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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, CO_2 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.

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 CO_2 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 CO_2 activation and use [4,5], CO_2 capture [6,7], and the conversion of CO_2 to useful substances [8–12]. One of the most promising utilization of CO_2 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 CO_2, 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 CO_2, 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 CO_2 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 CO_2, 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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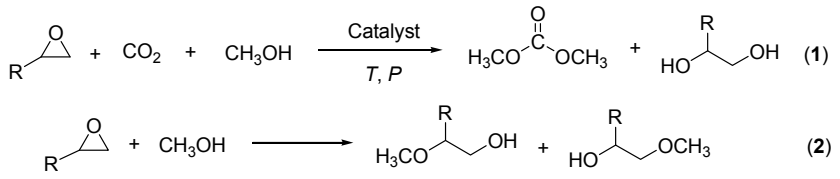


Scheme 1. One-pot synthesis of DMC (**1**) and its side reaction (**2**).

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.

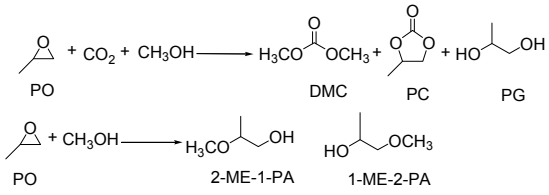
3. Results and discussion

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 $(i\text{-Pr})_2NH$ 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.



Entry	Catalyst	Conversion of PO [a] (%)	Yield [b] (%)			
			DMC	PC	PG	PM
1	None	54.3	0	0.7	0	53.6
2	$(i\text{-Pr})_2NH$	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.