

Highly efficient synthesis of diethyl carbonate via one-pot reaction from carbon dioxide, epoxides and ethanol over KI-based binary catalyst system

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ABSTRACT

The synthesis of diethyl carbonate (DEC) directly from carbon dioxide, ethylene oxide (EO), and ethanol via one-pot reaction is reported for the first time. The effects of catalyst species and reaction variables on the synthetic performance of DEC were systematically studied. The integration of easily available KI and sodium ethoxide as homogeneous binary catalyst system was found to be very active for the one-pot reaction, and 63.6% of the DEC yield could be achieved under relatively mild reaction conditions (443 K, 3 MPa CO₂ initial pressure, 2 h). The byproduct of 2-ethoxyethanol, which is predominantly formed via alcoholysis of EO by ethanol through ring-opening reaction, was produced with small amount (<5%) under optimized conditions. Additionally, the thermodynamic evaluation reveals that the standard molar enthalpy of one-pot reaction is exothermic ($\Delta_r H_m^\theta = -19.70$ kcal/mol < 0). In comparison with the direct synthesis of DEC from CO₂ and ethanol, the involvement of EO facilitates the formation of DEC, simultaneously with glycol produced. This strategy could also be successfully expanded to terminal epoxide substrates. Furthermore, a possible mechanism of the reaction was proposed on the basis of experimental results. This method provides a highly effective way to produce DEC via directly chemical utilization of CO₂ and shows promising application in the manufacture of diethyl carbonate on an industrial scale.

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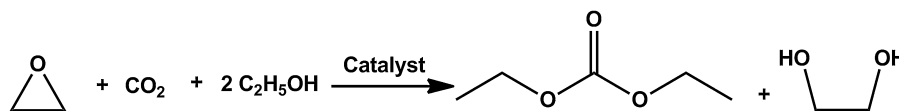
1. Introduction

Nowadays, atmospheric CO₂ concentration is continuously increasing mainly due to the huge and growing emission from the consumption of fossil fuels by human activities. CO₂ is considered to be the most significant greenhouse gas responsible for the global warming. Meanwhile, the chemical utilization of CO₂ as C1 feedstock arouses intense interest since CO₂ is renewable, inexpensive, nonflammable and nontoxic [1–4]. Numerous approaches of developing efficient route for CO₂ transformation into industrially interesting chemicals have attracted wide concerns in recent years [5,6]. Particularly, organic carbonates represent an important kind of carbonyl containing compound with wide applications in the fields of solvent, synthetic, additives, etc. [7–9]. Among them, diethyl carbonate (DEC) is an important homologue in the family of dialkyl carbonates, which has eco-friendly features and versatile applications. In the aspect of organic synthesis, DEC is a useful precursor

as a substitute for toxic phosgene [10]. It can be used as carbonylation or ethylation reagent due to the carbonyl group or ethyl group in its molecular structure [10,11]. DEC has also been considered as a replacement of methyl *tert*-butyl ether (MTBE) as fuel additive due to its high oxygen content (40.6 wt%). Additionally, DEC can be biodegraded to CO₂ and ethanol when released into the environment, showing eco-friendly feature and demonstrating a promising application as green solvent for synthesis and catalysis [12].

Conventionally, DEC was manufactured by the reaction of ethanol with toxic phosgene (COCl₂) [13]. Considerable efforts were devoted to develop non-phosgene routes by researchers in order to reduce or completely abandon the involvement of extreme toxic phosgene, e.g. transesterification reaction of dimethyl carbonate [14], oxidative carbonylation of ethanol [15–18], carbonylation of ethyl nitrite [19], electrochemical synthesis in the presence of ethyl iodide [20], decarbonylation of diethyl oxalate [21] and alcoholysis of urea or its derivative (ethyl carbamate) with ethanol [22,23]. Nevertheless, these routes suffer from disadvantages of toxic (phosgene, CO, ethyl nitrite) or expensive raw materials, easy deactivation of catalysts or low product yields, which restrict their practical applications.

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Scheme 1. One-pot process for DEC synthesis from ethylene oxide, CO₂ and ethanol.

The synthesis of diethyl carbonate (DEC) using CO₂ as building block is a promising route. Ideally, the process starts from CO₂ and ethanol, but the reaction hardly occurs spontaneously even under harsh conditions due to the thermodynamic limitations [24,25]. To address this issue, chemical dehydration reagent was usually involved to shift the reaction forwards to the carbonate side, leading to equivalent waste [26]. Although great efforts have been devoted to the synthesis of DEC from CO₂ over various catalysts [24–26], the effective utilization of CO₂ to synthesize DEC still remains a challenge and should be supplemented.

It is proposed that the addition of chemicals with high energy is favorable for the activation of the inert CO₂. Recently, in order to overcome the drawbacks of thermodynamic constrains, the usage of butylene oxide as a chemical water trap was reported [27,28]. According to the results [27], 15.6% ethanol conversion and 10% DEC yield were obtained over cerium (IV) oxide at 180 °C and 9 MPa pressure. Although the yield was 9-fold enhancement compared with the method without water removal, unfortunately, the DEC yield was not high enough in this system and needed to be improved. It is worth mentioning that the synthesis of cyclic carbonate from epoxide and CO₂ was well established in industrial manufacture. Furthermore, the transesterification of cyclic carbonate with ethanol to produce DEC was also proved to be feasible [29]. In principal, the DEC could be synthesized via the consequent two-step reaction. However, in view of the energy consumption, productivity and investment, the one-pot reaction directly from CO₂ was undoubtedly superior to the two-step separate reaction. Thus, the development of a more effective one-pot reaction to improve the productivity of DEC directly from CO₂ is highly desired.

With the aim of developing effective methods for activation and utilization of CO₂ to synthesize high-valued chemical of DEC, herein, we describe a new methodology for the synthesis of DEC through one-pot reaction from commodity chemicals of EO, carbon dioxide and ethanol, as shown in Scheme 1. In this process, glycol was simultaneously co-produced, which is also an important raw material in the manufacture of polyester fibers and fabric industry. The varied catalyst species and reaction variables, e.g. catalyst composition, reaction temperature, molar ratio of the reactants, reaction pressure, reaction time, were systematically evaluated. Subsequently, catalyst recyclability was also investigated. To the best of our knowledge, this is the first work to study one-pot reaction for efficient synthesis of DEC from ethylene oxide, CO₂ and ethanol. Additionally, thermodynamic calculation was used to predict the reaction spontaneity as a function of temperature. On the basis of the experimental results, a possible reaction mechanism was also proposed. Moreover, the scope of substrates was extended to terminal epoxides. In comparison with the reported processes, this route has provided an effective way to realize the synthesis of DEC directly from abundant CO₂ via one-pot reaction.

2. Experimental

2.1. Materials

Ethylene oxide (EO), propylene oxide (PO), tributylamine (Bu₃N), triethylamine (Et₃N), tetrabutyl ammonium iodide (Bu₄NI), tetramethyl ammonium iodide (Me₄NI), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), sodium ethoxide (EtONa),

La(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, were purchased from Sinopharm Chemical Reagent Co., Ltd. NaI was purchased from Tianjin Guangfu Fine Chemical Research Institute. KI, KCl, ethanol, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Zn(NO₃)₂·6H₂O, MgO were purchased from Xilong Chemical Industry Incorporated Co., Ltd. KBr was purchased from PIKE Technologies Spectroscopic Creativity. Magnesium carbonate (MgCO₃) was purchased from Adamas Reagent Co., Ltd. CO₂ (>99.9% purity) and N₂ (99.999% purity) were purchased from Beijing Qianxi Company. Potassium ethoxide (EtOK, 95% purity) was purchased from Sigma-Aldrich. Glycidyl isopropyl ether, glycidyl phenyl ether, butyl glycidyl ether, styrene oxide, 1,2-epoxycyclohexane and allyl glycidyl ether were purchased from TCI. All the chemicals were of analytical grade and used without further purification unless noted otherwise.

