from the reaction, thus improving the yield of propylene carbonate. Ammonium carbonate was added into the reaction as the coupling agent to significantly elevate the selectivity of propylene carbonate. In this case, the yield of propylene carbonate was found to closely related with the basicity. Under the optimal conditions, the yield of propylene carbonate could reach 10.5% with 100% of the selectivity.

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