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Article

Low pressure one-pot synthesis of dimethyl carbonate catalyzed by an alkali carbonate

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ABSTRACT

A mild and efficient protocol for the alkali carbonate-catalyzed one-pot synthesis of dimethyl carbonate (DMC) from epoxide, CO₂ and methanol was developed. The reaction conditions for the one-pot synthesis of DMC were investigated. Under the optimized conditions of initial pressure 0.5 MPa, 120 °C and catalyst loading of 7.5 mol%, 63.5% yield of DMC was achieved using ethylene oxide as the starting material. A mechanism for the catalysis by the alkali carbonate was proposed.

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1. Introduction

Global warming is of great concern as it can lead to alterations to the climate. For example, the rainfall distribution can change and the frequency of severe weather events, such as hurricanes and typhoons, can increase [1]. It is now well established that the release of CO₂ from anthropogenic activities such as fossil fuel burning is among the leading causes of global warming [2,3]. Therefore, considerable efforts have been directed towards the development of technologies for CO₂ activation and use [4,5], CO₂ capture [6,7], and the conversion of CO₂ to useful substances [8–12]. One of the most promising utilization of CO₂ is the synthesis of dimethyl carbonate (DMC). DMC is an environmentally benign substitute for toxic dimethyl sulfate, methyl iodide, and phosgene. DMC can also be used for the synthesis of polycarbonate resins, as a green solvent, as a capture agent for CO₂, and as a gasoline additive to increase octane number [13,14].

DMC was produced from methanol and phosgene for the first time in the 1910s, but this process was eliminated in recent years due to the use of the virulent phosgene [15]. There are now three other routes for the production of DMC. The first is the oxidative carbonylation of methanol using CuCl as catalyst. Its main drawback is the production of corrosive hydrogen chloride [16]. The second is the carbonylation of methyl nitrite over Pd/carbon. Here, the use of toxic CO is the main problem [17]. The third is the transesterification method in which a cyclic carbonate is formed first from an epoxide and CO₂, and subsequently a transesterification follows to produce DMC [18]. In recent years, other novel processes have been developed for the synthesis of DMC, such as the direct synthesis of DMC from CO₂ and methanol [19], the “one-pot, two-step” method [20], and the one-pot synthesis [21]. Among these, the one-pot synthesis of DMC from CO₂, epoxide and methanol (Scheme 1) is a simple and economic approach for the synthesis of DMC. However, a side reaction occurs due to the addition

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Scheme 1. One-pot synthesis of DMC (1) and its side reaction (2).

of methanol [21].

There are several reports on the one-pot synthesis of DMC using different catalysts [21–36]. Among these, alkali carbonates have attracted attention due to its cheapness, negligible eco-toxicity and basic properties. In 2001, Bhanage et al. [36] reported that 8.7% yield of DMC was obtained in 15 h from propylene oxide (PO) using 24.8 mol% K_2CO_3 as catalyst at 150 °C under 8 MPa CO_2 . In 2003, Cui et al. [35] achieved 51.5% yield of DMC in 3 h from ethylene oxide (EO) using 15.9 mol% K_2CO_3 as catalyst at 120 °C under 15 MPa CO_2 . Very recently, Yang et al. [23] obtained 38.7% yield of DMC after 6 h from cyclohexane oxide (CHO) using 0.8 mol% K_2CO_3 as catalyst at 150 °C under 2.6 MPa CO_2 (initial pressure at room temperature). It is clear from these results that a high reaction pressure is needed in the one-pot synthesis of DMC catalyzed by an alkali carbonate, and the highest yield of DMC was 50%. The one-pot synthesis of DMC under an initial pressure less than 2.0 MPa has not been reported. In this paper, we describe an efficient protocol for the direct synthesis of DMC under a low pressure from CO_2 , epoxide and methanol catalyzed by alkali carbonate.