2.2. Catalyst preparation

The typical solid basic catalysts, e.g. La₂O₃, CeO₂, MgO, MgAl-LDO, ZnMgO_x, were prepared according to the procedure mentioned in the literatures with slight modifications [30–34]. Specifically, La₂O₃ was prepared by precipitation method with mixed base solution. 25.98 g La(NO₃)₃·6H₂O was dissolved in 400 mL de-ionized water. The solution was slowly titrated by mixture of KOH and K₂CO₃ until pH = 10 at 85 °C. The precipitate was refluxed for 24 h, filtered and washed with de-ionized water until the pH of the filtrated water became neutral. The resultant catalyst was dried at 100 °C for 12 h and calcined at 550 °C in air for 6 h before use. CeO₂, MgO, MgAl-LDO, ZnMgO_x were prepared according to the methods used in the literatures with slight modifications, i.e. CeO₂ was obtained by calcining Ce(NO₃)₃·6H₂O at 800 °C for 3 h [31], MgO was obtained commercially and calcined at 650 °C for 3 h [32], MgAl-LDO was obtained by calcining the Mg–Al hydrotalcite precursor at 450 °C for 3 h in air [33], ZnMgO_x was obtained with molar ratio of Zn/Mg equal to 7/3 in initial solution and calcined at 800 °C for 4 h [34].

2.3. Catalytic activity test


In a typical catalytic evaluation, 45 mmol EO, 31.4 g ethanol and 0.2 g total amount of catalyst were added into a stainless autoclave reactor with an inner volume of 150 mL. CO₂ was introduced with an initial pressure of 3.0 MPa at room temperature, and the autoclave was completely sealed. The reactor was heated and stirred constantly at desired temperature (e.g. 423 K) during the reaction. The reaction was conducted in a batch operation mode. After the reaction, the reactor was cooled to room temperature and the residual gas was depressurized slowly passing through the trap with ethanol as an absorbent. The compositions of the resulting mixture were measured by GC–MS (Agilent 6890N/5975B). In order to quantitatively analyze the composition of the resulting mixture, the liquid products were analyzed by a gas chromatograph (Shimadzu) with a capillary column (Rtx-WAX 30 m × 0.25 mm × 0.25 μm) equipped with a flame ionization detector (FID) and an automatic sampler using an external standard technique. The yield of product was defined and calculated as follows:

$$\text{yield of product } Y_i(\%) = \frac{\text{mole of product } i}{\text{mole of epoxide charged}} \times 100\%$$

Table 1
The conversions and yields of the reaction with different catalysts.

Entry	Catalyst		EO conversion (%)	Yield (%)			
	I	II		DEC	EG	EC	EE
1	–	–	66.5	0	3.5	1.4	47.2
2 ^a	–	–	96.4	0	21.4	0	79.3
3	KI	–	97.3	5.5	8.3	80.8	4.0
4 ^b	KI	DBU	97.8	20.6	28.3	50.8	2.6
5 ^b	KI	Bu ₃ N	98.1	14.1	18.9	72.6	6.5
6 ^b	KI	Et ₃ N	97.7	21.5	25.5	64.1	2.8
7	KI	La ₂ O ₃	97.3	3.6	6.8	77.3	14.1
8	KI	CeO ₂	94.2	8.9	15.8	67.8	3.1
9	KI	MgO	97.4	5.8	9.2	79.1	4.0
10	KI	MgAl-LDO	97.3	9.4	16.3	68.3	4.2
11	KI	ZnMgO _x	96.3	6.4	10.6	74.5	4.0
12	KI	MgCO ₃	97.2	4.2	6.7	75.7	3.7
13	KI	EtONa	97.2	30.8	39.4	34.8	4.1
14	KBr	EtONa	95.4	29.6	39.2	44.4	6.5
15	KCl	EtONa	93.7	21.5	27.1	46.5	16.8
16	–	EtONa	80.6	11.6	16.8	19.1	42.6
17	NaI	EtONa	98.9	27.8	35.2	51.2	2.7
18	Bu ₄ NI	EtONa	99.0	31.6	39.6	53.1	3.5
19	Me ₄ NI	EtONa	98.9	29.0	35.4	53.9	2.9
20	NaI	EtOK	98.7	16.7	23.7	64.6	2.5
21 ^c	–	EtOK	84.7	12.8	21.6	33.1	28.3

Reaction conditions: 2.0 g EO, 31.4 g C₂H₅OH, 0.1 g catalyst I and 0.1 g catalyst II, CO₂ initial pressure of 3 MPa, reaction temperature of 423 K, reaction time of 3 h; magnetic stirring rate = 500 rpm.

EG: ethylene glycol. EC: ethylene carbonate. EE: 2-ethoxyethanol .

^a The reactor was charged with 3 MPa of nitrogen initial pressure instead of CO₂.

^b 100 μL of the liquid catalyst II was charged.

^c 0.2 g EtOK.

2.4. Catalyst recycling experiment

The mixture of ethanol, DEC, EE, EG and EC with relatively lower boiling points in the resulting mixture were removed by rotary evaporator under vacuum at consecutive heating temperatures of 60 °C and 150 °C, respectively. As a result, the binary catalysts of (KI + EtONa) with high viscosity could be successfully separated and recycled for the next run.

2.5. Thermodynamic evaluation

Calculation of thermodynamic evaluation for the processes involved in one-pot reaction for DEC synthesis from EO, CO₂ and ethanol was conducted by density-functional theory (DFT) in DMol³ package. The Becke exchange plus Lee–Yang–Parr correlation functional and all-electron core potentials were used. The double- ξ numerical polarization (DNP) basis set was adopted, which is comparable to the 6-31G(d, p) Gaussian type basis set. The DNP basis set incorporates d-type polarization into heavier atoms and p-type polarization into hydrogen atoms. To compute the enthalpy and free energy of a reaction, we first add up the DMol³ total energies for the reactants and products to obtain the finite temperature-corrected value for H and G for each component.

$$H_{\text{Torr}}^T(\text{component}) = E_{\text{total}} + H_T(\text{component}) \quad (1)$$

$$G_{\text{Torr}}^T(\text{component}) = E_{\text{total}} + G_T(\text{component}) \quad (2)$$

The enthalpy and free energy of reaction were simply computed as follows.

