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RESEARCH ARTICLE

Synthesis of cyclic carbonates and dimethyl carbonate using CO_2 as a building block catalyzed by MOF-5/KI and MOF-5/KI/K_2CO_3

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The synthesis of cyclic carbonates or dimethyl carbonate (DMC) using CO_2 as a building block is a very interesting topic. In this work, we found that the metal-organic framework-5 (MOF-5)/KI was an active and a selective catalytic system for the synthesis of cyclic carbonates from CO_2 and epoxides, and MOF-5/KI/K_2CO_3 was efficient for the preparation of DMC from CO_2, propylene, and methanol by a sequential route. The impacts of temperature, pressure, and reaction time length on the reactions were investigated, and the mechanism of the reactions is proposed on the basis of the experimental results.

Keywords carbon dioxide, cyclic carbonates, dimethyl carbonate (DMC), metal-organic framework-5 (MOF-5), sequential route, propylene oxide

1 Introduction

Dimethyl carbonate (DMC) has attracted much interest as an excellent solvent, a promising gasoline octane enhancer, nontoxic carbonylation and methylation reagent in place of virulent phosgene and dimethyl sulfate, and precursor for polycarbonate resins [1–3]. DMC can be synthesized on an industrial scale by the phosgene process or by the oxidative carbonylation of methanol process (Fig. 1) [4,5]. Because phosgene is highly toxic and the by-product HCl causes serious corrosion, the phosgene process is gradually out of use. For the oxidative carbonylation process, carbon monoxide is used, which, however, is a hazardous gas. Therefore, the development of green and safe processes for the DMC production has been an interesting topic.

In recent years, the development of green processes to prepare DMC based on utilizing carbon dioxide (CO_2) has received much attention because CO_2 is an abundant carbon resource and a greenhouse gas and can be used as a safe and cheap C1 building block to produce useful organic compounds as well as a nontoxic reaction media [6–8]. There are mainly two routes for the synthesis of DMC using CO_2. The first is by means of the reaction of methanol and CO_2 [9–16]. The yield of DMC in this route is low because of the thermodynamic limitations of the reaction. The second route is through the two-step transesterification process (Fig. 2). However, the main drawback of this process is that separation of the cyclic carbonates is required. It is attractive to integrate the coupling reaction of CO_2 with epoxides and the transesterification of cyclic carbonate with methanol into a one-pot reaction, and some catalysts have been prepared for the one-pot reaction [17–23]. Unfortunately, the one-pot method could produce large amounts of by-products from the alcoholysis of epoxides (Fig. 3). Therefore, the development of new routes synthesizing DMC from CO_2 is desirable. Recently, a simple route, in which the coupling reaction and the transesterification reaction took place in sequence, has been developed by He et al. This route can avoid the alcoholysis of epoxides and get a higher DMC yield [24]. The development of effective catalytic systems is crucial for this route.

In recent years, metal-organic frameworks (MOFs), which were formed by copolymerization of organic molecules with metal ions or metal ion clusters, have received much attention because of their zeolite-like properties, such as high internal surface area and microporosity, well-ordered porous structures, and high absorption capacity [25–29]. Various applications of MOFs, such as gas storage [30–32] and separation [33,34], have been studied. Applications of MOFs in catalysis have also been explored [35–47]. However, the exploration of their applications in different reactions is yet interesting.

MOF-5 [$Zn_4O(BDC)_3$, BDC = benzene-1,4-dicarboxylate] is a commonly used MOF. In this work, we studied the catalytic performance of MOF-5/KI/K_2CO_3 system for the synthesis of DMC from CO_2, propylene oxide, and methanol by a sequential route. It was demonstrated that the catalyst system could effectively catalyze both the coupling reaction of CO_2 with epoxides to the corresponding cyclic carbonates and the transesterification reaction of propylene carbonate with methanol to DMC and propylene glycol, achieving a high yield of DMC. We believe that this simple and cheap route to synthesize DMC has a great potential in industrial application.

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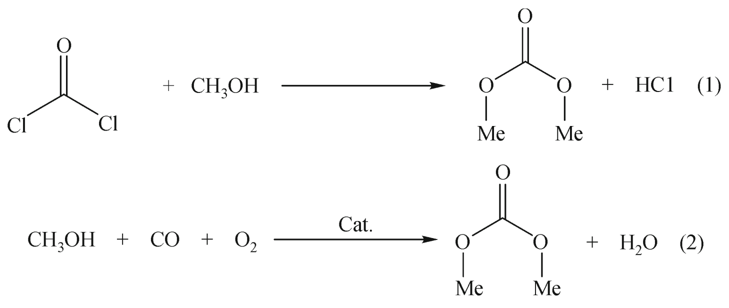


Figure 1 The phosgene process (1) and the oxidative carbonylation process (2).