2. Experimental

2.1. Materials

Propylene oxide, cyclohexene oxide, styrene oxide, epichlorohydrin and glycidyl phenyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene oxide was a gift from Liaoning Oxiranchem Co., Ltd. CO_2 was purchased from Dalian Guangming Special Gas Co., Ltd. The other chemicals were obtained commercially and used without any prior purification.

2.2. General procedure for the one-pot synthesis of DMC

The one-pot synthesis of DMC was carried out in a stainless steel autoclave reactor with a volume of 75 ml. A typical procedure was as follows: epoxide (14.3 mmol), methanol (214.5 mmol, 8.7 mL), Na_2CO_3 (5.0 mol%) and biphenyl (80 mg, an internal standard for GC analysis) were charged in the autoclave at room temperature. Then CO_2 was introduced into the reactor, which was heated to 120 °C for 6 h. After cooling, the reaction mixture was analyzed by gas chromatograph.

2.3. Techniques used

GC analysis was recorded on a gas chromatograph (Agilent 7820) equipped with a capillary column (HP-5, 30 m × 320 μm × 0.25 μm) using a flame ionization detector with a flow rate of 1

mL/min. The following parameters were used: oven temperature was held at 50 °C for 5 min and then increased linearly to 240 °C over 20 min with a final hold of 5 min.

3. Results and discussion

Due to the similar properties of 1-methoxy-2-propanol (1-ME-2-PA) and 2-methoxy-1-propanol (2-ME-1-PA), PM is used in this paper to represent both 1-ME-2-PA and 2-ME-1-PA. Propylene carbonate is abbreviated as PC, and 1,2-propanediol is abbreviated as PG.

3.1. The effect of the catalyst on the one-pot synthesis of DMC

The reaction of propylene oxide (PO), methanol and CO_2 was chosen as a model reaction to screen the catalysts under the conditions of 0.5 MPa, 120 °C, 6 h. The results are summarized in Table 1. No DMC was detected and a high yield of PM byproduct was obtained in the absence of a catalyst (Table 1, entry 1). More than 69.0% conversion of PO was obtained in the presence of different catalysts, and the yield of DMC varied from 2.0% to 44.5%. This showed that the catalyst was crucial to both the cyclo-addition of PO and the transesterification of PC. An organic base (*i*-Pr) $_2\text{NH}$ was relatively ineffective in the catalytic system for the synthesis of DMC (Table 1, entry 2). A high yield of PC and a low yield of PM were obtained in the

Table 1
Catalyst screening for the one-pot synthesis of DMC.

$ \begin{array}{c} \text{PO} + \text{CO}_2 + \text{CH}_3\text{OH} \longrightarrow \text{H}_3\text{CO}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{OCH}_3 + \text{PC} + \text{PG} \\ \\ \text{PO} + \text{CH}_3\text{OH} \longrightarrow \text{H}_3\text{CO}-\text{CH}(\text{R})-\text{CH}_2\text{OH} + \text{HO}-\text{CH}(\text{R})-\text{CH}_2\text{OCH}_3 \\ \text{PO} \qquad \qquad \qquad \text{2-ME-1-PA} \qquad \qquad \text{1-ME-2-PA} \end{array} $						
Entry	Catalyst	Conversion of PO ^a (%)	Yield ^b (%)			
			DMC	PC	PG	PM
1	None	54.3	0	0.7	0	53.6
2	(<i>i</i> -Pr) $_2\text{NH}$	69.1	2.0	16.9	3.2	50.2
3	KI	87.5	3.1	82.7	3.7	1.7
4	TBAI	94.8	9.3	82.1	10.5	3.4
5	NaH	77.4	6.7	20.1	7.5	50.6
6	CH_3ONa	82.0	21.3	19.4	23.6	41.3
7	NaOH	88.4	29.8	16.6	28.2	42.0
8	Na_2CO_3	87.9	43.0	18.5	42.7	26.4
9	K_2CO_3	88.2	42.7	15.6	40.4	29.9

Reaction conditions: PO (1 mL, 14.3 mmol), CH_3OH (8.7 mL, 214.4 mmol), catalyst (5.0 mol%), initial pressure 0.5 MPa, 120 °C, 6 h.