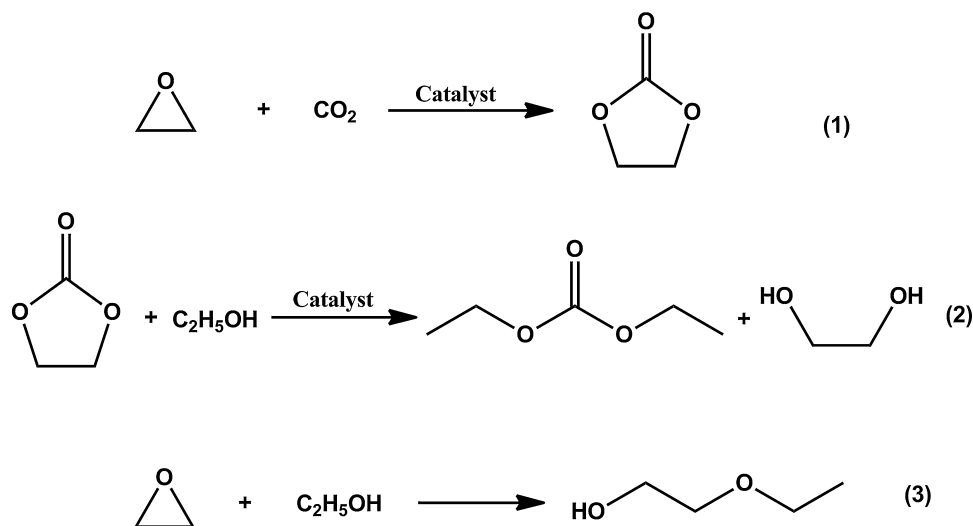
$$\Delta_r H_m^\theta = H_{\text{Torr}}^\theta(\text{product}) - E_{\text{Torr}}^\theta(\text{reactant}) \quad (3)$$

$$\Delta_r G_m^\theta = G_{\text{Torr}}^\theta(\text{product}) - G_{\text{Torr}}^\theta(\text{reactant}) \quad (4)$$

3. Results and discussion

3.1. Catalysts for the one-pot synthesis of DEC

The synthesis of DEC from EO, CO₂ and ethanol with or without catalyst were investigated and the corresponding results were summarized in Table 1. There is no detectable formation of DEC without any catalyst, entry 1, 2-ethoxyethanol (EE) is the main product, which is predominantly formed via alcoholysis of EO by ethanol through ring-opening reaction. This result indicated that the alcoholysis ring-opening reaction could occur spontaneously in the absence of catalyst and proton transfer from ethanol to EO occurs in this process, as shown in Scheme 2. Therefore, to facilitate the desired reaction, appropriate catalyst is necessary to be introduced. It should be worth mentioning that a small amount of ethylene glycol (EG) was also formed, which was probably derived from the hydrolysis of EO due to the existence of small amount of water in the system. To evaluate this conjecture, the reactor was charged with 3 MPa nitrogen gas instead of CO₂ to exclude the possibility of forming ethylene carbonate (EC) intermediate, entry 2. Interestingly, 21.4% EG was obviously formed in spite of slight experimental deviation in determining EO conversion and product yields. Since the possibility for formation of EG derived from EC via the pathway of transesterification reaction was exclusively eliminated, the possible reason can be attributed to that the small amount of water in the reaction system was consumed by EO to produce EG. In other words, EG could be produced via hydrolysis of EO with water. This can explain the phenomena of small difference between the DEC and EG yields in subsequent discussions. From the above results, it can be concluded that the reaction atmosphere has remarkable influence on the product productivity, that is, the nitrogen was more favorable for the transformation of EO and formation of EG and EE. When KI was used, entry 3, DEC can be formed with 5.5% yield, and the major product was EC (80.8%). Although the EC was considered to be the intermediate for DEC synthesis [35,36], this result was still not satisfactory due to too low DEC yield.



Scheme 2. The cycloaddition reaction of EO and CO₂ to produce EC (1) and the transesterification reaction of EC and ethanol to produce DEC and EG (2) ethanolysis of EO to EE (3).

It is worthy to note that the one-pot reaction in dimethyl carbonate synthesis was composed of two steps [1], cycloaddition reaction and subsequent transesterification reaction. Therefore, we deduced that the reaction proceeded in a similar pathway in the one-pot reaction for DEC synthesis. The possible reactions involved in this process were illustrated in Scheme 2. As reviewed in the literature [1], besides the ionic salts for the cycloaddition reaction, the employment of basic catalyst as co-catalyst was necessary to meet the requirement for effectively catalyzing the transesterification reaction. Therefore, some typical base catalysts were investigated with the combination of KI. When several homogeneous organic bases were used as co-catalysts [37,38], entries 4–6, the relatively stronger base of DBU catalyst gives higher DEC yield of 20.6%.

Additionally, the catalysts with appropriate acidic and basic properties were proved to be effective heterogeneous catalysts for transesterification reaction in previous reports [30–34]. Therefore, several typical solid basic catalysts with the combination of KI were tested, including single metal oxides or composites, i.e. La₂O₃, CeO₂, MgO, MgAl-LDO, ZnMgO_x and MgCO₃. These catalysts were also prepared as the method in experimental section or purchased commercially, entries 7–12. It is clear that EO conversion was as high as the results over homogeneous catalysts aforementioned, and all close to complete. However, in comparison with homogenous catalyst II aforementioned, the DEC yields over the combination of KI with heterogeneous catalysts were much inferior under identical reaction conditions, which were almost as low as the KI used alone. One possible reason was ascribed to the insolubility of the heterogeneous catalysts, thus few active sites can be accessible for the reactants during reaction.

Interestingly, the homogeneous binary catalyst system of KI/EtONa was found to be the most effective for the one-pot synthesis of DEC among the catalysts examined [39]. When the integration of KI and EtONa was used as the catalyst, entry 13, the one-pot synthesis of DEC can be conducted effectively. The product yields to DEC, EG, EC and EE of 30.8%, 39.4%, 34.8%, 4.1% with 97.2% EO conversion can be obtained, respectively. Additionally, small quantity of diglycol monoethylether was observed. To test the effect of different anion in catalyst I of potassium halide salt, KBr and KCl with varied halogen anions were examined under identical condition, entries 14–15. Obviously, the order of the catalytic activity among potassium salt was KI > KBr > KCl, which can be attributed to the varied nucleophilicity of the counter-anion. Apparently, the catalyst containing iodine with higher nucleophilicity demonstrated higher catalytic activity. Nevertheless, when the basic catalyst of

EtONa was employed alone, entry 16, the DEC yield was as low as 11.6%, and EE was the predominant product (42.6%), suggesting basic catalyst alone could not result in high desired product yields.

The influence of the cation type of iodonium salts on the catalytic performance was investigated and summarized in Table 1. As can be seen, there are slight difference between the iodonium salts with different cations, e.g. 27.8%, 31.6% and 29.0% DEC yields for the iodonium salt catalysts with Na⁺, Bu₄N⁺, Me₄N⁺ as cations, respectively. In association with the results aforementioned, it seems that the anion part, i.e. iodonium, has a critical role in the catalytic activity. It was considered that the transesterification reaction is probably the rate-determining step under the reaction conditions investigated. That is, the DEC production in this step depends more strongly on the part of basic catalyst. Thus, although there may be different catalytic activities towards the cycloaddition reaction, the amounts of iodonium salts were sufficient for effective catalyzing the first step of cycloaddition reaction. As a consequence, DEC yields did not show much difference. These results are consistent with the opinions that the transesterification reaction is the rate-determining step.

To verify the possible ion exchange between the binary catalysts during reaction, the catalytic performance of pure EtOK and its combination with NaI were tested, entries 20–21. The result showed that DEC yield is 16.7% when using the combination of NaI and EtOK, entry 20, which is much lower than the result obtained over the catalyst by combination of KI and EtONa. Additionally, the catalytic performance of pure EtOK was tested in the DEC synthesis for comparison, entry 21. As expected, 12.8% of low DEC yield was obtained over pure EtOK, meanwhile large amount of EE byproduct (28.3%) was formed. Based on these results obtained, it could be inferred that the exchange reaction between KI and EtONa in this reaction medium did not occur effectively.

