



One-step synthesis of dimethyl carbonate from carbon dioxide, propylene oxide and methanol over alkali halides promoted by crown ethers



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ABSTRACT

Crown ethers (i.e. [2,4]-dibenzo-18-crown-6 (DBC), 18-crown-6, 15-crown-5 and 12-crown-4) show obvious co-catalytic effect for alkali halides catalyzing one-step synthesis of dimethyl carbonate (DMC) from CO₂, propylene oxide and methanol. Especially, the DMC yield of KCl catalyst promoted by DBC can increase by more than five times and reach about 40% under mild reaction conditions (i.e., low mole ratio of methanol and epoxides: 7:3, low initial pressure of CO₂: 1.5 MPa, reaction temperature: 140 °C, time: 10 h). The optimized molar ratio of KCl to DBC is 2: 1. Due to the good complexing ability between DBC and K⁺, KCl and DBC formed an organometallic complex. Actually, DBC can not only promote the reaction rate and equilibrium of cycloaddition and transesterification reactions, but also prevent side reaction. Importantly, DBC can conveniently achieve high recovery ratio and show excellent reusability.

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1. Introduction

Dimethyl carbonate (DMC) is an important raw material in organic synthesis, fuel additive and electrolyte in lithium batteries. Several routes are known for DMC synthesis, e.g., oxidative carbonylation of methanol [1,2], transesterification [3,4], alcoholysis of urea [5–7], and direct synthesis from CO₂ and methanol [8–14]. Among them, the direct synthesis method and transesterification process have been considered to be an environmentally friendly and “green chemistry” process because of its utilization of CO₂. Thereinto, the conversion of direct synthesis method is very low because of the thermodynamic limitations. By comparison, transesterification process has been given much attention. Actually, the transesterification process can be divided into one-step and two-step methods. The two-step method involves the cycloaddition reaction of propylene oxide (PO) with CO₂ [15] and subsequently the transesterification reaction of propylene carbonate (PC) with methanol (Scheme 1). Unfortunately, this two-

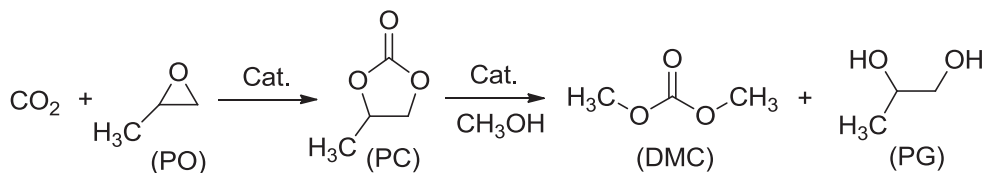
step method has the major disadvantages of high energy consumption, high investment and production costs which result from the separation of the intermediate cyclic carbonate [16,17]. To eliminate the drawbacks, the two-step processes are integrated into the one-step synthesis of DMC from CO₂, PO and methanol (Scheme 2), which has been given increasing attention.

For one-step synthesis of DMC, it has been reported that there are several supported catalysts [18–27], which have been prepared *via* loading inorganic bases (e.g., KOH and K₂CO₃), organic bases (e.g., choline hydroxide) or alkali halides (e.g., KI) on the MgO, ZnO, rare earth oxide (REO, RE = La, Ce, Y, Nd), smectite or 4A molecular sieve and so on as support. Furthermore, *n*-Bu₄NBr/*n*-Bu₃N, K₂CO₃/BrBu₃PPEG₆₀₀₀PBu₃Br and ionic liquid (e.g., [bmim]BF₄ and [bmim]Br) have also been employed [17,28,29]. However, the formation of by-products such as 1-methoxy-2-propanol (1) and 2-methoxy-1-propanol (2) from the side reaction like methanolysis of propylene oxide (Scheme 3) is usually unavoidable. Furthermore, these catalysts are not highly effective [24] or stable [16,20,26], or are difficult to recycle [16,28,29], and need rigorous reaction conditions (e.g., high pressure of supercritical CO₂) [21,27,28]. For example, most of supported catalysts present a lower yield of DMC (only 16.8%) [24] under a mild reaction condition (e.g., initial pressure of CO₂: 3 MPa, mole ratio of methanol and epoxides: 3:1), and the

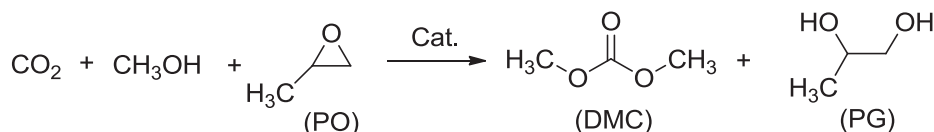
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Scheme 1. The route of two-step synthesis of DMC.