^a Sum of the yields of DMC, PC and PM.

^b Average of two runs, determined by GC using an internal standard technique.

presence of KI or TBAI (Table 1, entries 3 and 4), which demonstrated that KI and TBAI efficiently catalyzed the cyclo-addition of PO with CO₂ and decreased the alcoholysis of PO. NaH, NaOH and CH₃ONa gave yields of DMC less than 30%, and a high yield of PM was obtained (Table 1, entries 5–7). Although NaOH and CH₃ONa are stronger alkalis than the other catalysts used, they were less effective for the formation of DMC compared to Na₂CO₃ and K₂CO₃ (Table 1, entries 6 and 7 versus 8 and 9). The reason for this may be that high alkalinity catalysts have a high activity for the alcoholysis of PO [37]. This indicated that a catalyst with suitable alkalinity was essential to the efficient synthesis of DMC. We chose Na₂CO₃ as the catalyst for further research.

3.2. The effect of pressure on the synthesis of DMC

The effect of pressure on the one-pot synthesis of DMC was tested using the same model reaction in the presence of 5.0 mol% Na₂CO₃ under the conditions of 120 °C and 6 h. The experimental results are shown in Fig. 1. Higher than 77.5% PO conversion was obtained with an initial pressure range of 0 to 3.5 MPa, and lower than 74.5% PO conversion were obtained with an initial pressure range of 4.0 to 5.5 MPa. The yields of DMC and PG reached 43.0% and 42.7%, respectively, with an initial pressure of 0.5 MPa and decreased with the increase of initial pressure from 0.5 to 3.5 MPa. Further increasing of the initial pressure resulted in a slight increase in the yield of DMC. In the whole initial pressure range from 0 to 5.5 MPa, the yield of PM reached a maximum in the absence of CO₂ and remained roughly constant with an initial pressure higher than 0.5 MPa. It is clear from Fig. 1 that the conversion of PO and the yields of DMC, PC and PG changed when the initial pressure was increased from 3.5 to 4.0 MPa, and the yield of DMC reached 25.0% with an initial pressure higher than 4.5 MPa. The reason for this may be that the reaction mixture is in the supercritical

state when the reaction pressure is higher than 7.8 MPa (initial pressure of 4.0 MPa) at 120 °C, which is in accordance with previous reports [31,33,35]. With further increasing of the loading of Na₂CO₃ to 7.5 mol%, a similar effect of the pressure on both the yields of products and the conversion of PO was observed (Fig. 2). The results in Fig. 1 and Fig. 2 demonstrated that the optimal initial pressure for the one-pot synthesis of DMC catalyzed by Na₂CO₃ was 0.5 MPa (reaction pressure, 1.0 MPa). A higher pressure is unfavorable for both the conversion of PO and yield of DMC.

3.3. The effect of temperature on the synthesis of DMC

The effect of reaction temperature on the one-pot synthesis of DMC was investigated using the same model reaction in the presence of 5.0 mol% Na₂CO₃ under the conditions of initial pressure 0.5 MPa and 6 h. The results are shown in Fig. 3. A slight effect of the reaction temperature on PO conversion was observed, and higher than 86.5% conversions were obtained at temperatures from 110 to 150 °C. The yields of DMC and PG increased to 43.0% and 42.7%, respectively, at 120 °C and remained roughly constant at higher temperatures. From the effects of temperature on both the yields of PC and PM, we chose 120 °C as the optimal reaction temperature.

3.4. The effect of reaction time on the synthesis of DMC

The effect of reaction time on the one-pot synthesis of DMC was tested using the same model reaction in the presence of 5.0 mol% Na₂CO₃ and the conditions of 120 °C and initial pressure 0.5 MPa. The reaction time in the range of 2 to 8 h was investigated. The results are shown in Fig. 4. The PO conversion was 67.3% after 2 h and reached 88.1% in 4 h and remained roughly constant with extended reaction time. The yields of DMC and PG increased with extended reaction time and re-

Fig. 1. Effect of pressure on the synthesis of DMC in the presence of 5.0 mol% Na₂CO₃. Reaction conditions: PO (1.0 mL, 14.3 mmol), CH₃OH (8.7 mL, 214.4 mmol), Na₂CO₃ (75.7 mg, 5.0 mol%), 120 °C, 6 h. Yields and conversions are the average of two runs determined by GC using an internal standard technique.