In association with the above results, among the catalysts tested, the combination of KI and sodium ethoxide (EtONa) was proved to be an easily available and effective binary catalyst system and used in the consequent investigation. To simplify the discussion, DEC yield was used to evaluate the catalytic performance irrespective of other product yields in some discussions.

3.2. Effect of KI to sodium ethoxide

The effect of KI/(KI + EtONa) composition on the yield of product was shown in Fig. 1. The reaction was studied over 0.2 g total weight of KI and EtONa with varied weight ratio at 423 K and CO₂

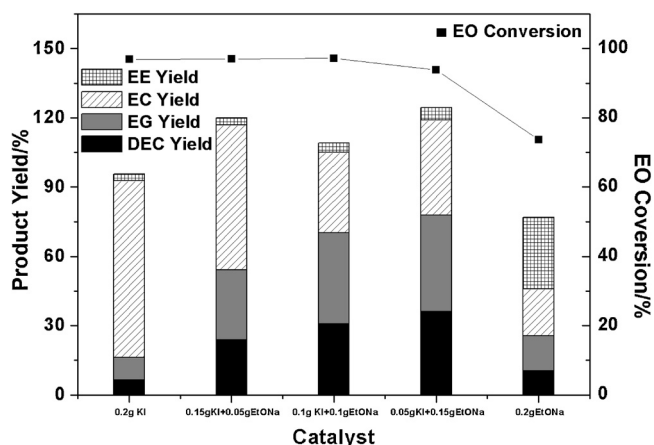


Fig. 1. Effect of KI/(KI+EtONa) composition on the synthesis of DEC. Conditions: 0.2 g total catalyst amount, 2.0 g EO, 31.4 g ethanol, 423 K, 3 MPa initial CO₂ pressure, 3 h, 500 rpm magnetic stirring rate. ■ EO conversion; ■ EE Yield; ■ EC Yield; ■ EG Yield; ■ DEC Yield.

initial pressure of 3 MPa. It was found that the catalyst composition had significant effect on the DEC synthesis. In the case of single 0.2 g KI without EtONa, EO was consumed close to complete. However, the DEC yield was found to be as low as 6.4%, indicating KI was effective for the cycloaddition reaction to produce EC (76.4%), but not effective enough for the DEC production. The DEC increased with the elevation of EtONa content, and reached maximum yield of 36.1% over the catalyst with the combination of 0.05 g KI and 0.15 g EtONa. However, when 0.2 g EtONa was used as single component catalyst, merely 10.4% of DEC yield was obtained with 73.7% EO conversion, simultaneously byproduct EE was significantly increased to 30.9%. Moreover, it is accepted that the transesterification was reverse reaction, and it was probably the rate-determining step in analogous system. Therefore, in the premise of providing sufficient catalyst amount for cycloaddition reaction, the larger usage of basic catalyst was more favorable for the transesterification reaction, leading to higher DEC yield. Thus, the preferred weight ratio of KI/EtONa is 1:3.

3.3. Effect of reaction temperature

To investigate the effect of reaction temperature on the catalytic activity, the reaction was carried out in the range of 403–453 K at ethanol/EO of 15 and CO₂ initial pressure of 3 Mpa, as shown in Fig. 2. Within the range of investigation, close to complete conversion of EO was obtained and EG yield as a function of reaction temperature has the same tendency as that of DEC. To simplify the discussion, the DEC yield reflecting the reaction performance will be used alone in subsequent section, unless otherwise specified. It can be seen that the DEC yield increased monotonically with the increasing reaction temperature. The DEC yield was as low as 13.5% when the temperature was 403 K. In contrast, the EC yield was 70.2%, suggesting the cycloaddition reaction between the EO and CO₂ to form ethylene carbonate progressed rapidly. The DEC yield gradually increased with subsequent elevating reaction temperature. The relatively higher DEC yield of 65.5% was obtained when the temperature was 443 K. The DEC yield did not increase significantly when the temperature further increased to 453 K. This result indicated that the reaction temperature has great impact on the catalytic behavior of the one-pot reaction, and relatively higher reaction temperature was more favorable for the DEC production. In comprehensive consideration of the economical and reactivity of the process, 443 K was chosen as the preferential temperature.

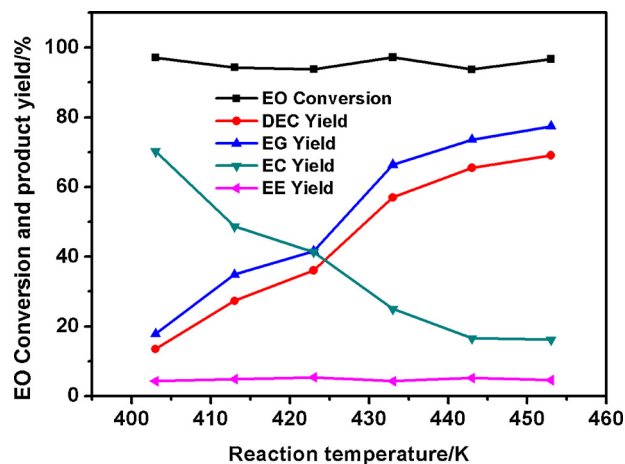


Fig. 2. Effect of reaction temperature on the synthesis of DEC. Conditions: 0.05 g KI, 0.15 g EtONa, 2.0 g EO, 31.4 g ethanol, 3 MPa of initial CO₂ pressure, 3 h, 500 rpm stirring rate.

3.4. Effect of molar ratio of ethanol to EO

The influence of the feed molar ratio of EtOH/EO was investigated at 423 K for 3 h at the pressure of 3 MPa CO₂, and the results were plotted in Fig. 3. When the ratio was 6, the DEC yield of 49.5% could be obtained. When the molar ratio was increased to 10, 62.2% DEC yield and 72.9% EG yield with 98.0% EO conversion could be obtained. The reaction reached equilibrium at this ratio in the batch model, which was consistent with the results verified in the literature [29]. When the molar ratio was further increased to the range of 15–30, the DEC yield did not show significant increase even in such excess of ethanol.

The possible reasons were conjectured as follows. On the one hand, it can be seen that the higher EG yield was produced at higher molar ratio of EtOH/EO. It should be noted that the small quantity of water was contained in the ethanol used, which suggested that the higher EtOH/EO would result in the increased molar ratio water (H₂O)/EO. That is, the hydrolysis of EO occurred more easily and seriously at higher EtOH/EO. Undoubtedly, this parallel reaction would lead to decreased amount of EO involved in the desired one-pot reaction from CO₂, EO and ethanol. Moreover, this result also could explain the phenomenon of decreased amount of ethylene carbonate with increasing the ethanol amounts due to the competitive reaction of EO hydrolysis. As a result, the cycloaddition

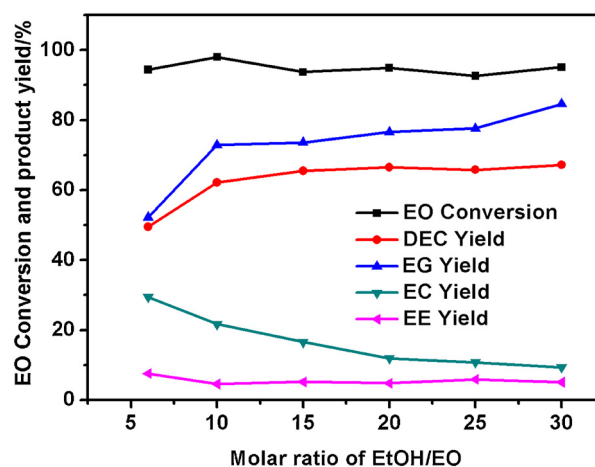


Fig. 3. Effect of molar ratio of EtOH/EO on the synthesis of DEC. Conditions: 0.05 g KI, 0.15 g EtONa, 31.4 g ethanol, 3 MPa initial CO₂ pressure, 443 K, 3 h, 500 rpm stirring rate.