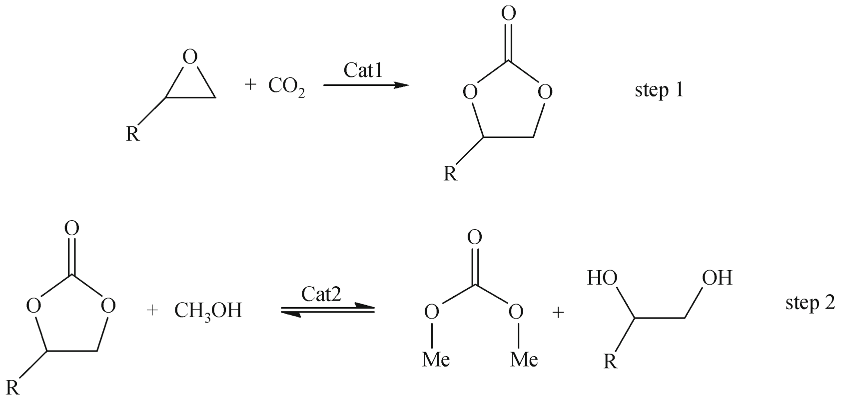


Figure 2 The two-step transesterification process.

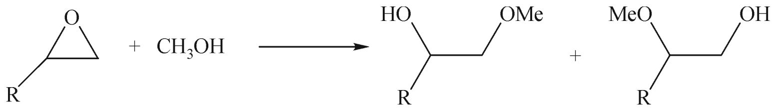


Figure 3 The alcoholysis of epoxides.

2 Experimental

2.1 Material and apparatus

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.99%. Propylene oxide (PO), methanol, epichlorohydrin, $Zn(NO_3)\cdot 6H_2O$, KI, KCl, KBr, K_2CO_3, ZnO, and triethylamine that were of analytical grade were provided by Beijing Chemical Reagents Company. Benzene-1, 4-dicarboxylic acid was of analytical grade and was provided by Aldrich Chemical Company. Other epoxides were purchased from ACROS ORGANICS. All chemicals were used as received.

Thermogravimetric (TG) analysis of MOF-5 was performed on NETZSCH STA 409 PC/PG thermogravimetric analysis system in N_2 atmosphere at a heating rate of $20°C\cdot min^{-1}$. The X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (D/MAX-RC) operated at 40 kV and 200 mA with Cu Kα radiation. Fourier transform infrared (FTIR) spectra were determined using a Bruker Tensor 27 spectrometer, and the sample was prepared by KBr pellet method.

2.2 Preparation of MOF-5

The procedures to prepare MOF-5 were similar to that reported in Ref. [48]. Briefly, $Zn(NO_3)\cdot 6H_2O$ (1.21 g, 4 mmol), benzene-1,4-dicarboxylic acid (0.32 g, 2 mmol), and 40 mL N,N-dimethylformamide were added into a 100-mL flask equipped with a magnetic stirrer. The flask was put into an oil bath at 60°C. Then, triethylamine (1.6 g) were added into the mixture. The mixture was maintained at 60°C for 4 h with stirring. The formed MOF-5 was collected by filtration, washed using N, N-dimethylformamide, and then dried at 60°C for 12 h under a vacuum. X-ray diffraction patterns, thermograms, and FTIR spectra of the MOF-5 prepared in this work agree well with those reported by other authors [48].

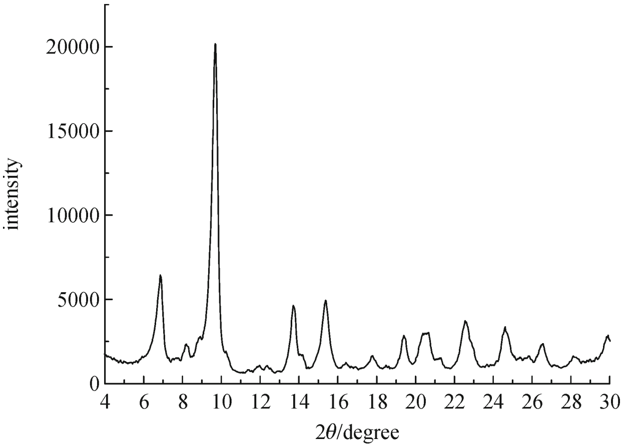
2.3 Typical procedures for DMC synthesis from propylene oxide, CO_2,and methanol