Fig. 2. Effect of pressure on the synthesis of DMC in the presence of 7.5 mol% Na₂CO₃. Reaction conditions: PO (1.0 mL, 14.3 mmol), CH₃OH (8.7 mL, 214.4 mmol), Na₂CO₃ (113.6 mg, 7.5 mol%), 120 °C, 6 h. Yields and conversions are the average of two runs determined by GC using an internal standard technique.

Fig. 3. Effect of temperature on the synthesis of DMC. Reaction conditions: PO (1 mL, 14.3 mmol), CH₃OH (8.7 mL, 214.4 mmol), Na₂CO₃ (75.7 mg, 5.0 mol%), initial pressure 0.5 MPa, 6 h. Yields and conversions are the average of two runs determined by GC using an internal standard technique.

mained roughly constant at 43.0% and 42.7%, respectively, after 6 h. The yield of PC decreased with extended reaction time and remained roughly constant at 15.4% after 4 h. A slight effect of reaction time on the PM yield was observed. A reaction time of 6 h was suitable for further studies.

3.5. The effect of Na₂CO₃ loading on the synthesis of DMC

The effect of Na₂CO₃ loading on the one-pot synthesis of DMC was tested using the same model reaction and the conditions of initial pressure 0.5 MPa, 120 °C and 6 h. The results are shown in Fig. 5. 54.3% PO conversion was obtained in the absence of Na₂CO₃ and higher than 80.0% conversions were ob-

Fig. 4. Effect of reaction time on the synthesis of DMC. Reaction conditions: PO (1 mL, 14.3 mmol), CH₃OH (8.7 mL, 214.4 mmol), Na₂CO₃ (75.7 mg, 5.0 mol%), initial pressure 0.5 MPa, 120 °C. Yields and conversions are the average of two runs determined by GC using an internal standard technique.

tained when the Na₂CO₃ loading was increased to 10.0 mol%, which indicated that Na₂CO₃ promoted the conversion of PO. In the range of Na₂CO₃ loading from 1.5 to 10.0 mol%, the yields of DMC and PG increased with the increase of Na₂CO₃ loading, but the yield of PC decreased. The yield of PM decreased with the increase of Na₂CO₃ loading and remained roughly constant when the Na₂CO₃ loading was above 5.0 mol%. A Na₂CO₃ loading of 7.5 mol% was selected for the one-pot synthesis of DMC.

3.6. The effect of methanol amount on the synthesis of DMC

The effect of methanol amount on the one-pot synthesis of DMC was tested using the same model reaction in the presence of 7.5 mol% Na₂CO₃ and the conditions of initial pressure 0.5 MPa, 120 °C, 6 h. The results are shown in Fig. 6. A slight effect of methanol amount on the PO conversions was observed within the methanol amount range of 10 to 20 molar equivalents. When the methanol amount was increased from 5 to 15 molar equivalents, the yield of DMC increased from 33.5% to 45.6%, and the yield of PC increased from 11.7% to 15.1%. On further increasing the methanol amount to 20 molar equivalents, the yield of DMC decreased to 38.4%. Therefore, the best amount of methanol was 15 molar equivalents in the present reaction.