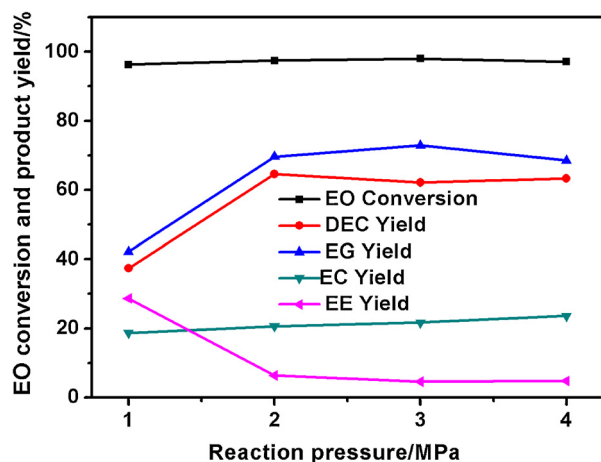


Fig. 4. Effect of reaction pressure on the synthesis of DEC. Conditions: 0.05 g KI, 0.15 g EtONa, 3.0 g EO, 31.4 g ethanol, 443 K, 3 h, 500 rpm stirring rate.

reaction of EO with CO₂ to produce ethylene carbonate was impaired to some degree.

On the other hand, we noted that the EO conversion decreased at higher molar ratio of EtOH/EO above 10, suggesting the declined amount of EO was converted in the reaction. In terms of the lower conversion of EO, in fact, the relative amount of DEC to the consumed amount of EO was increased with increasing the molar ratio of EtOH/EO. These results are in accordance with the feature of the equilibrium reaction.

From the results aforementioned, it could be seen that the DEC yield increased slowly with the increased molar ratio of EtOH/EO due to the competitive reaction of EO hydrolysis. In contrast, the corresponding concentration of DEC in the resulting mixture would be decreased sharply with the increased molar ratio. Conclusively, from a practical view, the relatively higher EtOH/EO molar ratio of 10 was the more suitable feed ratio to reduce the energy consumption in the sector of separation.

3.5. Effect of reaction pressure

The influence of initial CO₂ pressure on the reaction was investigated in the range of 1–4 MPa, as depicted in Fig. 4. It was found that the initial pressure had significant influence on the DEC synthesis, especially in the region of low pressure, i.e. below 3 MPa. When the initial reaction pressure was as low as 1 MPa, 37.4% DEC yield was obtained, simultaneously with 28.7% of a high EE yield. As mentioned above, EE was formed by alcoholysis of EO, which is competitive with the cycloaddition reaction to form EC. It was reasonable to propose that the low pressure of CO₂ did not provide sufficient concentration of CO₂ to make cycloaddition reaction progressed rapidly. To our delight, the increase of the initial pressure to 2 MPa could effectively promote the DEC yield, while the side-reaction for EE formation was suppressed to a great extent. The DEC yield can be drastically increased to 64.2%, meanwhile, the EE yield was decreased to 6.4%. Further increase the pressure to 3 MPa and 4 MPa led to approximately constant DEC and EG yields, while the EE yields could be further decreased to 4.6% and 4.8%, respectively. On the premise of ensuring to achieve high product yields, the reaction conducted at relatively lower pressure was favorable to alleviate the risk of operation and reduce the production cost. For comprehensive consideration, the initial CO₂ pressure of 3 MPa was more favorable for obtaining maximum DEC productivity with less amount of undesired byproduct.

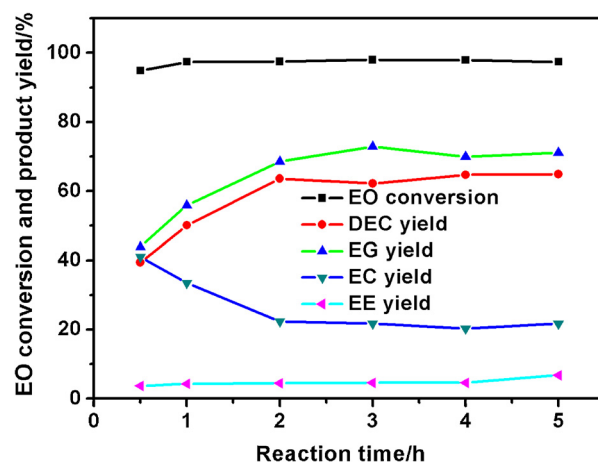


Fig. 5. Effect of reaction time on the synthesis of DEC. Conditions: 0.05 g KI, 0.15 g EtONa, 3.0 g EO, 31.4 g ethanol, 3 MPa initial CO₂ pressure, 443 K, 500 rpm stirring rate.

3.6. Effect of reaction time

The dependence of the reaction time on the synthesis of DEC was monitored in the range of 0.5–5 h, as illustrated in Fig. 5. The DEC yield was increased monotonically at the initial stage. On the contrary, the EC yield was gradually decreased. This clearly confirmed EC was the reaction intermediate, and consumed gradually with the reaction progress. 39.4% DEC yield and 43.9% EG yield with 94.9% EO conversion could be obtained at the initial stage of 0.5 h, simultaneously with EC yield of 41.0%. The high EO conversion indicated that the cycloaddition reaction progressed rapidly and close to be completed within the initial 0.5 h [41,42]. As declared in the literature [40], the polar solvent environment provided by the hydroxyl substance was favorable to the cycloaddition reaction. To illustrate the role of ethanol, the performance of cycloaddition reaction between EO and CO₂ in the absence of ethanol within 0.5 h was tested. In comparison with the result in the presence of ethanol, merely 2.2% of EC yield was observed in the absence of ethanol under the identical reaction condition. For comparison, the catalytic activity was determined by turnover frequency (TOF), which is calculated based on the mol of EC produced per mol of KI catalyst per hour. It is worth mentioning that the DEC was formed from EC via transesterification reaction. Therefore, the total amount of EC and DEC reflected the actual EC amount formed during reaction. The calculated TOF for the reaction in the presence of ethanol was 353 h⁻¹, while the calculated TOF value was only 10 h⁻¹ in the absence of ethanol. This result ambiguously confirmed that the ethanol had significant impact on accelerating the cycloaddition reaction. Accordingly, it could be deduced that KI played a major role in the catalytic activity and ethanol had a promotional effect in the stage of cycloaddition reaction.