In a typical reaction, the cycloaddition reaction of CO_2 and propylene oxide was conducted in a 22 mL stainless steel reactor equipped with a magnetic stirrer. In the reaction, propylene oxide (20 mmol), 0.5 mmol KI, 0.5 mmol K_2CO_3, and 0.1 g MOF-5 were added into the reactor. After it was sealed, the reactor was put into a constant-temperature air bath of 90°C. CO_2 was then charged into the reactor to a pressure of 4 MPa, and the stirrer was started. After a reaction time of 2 h, the reactor was placed into ice water, and the excess CO_2 was released slowly. After that, 200 mmol methanol was added into the reactor, and the reactor was placed into a constant-temperature air bath of 130°C. The transesterification reaction was carried out for 2 h. When the reactor was cooled to room temperature, *n*-butanol was added into the reactor as an internal standard. The reaction mixture was analyzed by GC (Agilent 6820) equipped with a flame-ionized detector and further identified by GC–MS.

3 Results and discussion

3.1 Catalyst characterization

The powder XRD pattern of the MOF-5 is given in Fig. 4, which agreed perfectly with the result reported by Huang et al. [48]. MOF-5 has good thermal stability, as can be learned from the thermogram shown in Fig. 5. The weight loss below 280°C resulted from the occluded solvent DMF and water. MOF-5 began to decompose above 380°C, which is much higher than the reaction temperatures of the cycloaddition reaction (90°C) and the transesterification reaction (130°C). The FTIR spectrum of the MOF is provided in Fig. 6. IR spectra show the expected strong characteristic adsorptions for the symmetric and asymmetric vibrations of BDC (1610 – 1550 $cm^{-1}$and 1420 – 1335 cm^{-1}) and adsorbed water (3500 – 3200 cm^{-1}). There were no absorptions of protonated BDC (1715 – 1680 cm^{-1}), which confirmed complete deprotonation of H_2BDC by TEA in MOF-5.



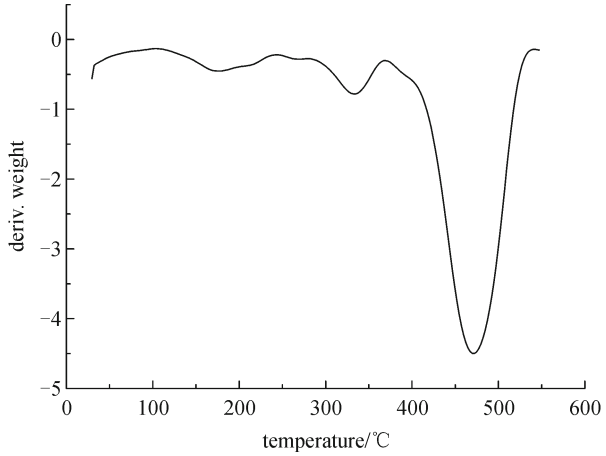


Figure 5 Thermogram of MOF-5.

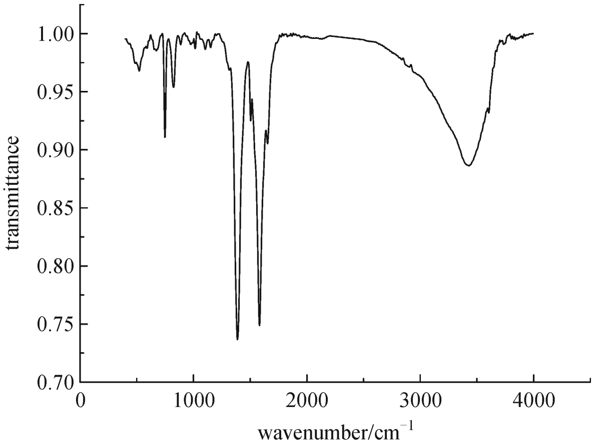


Figure 6 FTIR spectra of MOF-5.