3.7. Scope and limitation of the substrates

Using the optimized conditions, we further studied the generality of the one-pot synthesis of DMC using different epoxides. The reactions of ethylene oxide (**A**), styrene oxide (**B**), epichlorohydrin (**C**), glycidyl phenyl ether (**D**) and cyclohexene oxide (**E**) were investigated under the conditions of 120 °C, 6 h, 0.5 MPa. The results are summarized in Table 2. **A** and **B** exhibited efficient reactivity giving 63.5% and 59.0% yields of DMC, respectively (Table 2, entries 1 and 2). PO provided 45.6% yield of DMC (Table 2, entry 3). **C**, **D** and **E** gave 31%–36% yields of

Fig. 5. Effect of Na₂CO₃ loading on the synthesis of DMC. Reaction conditions: PO (1 mL, 14.3 mmol), CH₃OH (8.7 mL, 214.4 mmol), initial pressure 0.5 MPa, 120 °C, 6 h. Yields and conversions are the average of two runs determined by GC using an internal standard technique.

Fig. 6. Effect of methanol amount on the synthesis of DMC. Reaction conditions: PO (1 mL, 14.3 mmol), Na_2CO_3 (7.5 mol%), 0.5 MPa, 120 °C, 6 h. Yields and conversions are the average of two runs determined by GC using an internal standard technique.

DMC. Hence, the order of reactivity for DMC formation under the same reaction conditions was $\text{A} > \text{B} > \text{PO} > \text{C} > \text{D} > \text{E}$.

3.8. Possible mechanism

Based on previous reports [28,38,39] and the results presented above, a mechanism portraying the probable sequence of events is shown in Scheme 2. The CO_3^{2-} group of the alkali carbonate attacks the carbon atom of the epoxide resulting in the ring opening of the epoxide (Step 1). Then, an interaction occurs between the oxygen anion and CO_2 , and an alkylcarbonate anion is formed (Step 2). Next, the alkylcarbonate anion is transformed into a cyclic carbonate (Step 3). Then methanol is activated by the carbonate anion to generate a hydrogen bond complex ($\text{CH}_3\text{OH} \cdots \text{CO}_3^{2-}$) (Step 4), which reacts with the cyclic carbonate to form an intermediate (Step 5), and DMC is

Scheme 2. Proposed mechanism for the one-pot synthesis of DMC.

subsequently produced (Step 6).

4. Conclusions

Alkali carbonate-catalyzed one-pot synthesis of DMC and 1,2-diols from epoxide, methanol, and CO_2 was investigated. Under the optimized conditions of 120 °C and initial pressure of 0.5 MPa, Na_2CO_3 exhibited good catalytic activity and provided the highest DMC yield of 63.5% in 6 h with ethylene oxide. The results demonstrated that a low pressure is favorable for the one-pot synthesis of DMC.

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Table 2

Scope and limitation of the substrate

Entry	Epoxide	Yield of DMC ^a (%)
1	(A)	63.5
2	(B)	59.0
3	(C)	45.6
4	(D)	35.5
5	(E)	33.5
6	(F)	31.2

Reaction conditions: Epoxide (14.3 mmol), CH_3OH (8.7 mL, 214.4 mmol), Na_2CO_3 (7.5 mol%), initial pressure 0.5 MPa, 120 °C, 6 h.

^a Average of two runs determined by GC using an internal standard technique.

Graphical Abstract

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Low pressure one-pot synthesis of dimethyl carbonate catalyzed by an alkali carbonate

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This work developed a protocol of alkali carbonate-catalyzed one-pot synthesis of dimethyl carbonate (DMC) from epoxide, CO_2 , and methanol. 63.5% yield of DMC was achieved with an initial CO_2 pressure of 0.5 MPa and ethylene oxide as reactant.

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低压下碱金属碳酸盐催化一步法合成碳酸二甲酯

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摘要: 报道了低压下碱金属碳酸盐催化环氧化物、 CO_2 和甲醇一步合成碳酸二甲酯(DMC)的方法, 系统考察了反应条件对一步合成DMC的影响规律。在最优反应条件下(初始压力0.5 MPa, 反应温度120 $^{\circ}\text{C}$, 碳酸钠7.5 mol%), 以环氧乙烷为起始剂的DMC收率达到63.5%。提出了碱金属碳酸盐催化一步法合成DMC的可能反应机理。

关键词: 碳酸二甲酯; 环氧化物; 碱金属碳酸盐; 一步法; 低压

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