When the reaction time prolonged to 1 h, 50.1% increased DEC yield with 97.4% EO conversion could be obtained. The DEC and EG yield further increased to 63.6% and 68.6% at 2 h, respectively, with the consumption of EC intermediate. The DEC and EG yield did not significantly change when the reaction time further prolonged to 3–5 h in subsequent investigation. It is well known that the transesterification reaction is reversible, and product yields would not increase when reaching the equilibrium yields in the batch mode. As reported previously [29], 63% DEC yield is the equilibrium value when the molar ratio of ethanol/EC is 10 under the boiling point of reaction mixture. In spite of some difference between these two systems, e.g. additional composition of CO₂ existing in our system or different reaction temperature, it was conjectured that the reaction was presumably close to or reached the equilibrium in such a

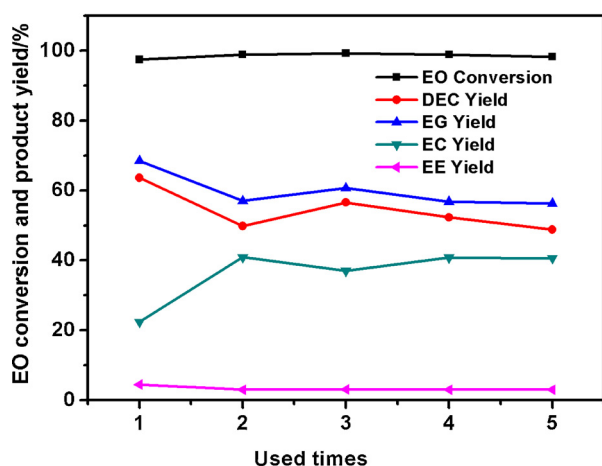


Fig. 6. Catalyst recycling on the synthesis of DEC. Conditions: 0.05 g KI, 0.15 g EtONa, 3.0 g EO, 31.4 g ethanol, 3 MPa initial CO₂ pressure, 443 K, 3 h, 500 rpm stirring rate. Note: The reaction time for the used times of 1 and 2 is 2 h.

condition. Therefore, reaction time of 2 h was enough for achieving excellent DEC yield. In comparison with the method directly from CO₂ and ethanol, the DEC production was greatly improved with EO involved because the equilibrium restriction was effectively circumvented. It should be mentioned that residual EC as reaction intermediate could be recycled, and further transformed into DEC through reaction distillation to shift the equilibrium towards product side in continuous reaction mode. Thus, this process provides an effective method to synthesize DEC through direct utilization of CO₂.

3.7. Catalyst recyclability

The experiment of catalyst recyclability was conducted and the results are shown in Fig. 6. It can be seen that nearly complete conversions of EO were obtained during the recycling experiment. In comparison with the result obtained over fresh catalyst, the DEC yield decreased from 63.6% to 49.8% when the catalyst was used for the second run. To our delight, when the reaction time was prolonged to 3 h, 56.6% of relatively higher DEC yield could be obtained. In subsequent recycling investigations, although DEC yield was slowly decreased with the increased recycling number, still 48.8% DEC yield could be obtained even at the fifth use of catalyst.

It is worth mentioning that about 3% amount of total weight was sampled for each analysis, suggesting the same amount of homogenous catalyst was simultaneously lost. Therefore, although the possibility of catalyst deactivation to some degree cannot be completely excluded, the decreasing amount of catalyst in the reaction system along with the increased running cycles is probably responsible for the declined activity after first cycle. In addition, in comparison with the fresh catalyst, lower yields of byproduct of EE (<3.1%) were observed during the recycling experiment. To some extent, it can be deduced that the catalyst could be basically recycled without significant decline in catalytic activity.

Table 2

Thermodynamic data of various substrates and products in the reaction.

Substrate	E_{total} (Ha)	H (kcal/mol)	H_{Totr}^{θ} (kcal/mol)	S^{θ} (kcal/mol/K)	C_p (kcal/mol/K)
DEC	-422.255	99.673	-264869.562	95.143	34.631
CO ₂	-188.616	9.685	-118348.741	39.062	9.994
C ₂ H ₅ OH	-155.038	52.297	-97235.598	64.61	15.834
EG	-230.26	56.031	-144434.422	72.661	19.643
EO	-153.792	37.648	-96468.370	59.445	11.46
EC	-342.437	49.365	-214323.531	72.565	20.577
EE	-308.87	91.658	-193727.356	82.615	27.111

3.8. Thermodynamic evaluation of the DEC synthesis via direct route from ethylene oxide, CO₂ and ethanol








Thermodynamic evaluation of the DEC synthesis via direct route from EO, CO₂ and ethanol was calculated based on the density-functional theory (DFT). The results of a vibrational analysis or Hessian evaluation in DFT calculations can be used to compute enthalpy (H), entropy (S), free energy (G), and heat capacity at constant pressure (C_p) as functions of temperature. The DMol³ total energy yields the total electronic energy E_{total} at 0K. The various translational, rotational, and vibrational components are used to compute H , S , G , and C_p . The thermodynamic data of various substrates and products involved in the reaction are calculated for the first time and summarized in Table 2. The standard molar enthalpy change can be calculated in accordance of the equation $\Delta_r H_m^{\theta} = \sum \nu H_i^{\theta}$, where the ν represents the stoichiometric coefficient. Based on the obtained data it can be concluded that the desired reaction is exothermic ($\Delta_r H_m^{\theta} = -19.70$ kcal/mol < 0). Hence, elevating the reaction temperature would go against the production of DEC. The standard molar free energy change can be calculated in accordance of the EQ.4. Based on the obtained data it can be concluded that the desired reaction is spontaneous ($\Delta_r G_m^{\theta} = -1.85$ kcal/mol < 0). As mentioned in the literature [27], the $\Delta_r G_m^{\theta}$ for the direct synthesis of DEC from ethanol and CO₂ is 35.85 kJ/mol > 0, indicating the reaction cannot occur spontaneously. Therefore, in comparison with the direct route aforementioned, the involvement of EO facilitates the synthesis of DEC via one-pot reaction from CO₂, EO and ethanol, and makes the process conduct effectively. Meanwhile, the side reaction of ethanolysis of EO is also exothermic ($\Delta_r H_m^{\theta} = -23.4$ kcal/mol < 0), exhibiting more significant thermal effect in comparison with the main reaction. Therefore, controlling appropriate reaction temperature is important to achieve higher DEC production, as also evidenced by experimental results.

3.9. Scope of the epoxides

The applicability for a variety of terminal epoxide substrates, e.g. propylene oxide, styrene oxide, glycidyl phenyl ether, glycidyl isopropyl ether, butyl glycidyl ether, allyl glycidyl ether, 1,2-epoxycyclohexane, for one-pot synthesis of DEC over binary system KI/EtONa was surveyed at 443 K and 3 MPa of CO₂ initial pressure. The compositions of the resulting mixture were measured by GC-MS, and the results showed that the products primarily consisted of diethyl carbonate, 1,2-diol, cyclic carbonate, and mono- or di-ether formed by ring-opening reaction. Besides, small quantity or trace of aldehyde was observed when SO was employed as substrate. The corresponding results are summarized in Table 3.

For the synthesis of DEC from propylene oxide, CO₂ and ethanol, entry 1, 46.0% DEC yield with 100% propylene oxide conversion could be obtained within 4 h. 48.7–57.9% DEC yields can be obtained within 4–5 h, entries 2–5. Although the obvious influence of the electronic property of the substitute on the ring of the epoxides on reaction performance was described in previous literature [43], it was not the case in this work. There was no significant difference between the DEC yields with high substrate conversions, which

Table 3
DEC synthesis from various epoxide substrates via one-pot reaction.

Entry	Substrate	t (h)	Con. (%)	DEC Yield (%)	DEC Sel. (%)	Cyclic carbonate yield (%) ^a
1		4	100	46.0	46.0	31.2
2		5	98.6	53.5	54.3	2.1
3		4	93.8	57.9	61.7	8.5 ^b
4		4	96.2	48.7	50.6	5.6
5		5	98.2	54.5	55.4	8.3
6		4	97.5	36.6	37.5	13.6
7		4	57.1	14.4	25.2	14.7

Reaction conditions: 0.05 g KI, 0.15 g EtONa; epoxide, 30 mmol; ethanol, 27.6 g (600 mmol); CO₂ initial pressure, 3 MPa; reaction temperature, 443 K.