3.2 Cycloaddition of CO_2 with epoxides

First, the activity of different catalysts was tested using the reaction of PO and CO_2 to produce propylene carbonate (PC), and the results are summarized in Table 1. When we used only KI as a catalyst, the yield of PC was low (entry 1). MOF-5 itself was not active (entry 2). In the presence of various potassium salts, MOF-5 could catalyze the coupling reaction, and MOF-5/KI was the most effective (entries 3–7). The different activity of various catalyst systems could result from the nucleophilicity and leaving ability of the counter-anion of different potassium salts. In addition, it can be observed that MOF-5 has a higher activity than ZnO, and the reason may be

Table 1 Coupling of CO_2 and propylene oxide catalyzed by different catalysts[a)]

entry	catalyst	yield/%[c)]
1	KI	0.1
2[b)]	MOF-5	0
3[b)]	MOF-5 + KOH	0.1
4[b)]	MOF-5 + K_2CO_3	0.1
5[b)]	MOF-5 + KCl	0.2
6[b)]	MOF-5 + KBr	1.2
7[b)]	MOF-5 + KI	98
8[b)]	ZnO + KI	5
9[d)]	MOF-5 + KI + K_2CO_3	98
10	MOF-5(2nd) + KI(fresh)	98
11	MOF-5(3rd) + KI(fresh)	98

a) Typical reaction conditions were a stainless autoclave of 22 mL, 20 mmol PO with 2.5 mol% catalyst, CO_2 pressure 6 MPa, reaction temperature 90°C, and reaction time 2 h.
b) 0.1 g MOF-5 or ZnO was added.
c) Yields were determined by GC versus an internal standard.
d) The amount of K_2CO_3 added was 2.5 mol%.

that MOF-5 is a porous material with high surface area [48], which makes for the access of reactants to the active sites (Zn_4O) of MOF-5. To examine the effect of K_2CO_3 on the coupling reaction catalyzed by MOF-5/KI, we used MOF-5/KI/K_2CO_3 to conduct the cycloaddition of CO_2 and PO (entry 9). The result showed that K_2CO_3 did not affect the activity of MOF-5/KI.

The reusability of the MOF-5 was also studied at the reaction condition used in entry 7, and the results are also summarized in Table 1 (entries 10, 11). Obviously, the activity and selectivity of the MOF-5 remained after reusing for three times.

The pressure of CO_2 is an important reaction parameter for the coupling reaction of CO_2 with epoxides. To study the effect of CO_2 pressure on PC yield, the reaction was conducted with MOF-5/KI catalyst system at 90°C within the pressure range of 2–12 MPa for 2 h, and the results are shown in Fig. 7. It can be learned in Fig. 7 that CO_2 pressure had little effect on the PC yield at low CO_2 pressure (2–6 MPa), and then, the yield of the PC decreased with the pressure increase (from 6 MPa to 12 MPa). The main reason for this may be that MOF-5 is a good absorbent, and concentrations of PO and CO_2 in the vicinity of the catalyst were high enough at low pressure. However, more PO was extracted into the CO_2-rich phase at higher pressures because the solvent power of CO_2 increases with pressure, which reduced the concentration of PO in the vicinity of the catalyst. Therefore, the yield decreased with increasing pressure at higher pressures.

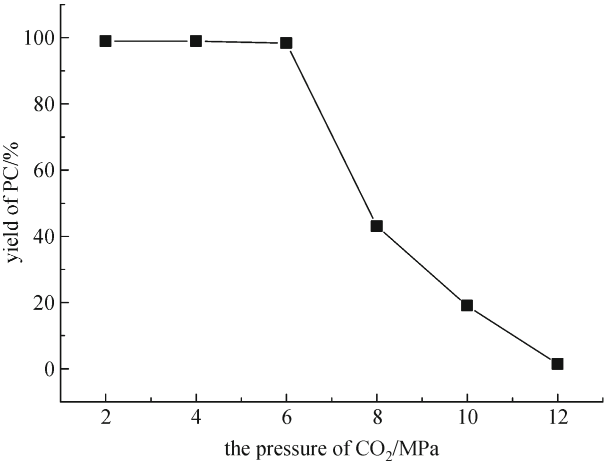


Figure 7 The effect of CO_2 pressure on PC yield. Reaction conditions were 20 mmol PO with 2.5 mol% KI, 0.1 g MOF-5, reaction temperature 90°C, and reaction time 2 h.