Scheme 2. The route of one-step synthesis of DMC.

yield of DMC only reaches to 34% under a relative rigorous reaction condition (e.g., initial pressure of CO₂: 8 MPa [19,22,23,25], mole ratio of methanol and epoxides: 9:1 [23]), while the yield of DMC of 57% needs an especially rigorous reaction condition (e.g., initial pressure of supercritical CO₂ [21,27,28]: 16.5 MPa, mole ratio of methanol and epoxides: 20:1 or even 40:1 [20,28]). Therefore, our aim is to achieve higher DMC yield, especially under mild reaction conditions, which is important from the point of industrial application.

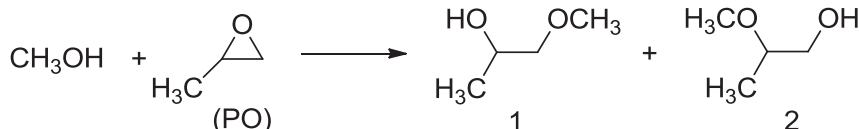
The analysis of the above literature demonstrates that the cheap alkali halides have received considerable attention. Unfortunately, the solubility of alkali halides is quite low in organic solvents (e.g., the solubility of KCl is less than 0.5 g/100 g in methanol at room temperature), which leads to lower interface between catalysts and reactants and, as a consequence, lower catalytic performance. It is well known that crown ethers and alkali halides can form an organometallic complex due to the good complexing ability between crown ethers and alkali metal ions [30,31]. This complexation is not only beneficial to solution of alkali halides in reactant system, but it also promotes more “bare anions” used as free nucleophilic groups, which will increase the probability of the nucleophilic reaction (i.e., the first step cycloaddition reaction of one-step synthesis of DMC, as shown in Scheme 1) [16] and, as a consequence, high yield of DMC.

Accordingly, some typical crown ethers (i.e., [2,4]-dibenzo-18-crown-6 (DBC), 18-crown-6, 15-crown-5 and 12-crown-4) were chosen as cocatalysts, aiming to promote the catalytic performance of alkali halides for one-step synthesis of DMC under mild reaction conditions, which has not been reported, to the best of our knowledge.

2. Experimental section

2.1. Chemical reagents

All the chemical reagents were purchased from Shanghai Chemical Reagent Ltd. They were of analytical grade and were used without further purification.



Scheme 3. Side reaction in one-step synthesis of DMC.

2.2. Evaluation of catalytic performance

The one-step synthesis of DMC from carbon dioxide, epoxides and methanol was carried out in a sealed Teflon-lined stainless steel high pressure autoclave with inner volume of 50 mL provided with a magnetic stirrer and an electric heater. Typical conditions and procedures are described as follows: a certain amount of methanol, propylene oxide (PO), catalyst and cocatalyst were added into the above autoclave. Alkali halides were used as catalysts, several typical crown ethers (i.e., [2,4]-dibenzo-18-crown-6 (DBC), 18-crown-6, 15-crown-5 and 12-crown-4) were used as cocatalysts, and polyethylene glycol (MW = 4000, abbreviated as PEG₄₀₀₀) was used as comparison for the crown ether. Then CO₂ (gas, > 99.99%) was injected up to a certain pressure at room temperature. The autoclave was heated to a certain temperature and the mixture was stirred at that temperature for several hours. After the reaction, the autoclave was cooled to about 10 °C with ice-water mixture and then depressurized. The liquid reaction mixture was analyzed by gas chromatograph (GC 2060) equipped with a capillary column (HP-INNOWAX, 30 m × 0.32 mm × 0.25 μm) and flame ionization detector (FID) using *n*-butyl alcohol as an internal standard, and further identified by gas chromatography-mass spectrometry (Agilent 7890-5975C) by comparing retention times and fragmentation patterns with authentic samples. The temperature of the GC column was set at 60 °C for 3 min and then was programmed to rise to 80 °C at the rate of 5 °C min⁻¹, and further reached 220 °C at the rate of 30 °C min⁻¹ and remained at that temperature for 3 min.

2.3. Calculation of yields

All of the yields in this work are based on the starting PO [21,28], as that PO is the limiting reactant and one mole of PO can produce one mole of DMC. The yields are defined in this work as follows: yield of product (i) = moles of product (i)/moles of propylene oxide added × 100%. Furthermore, one-step synthesis of DMC (as shown in Scheme 2) has been considered undergoing the two processes of cycloaddition reaction (the first step reaction) and subsequent transesterification reaction (the second step reaction), as shown in

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