^a Yield based on external standard method.

^b Yield based the product peak area ratio by GC analysis.

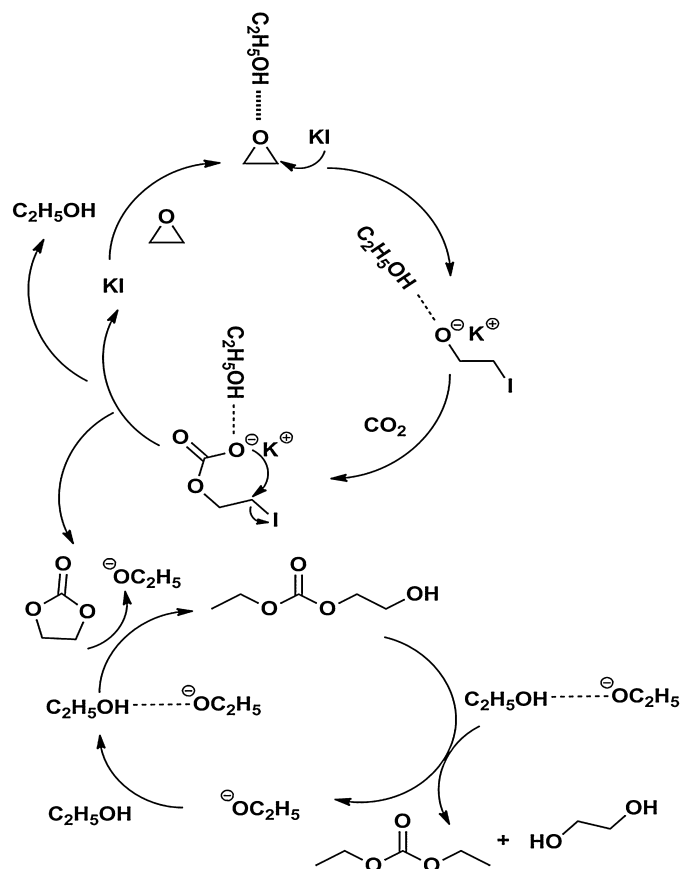
was irrespective of the kind of substitute, e.g. alkyl, phenyl, alkoxy substituted epoxides. Hence, the different substitutes did not have crucial impact on the DEC formation, and good yields can be obtained under reaction conditions. In addition, 36.6% of moderate DEC yield was obtained when glycidyl isopropyl ether was employed as substrate, entry 6.

Particularly, 14.4% of lowest DEC yield was obtained when using 1,2-epoxycyclohexane as substrate, entry 7. The low DEC yield might be attributed to its special molecular structure, which hampered the nucleophilic attack from iodine. As a result, the special structure with more hindrance decreased the rate of ring opening. Obviously, a large amount of 1,2-epoxycyclohexane was not efficiently converted, probably leading to insufficient intermediate of cyclic carbonate for subsequent transesterification reaction. Meanwhile, 2.1–31.2% yields of corresponding cyclic carbonates were also produced for the various epoxides, entries 1–7. In general, it can be concluded that this strategy can be successively expanded to terminal epoxide substrates, and those with less hindrance exhibit higher reactivity.

3.10. A plausible mechanism for the one-pot synthesis of diethyl carbonate in the presence of KI/EtONa

The plausible mechanism for the one-pot synthesis of diethyl carbonate from EO, CO₂ and ethanol in the presence of binary catalyst KI/EtONa is illustrated in Scheme 3. Based on the experimental results, the process is considered to be the integration of two-step reaction. For the first cycle, the reaction is initiated by hydrogen bonding between the hydrogen atom of hydroxy group in ethanol and oxygen atom of the epoxide, which could induce the activation of the epoxy ring [44–46,40]. Unlike the process of ethanolysis of EO to form EE, the proton transfer does not occur in this hypothesis. Simultaneously, the K⁺ cation stabilizes the anionic group via static electric interaction, followed by the ring opening step. Subsequently, I⁻ from KI attacks the carbon atom of the hydrogen bonded epoxide. Then, the oxygen anion of the opened epoxy ring interacts with the CO₂ to form an ethylcarbonate anion, which is converted into ethylene carbonate through the intramolecular ring closure step. Meanwhile, the KI and ethanol are completely

regenerated. It is worth mentioning that byproduct of EE is mainly formed through alcoholysis of the epoxide, suggesting it is competitive with cycloaddition reaction. This speculation can be confirmed by the reaction between ethanol and EO in the blank experiment,



Scheme 3. A plausible mechanism for the one-pot synthesis of diethyl carbonate from EO, CO₂ and ethanol in the presence of KI/EtONa.

as already discussed in catalyst screening section. Presumably, the reaction rate was greatly enhanced through the stabilization of the transition states with the assistance of ethanol, which accounts for the greatly enhanced catalytic performance.

The ternary synergistic performance of K^+ cation, the hydroxyl group, I^- anion is proposed to form an effective catalytic system. For the second cycle, after the cycloaddition reaction, the ethylene carbonate formed during the process is activated by $C_2H_5O-C_2H_5OH$, which originates from the interaction of basic $C_2H_5O^-$ anion and ethanol. The anionic group $C_2H_5O^-$ is released simultaneously with the formation of ethyl (2-hydroxyethyl) carbonate. Subsequently, the similar $C_2H_5O-C_2H_5OH$ attacks the methylene group at the side of $HOCH_2CH_2-$ group in ethyl (2-hydroxyethyl) carbonate, resulting in the production of diethyl carbonate and ethylene glycol. Eventually, the released $C_2H_5O^-$ reforms $C_2H_5O-C_2H_5OH$ with ethanol. With respect to the reaction mechanism, KI is the actual catalyst for the cycloaddition reaction and the catalytic activity is greatly promoted with the aid of ethanol, while the basic catalyst of sodium ethoxide is the valid component for the transesterification of EC to effectively produce DEC and EG.

4. Conclusions

In conclusion, a highly efficient approach to synthesize DEC directly from carbon dioxide, ethanol and EO was successively developed. Among the various catalysts tested, the integration of easily available KI and sodium ethoxide was found to be the most effective binary system for the one-pot reaction. The production of DEC can be maximized by optimizing reaction conditions, and the process can be performed efficiently under relatively mild conditions. Under optimized conditions, 63.6% of DEC yield and 68.5% of co-produced glycol yield with 97.5% EO conversion could be achieved at 443 K and 3 MPa CO_2 initial pressure within 2 h. To some extent, the catalyst could be basically recycled without significant decline of the catalytic activity. The thermodynamic evaluation showed that the reaction is exothermic ($\Delta_r H_m^\theta = -19.7 \text{ kcal/mol} < 0$). In comparison with the direct synthesis of DEC from CO_2 and ethanol, the involvement of EO greatly improved the formation of DEC since the equilibrium limitations were effectively overcome, simultaneously with the important chemicals of glycol co-produced. Based on the experimental results, the corresponding catalytic mechanism was proposed. For the first cycle, the reaction of EO and CO_2 occurred to form ethylene carbonate via cycloaddition reaction. In this step, ethanol was found to exhibit promotional effect, and the reaction proceeded very effectively. For the second cycle, the transesterification of EC with ethanol occurred to produce DEC and EG. Moreover, this strategy was also proved to be effective for other terminal epoxides and produced DEC efficiently, indicating the universality of this method. Compared with other current routes, this work has provided a facile route to synthesize DEC directly from CO_2 and shows promising application on an industrial scale with respect to the merits of high efficiency, energy saving and eco-friendly feature.