Figure 8 demonstrates the dependence of the yield of PC on the temperature at CO_2 pressure of 6 MPa within the temperature range of 60°C–110°C, and the reaction lasted for 2 h. It was shown that the activity of the catalyst was strongly affected by the reaction temperature. The yield of PC increased with increasing temperature, and it reached 98% at 90°C. Then, the PC yield was kept almost constant with the further increase of the temperature, hinting that 90°C is the optimal temperature for the reaction under our reaction conditions.

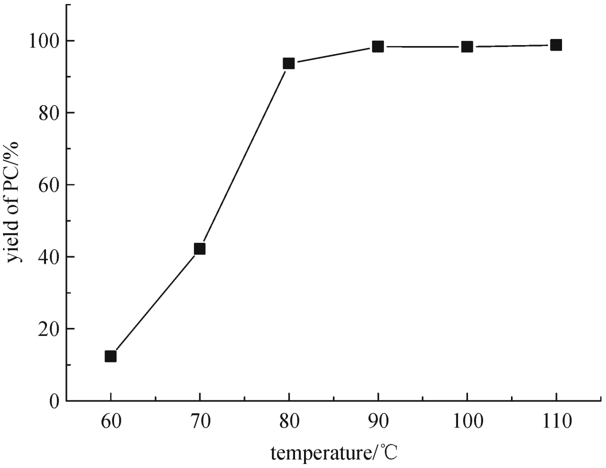


Figure 8 The effect of reaction temperature on PC yield. Reaction conditions were 20 mmol PO with 2.5 mol% KI, 0.1 g MOF-5, CO_2 pressure 6 MPa, and reaction time 2 h.

The influence of reaction time on PC yield is given in Fig. 9. The coupling reaction was conducted at 90°C and 6 MPa of CO_2. It can be seen in Fig. 6 that the conversion of PO was incomplete, and the PC yield was low at short reaction time. The yield of PC could reach 98% at 2 h. No obvious increase in the PC yield was observed with prolonged reaction time, indicating that the reaction time of 2 h was suitable for our catalyst system.

Under the catalyst system of MOF-5/KI, coupling reactions of CO_2 with different epoxides (Fig. 10) were also studied at 6 MPa without using any solvent, and the results are summarized in Table 2. The results showed that the catalyst system was active for all epoxides studied. PO (Table 1, entry 7) and glycidyl phenyl ether (Table 2, Entry 1) were the most active substrates and yielded a large amount of the corresponding cyclic carbonates in a short reaction time. Epichlorohydrin (Table 2, Entry 2) showed less activity and required a longer time (4 h) for obtaining high yield (94%) of the desired product, which may result from the reduced electron density of the epoxide oxygen atom caused by the electron-withdrawing CH_2Cl group. A much longer reaction time (7 h) was needed to get a high product yield (95%) when styrene oxide (Table 2, Entry 3) was used as substrate, which is probably due to the low reactivity of its β-carbon center. Among the substrates used, cyclohexene oxide (Table 2, Entry 4) showed the lowest activity for coupling with CO_2 among the substrates used. Only 20% yield of product was achieved when the reaction was carried out at 90°C for 24 h. The poor reactivity results mainly from the high steric hindrance.

Based on the results discussed above, we propose a plausible mechanism for this chemical fixation reaction (Fig. 11). The coupling reaction is initiated by coordination of Zn_4O clusters in MOF-5 as a Lewis acidic site with the oxygen atom of epoxide. Second, the I^- generated from KI attacks the less-hindered carbon atom of the coordinated epoxides, followed by ring opening step. Then, the interaction occurred between the oxygen anion of the opened epoxy ring

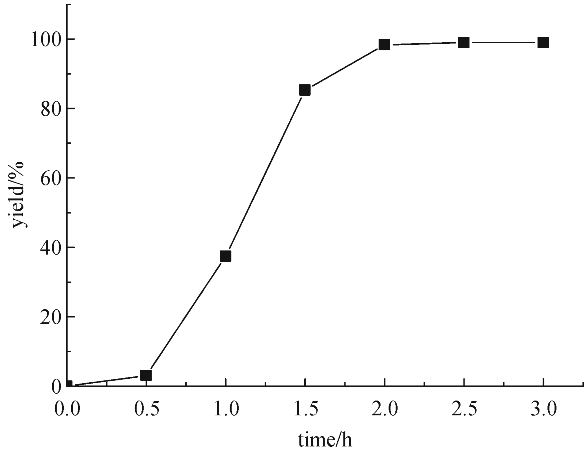
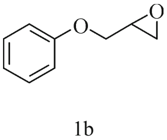
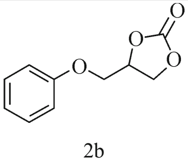
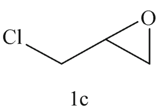
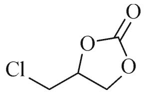
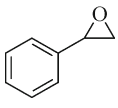
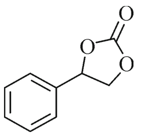
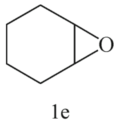
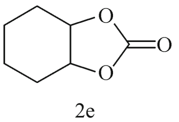


Figure 9 The influence of reaction time on PC yield. Reaction conditions were 20 mmol PO with 2.5 mol% KI, 0.1 g MOF-5, CO_2 pressure 6 MPa, and reaction temperature 90°C.

a: R = CH_3, b: R = $PhOCH_2$, c: R = $ClCH_2$, d: R = Ph, e: R = $-(CH_2)_4-$

Figure 10 Coupling of CO_2 with different epoxides.

Table 2 Various carbonates synthesis catalyzed by MOF-5 in the presence of KI [a)]

entry	epoxides	products	time/h	yield/%
1	 1b	 2b	2	97
2	 1c	 2c	4	94
3	 1d	 2d	7	95
4	 1e	 2e	24	20

a) Reaction conditions were epoxide 20 mmol with 2.5 mol% KI, 0.1 g MOF-5, CO_2 pressure 6 MPa, and reaction temperature 90°C.

and CO_2, and this can form an alkylcarbonate anion, which is converted into the corresponding cyclic carbonate through the ring close step.

3.3 Transesterification of PC with methanol

Transesterification of cyclic carbonate with methanol, the second step reaction in Fig. 2, is one of the important routes to produce DMC. We examined the activity of various catalysts for the reaction of PC with methanol, and the results are summarized in Table 3. All the catalyst systems with K_2CO_3 showed good activity. We chose the MOF-5/K_2CO_3 system to study the influence of other conditions on DMC yield. The effect of reaction time on the DMC yield using MOF-5/K_2CO_3 system is shown in Fig. 12. The yields of DMC and propylene glycol (PG) increased with increasing reaction time in the beginning and became constant after 2 h. This implies that the transesterification reaction reached an equilibrium after 2 h under the reaction conditions. We also studied the effect of reaction temperature on the DMC and PG yields, and the results are shown in Fig. 13. As reaction temperature was increased, the DMC and PG yields increased within the temperature range studied.

The molar ratio of methanol to PC is an important reaction parameter as transesterification is a reversible reaction. The yield of the reaction at different methanol to PC molar ratios is summarized in Table 4. As expected, the yield increased with increasing methanol to PC ratio.