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References

- [1] T. Sakakura, J.C. Choi, H. Yasuda, *Chem. Rev.* 107 (2007) 2365–2387.
- [2] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, T.E. Müller, *Energy Environ. Sci.* 5 (2012) 7281–7305.
- [3] S.N. Riduan, Y. Zhang, *Dalton Trans.* 39 (2010) 3347–3357.
- [4] J. Ma, N. Sun, X. Zhang, N. Zhao, F. Xiao, W. Wei, Y. Sun, *Catal. Today* 148 (2009) 221–231.
- [5] E.A. Quadrelli, G. Centi, J.L. Duplan, S. Perathoner, *ChemSusChem* 4 (2011) 1194–1215.
- [6] I. Omae, *Coord. Chem. Rev.* 256 (2012) 1384–1405.
- [7] B. Schöffner, F. Schöffner, S.P. Verevkin, A. Börner, *Chem. Rev.* 110 (2010) 4554–4581.
- [8] W.L. Dai, S.L. Luo, S.F. Yin, C.T. Au, *Appl. Catal., A* 366 (2009) 2–12.
- [9] T. Sakakura, K. Kohno, *Chem. Commun.* (2009) 1312–1330.
- [10] J. Shang, S. Liu, X. Ma, L. Lu, Y. Deng, *Green Chem.* 14 (2012) 2899–2906.
- [11] B. Xue, J. Xu, P. Liu, L. Lv, C. Xu, Y. Li, K. Zhang, *J. Mol. Catal. A: Chem.* 357 (2012) 50–58.
- [12] P. Arockiam, V. Poirier, C. Fischmeister, C. Bruneau, P.H. Dixneuf, *Green Chem.* 11 (2009) 1871–1875.
- [13] I.E. Muskat, F. Strain, US Patent 2,379,250, 1941.
- [14] H.P. Luo, W.D. Xiao, *Chem. Eng. Sci.* 56 (2001) 403–410.
- [15] B.C. Dunn, C. Guenneau, S.A. Hilton, J. Pahnke, E.M. Eyring, J. Dworzanski, H.L.C. Meuzelaar, J.Z. Hu, M.S. Solum, P.J. Pugmire, *Energy Fuels* 16 (1) (2002) 177–181.
- [16] D.N. Briggs, K.H. Lawrence, A.T. Bell, *Appl. Catal., A* 366 (2009) 71–83.
- [17] D.N. Briggs, G. Bong, E. Leong, K. Oei, G. Lestari, A.T. Bell, *J. Catal.* 276 (2010) 215–228.
- [18] H. Xiong, W. Mo, J. Hu, R. Bai, G. Li, *Ind. Eng. Chem. Res.* 48 (2009) 10845–10849.
- [19] X.B. Ma, M.M. Fan, P.B. Zhang, *Catal. Commun.* 5 (12) (2004) 765–770.
- [20] L. Zhang, D. Niu, K. Zhang, G. Zhang, Y. Luo, J. Lu, *Green Chem.* 10 (2008) 202–206.
- [21] C. Hao, S. Wang, X. Ma, *J. Mol. Catal. A: Chem.* 306 (2009) 130–135.
- [22] D. Wang, B. Yang, X. Zhai, L. Zhou, *Fuel Process. Technol.* 88 (2007) 807–812.
- [23] H. An, X. Zhao, L. Guo, C. Jia, B. Yuan, Y. Wang, *Appl. Catal., A* 433–434 (2012) 229–235.
- [24] W. Wang, S. Wang, X. Ma, J. Gong, *Catal. Today* 148 (2009) 323–328.
- [25] O. Arbeláez, A. Orrego, F. Bustamante, A.L. Villa, *Top. Catal.* 55 (2012) 668–672.
- [26] M. Honda, S. Kuno, N. Begum, K. Fujimoto, K. Suzuki, Y. Nakagawa, K. Tomishige, *Appl. Catal., A* 384 (2010) 165–170.
- [27] E. Leino, P. Mäki-Arvela, K. Eränen, M. Tenho, D.Y. Murzin, T. Salmi, J.P. Mikkola, *Chem. Eng. J.* 176–177 (2011) 124–133.
- [28] E. Leino, P. Mäki-Arvela, V. Eta, N. Kumar, F. Demoisson, A. Samikannu, A.R. Leino, A. Shchukarev, D.Y. Murzin, J.P. Mikkola, *Catal. Today* 210 (2013) 47–54.
- [29] P. Qiu, L. Wang, X. Jiang, B. Yang, *Energy Fuels* 26 (2012) 1254–1258.
- [30] L. Jin, Y. Zhang, J.P. Dombrowski, C.H. Chen, A. Pravatas, L. Xu, C. Perkins, S.L. Suib, *Appl. Catal., B* 103 (2011) 200–205.
- [31] M. Tamura, S.M.A.H. Siddiki, K. Shimizu, *Green Chem.* 15 (2013) 1641–1646.
- [32] C. De, B. Lu, H. Lv, Y. Yu, Y. Bai, Q. Cai, *Catal. Lett.* 128 (2009) 459–464.
- [33] D.G. Cantrell, L.J. Gillie, A.F. Lee, K. Wilson, *Appl. Catal., A* 287 (2005) 183–190.
- [34] H.V. Lee, Y.H. Taufiq-Yap, M.Z. Hussein, R. Yunus, *Energy* 49 (2013) 12–18.
- [35] C. Ngamcharussrivichai, P. Nunthasanti, S. Tanachai, K. Bunyakiat, *Fuel Process. Technol.* 91 (2010) 1409–1415.
- [36] B.M. Bhanage, S. Fujita, Y. Ikushima, K. Torii, M. Arai, *Green Chem.* 5 (2003) 71–75.
- [37] Y. Kishimoto, I. Ogawa, *Ind. Eng. Chem. Res.* 43 (2004) 8155–8162.
- [38] J.S. Tian, C.X. Miao, J.Q. Wang, F. Cai, Y. Du, Y. Zhao, L.N. He, *Green Chem.* 9 (2007) 566–571.
- [39] Y. Zhang, Z. Ji, R. Xu, Y. Fang, *Chem. Eng. Technol.* 35 (4) (2012) 693–699.
- [40] J. Ma, J. Liu, Z. Zhang, B. Han, *Green Chem.* 14 (2012) 2410–2420.
- [41] H. Cui, T. Wang, F. Wang, C. Gu, P. Wang, Y. Dai, *Ind. Eng. Chem. Res.* 42 (2003) 3865–3970.
- [42] H. Cui, T. Wang, F. Wang, C. Gu, P. Wang, Y. Dai, *Ind. Eng. Chem. Res.* 43 (2004) 7732–7739.
- [43] J. Li, L. Wang, S. Liu, X. Li, F. Shi, Y. Deng, *Chem. Lett.* 39 (2010) 1277–1278.
- [44] B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, *Appl. Catal., A* 219 (2001) 259–266.
- [45] J.Q. Wang, J. Sun, C.Y. Shi, W.G. Cheng, X.P. Zhang, S.J. Zhang, *Green Chem.* 13 (2011) 3213–3217.
- [46] J. Tharun, G. Mathai, A.C. Kathalikkattil, R. Roshan, J.Y. Kwak, D.W. Park, *Green Chem.* 15 (2013) 1673–1677.