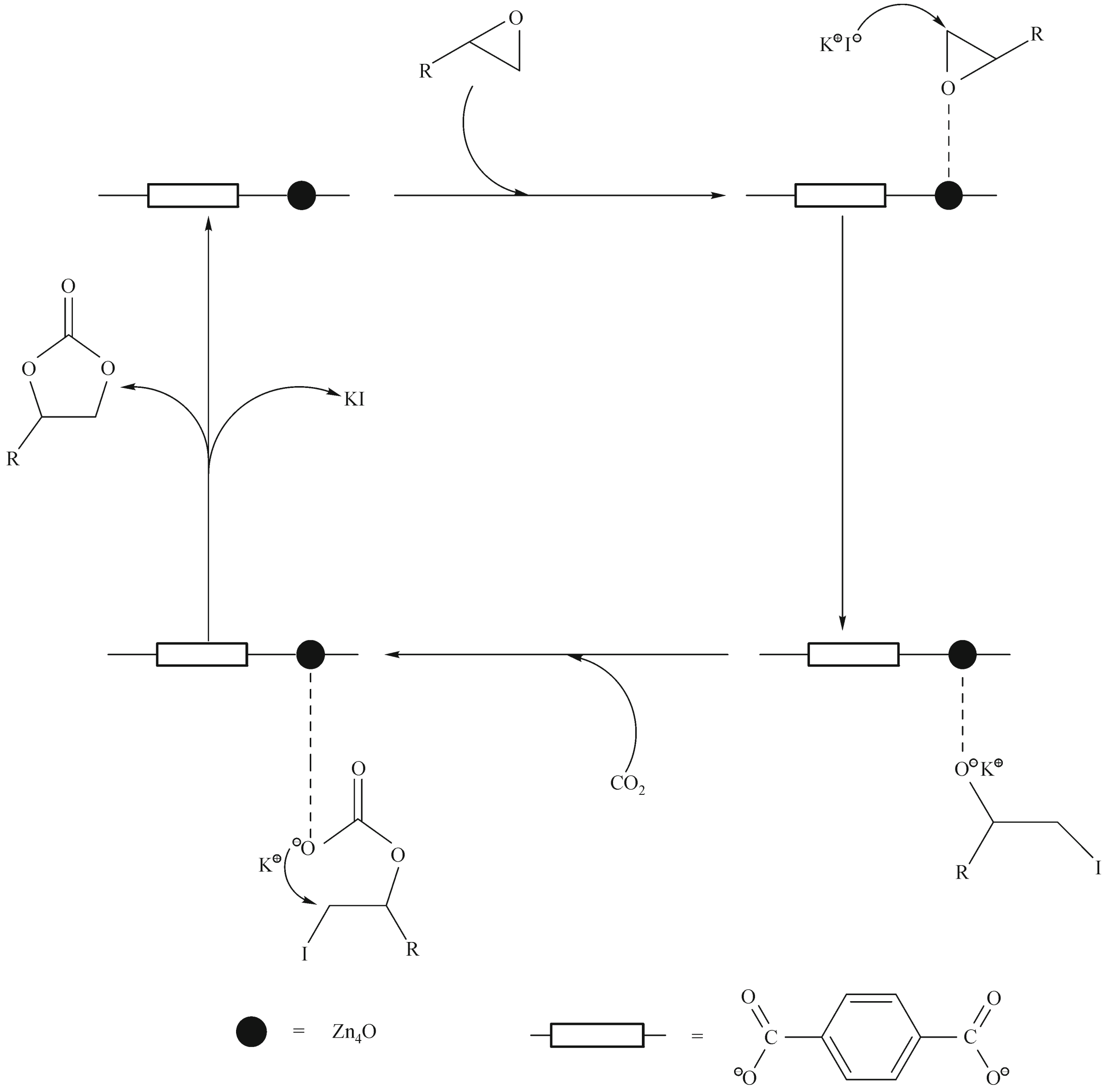


Figure 11 A plausible reaction mechanism for the coupling reaction of CO_2 with epoxide catalyzed by MOF-5 and KI.

Table 3 Transesterification of PC and methanol[a)]

entry	catalyst	PC conversion/%	yield/%[b)]	
			DMC	PG
1[c)]	KI	17	17	17
2[c)]	K_2CO_3	63	60	63
3[d)]	MOF-5	16	15	16
4[c), d)]	MOF-5 + KI	7	6	7
5[c), d)]	MOF-5 + K_2CO_3	64	60	63
6[c), d)]	MOF-5 + K_2CO_3 + KI	63	60	62

a) The typical reaction conditions were a stainless autoclave of 22 mL, 20 mmol PC, 0.2 mol methanol, reaction temperature 130°C, and reaction time 2 h.
b) Yields were determined by GC versus an internal standard.
c) 2.5 mol% KI or/and K_2CO_3 was added.
d) The amount of MOF-5 was 0.1 g.

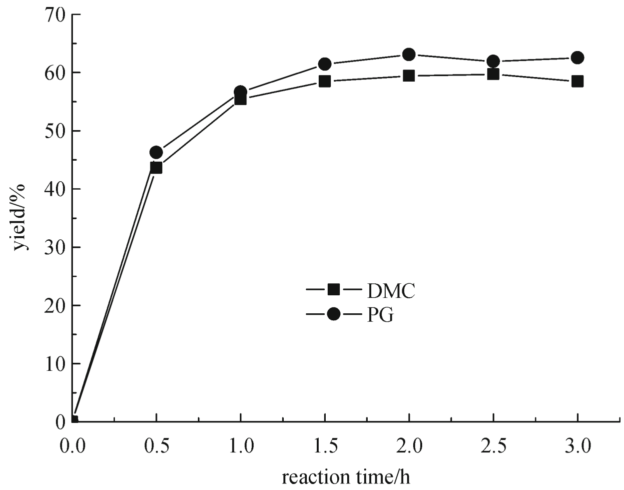


Figure 12 Influence of reaction time on the transesterification reaction of PC and methanol. Reaction conditions are 20 mmol PC with 2.5 mol% K_2CO_3, 200 mmol methanol, 0.1 g MOF-5, and reaction temperature 130°C.

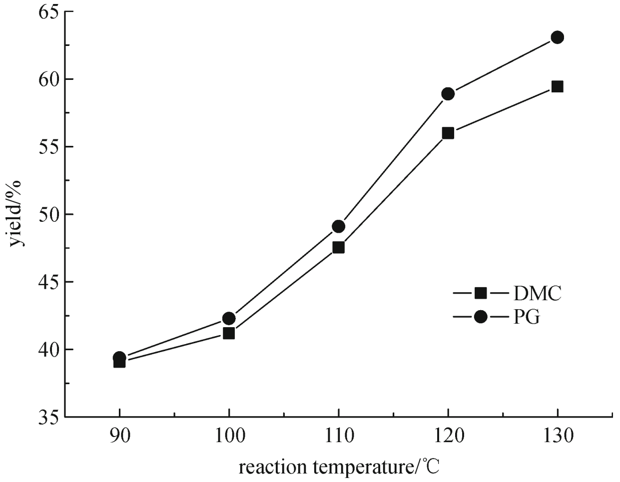


Figure 13 Influence of reaction time on the transesterification reaction of PC and methanol. Reaction conditions are 20 mmol PC with 2.5 mol% K_2CO_3, 200 mmol methanol, 0.1 g MOF-5, and reaction time 2 h.

3.4 DMC synthesis from CO_2, propylene oxide and methanol by a sequential route

To select a suitable route for our catalyst system MOF-5/KI/K_2CO_3, we conducted the reaction under various routes, and the results are shown in Table 5. The one-pot route (entries 1–7) produced a large amount of by-products, and the DMC yield was low. When the reaction was conducted under a sequential route (Fig. 14), there were no by-products produced, and the DMC yield was high (entry 8).

3.5 Reaction mechanism by a sequential route

Based on the above results, we proposed a plausible mechanism for the DMC synthesis by a sequential route (Fig. 15). First, propylene carbonate was formed from the coupling reaction CO_2 and propylene oxide catalyzed by MOF-5/KI. Then, the formed PC reacted with methanol in the presence of K_2CO_3 to form DMC.

4 Conclusion

MOF-5/KI system could catalyze the cycloaddition of CO_2 and PO to produce PC effectively, and a yield of 98% can be achieved at 90°C within the pressure range of 2–6 MPa with a reaction time of 2 h. The catalytic system is also efficient for the cycloaddition of CO_2 and epoxides, and high yields can be obtained under suitable conditions. MOF-5/KI/K_2CO_3 system is efficient for the preparation of DMC from CO_2, propylene, and methanol by a sequential route, and the selectivity for the desired products can be 100% under suitable conditions. We believed that the highly efficient catalytic systems have a

Table 4 The effect of molar ratio of methanol to PC on the yield of DMC and PG[a)]

entry	molar ratio of methanol to PC	PC conversion/%	yield/%[b)]	
			DMC	PG
1	5	47	43	45
2	10	64	60	63
3	15	71	67	68
4	20	76	75	76

a) Typical reaction conditions were a stainless autoclave of 22 mL, 4.9 wt% MOF-5 of PC, 2.5 mol% K_2CO_3, reaction temperature 130°C, and reaction time 2 h.
b) Yields were determined by GC versus an internal standard.

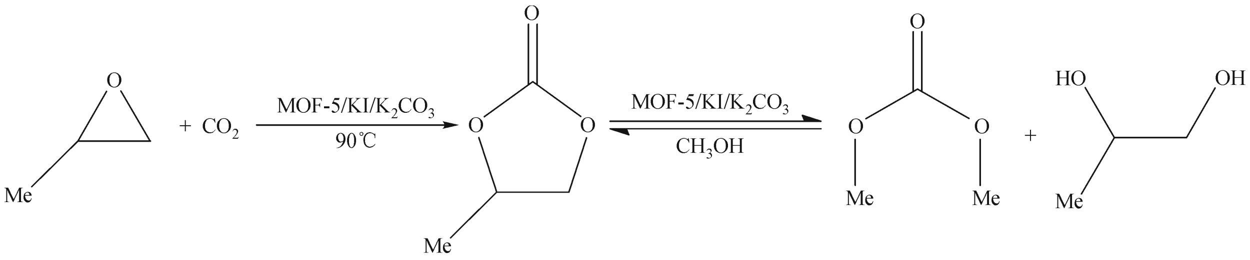
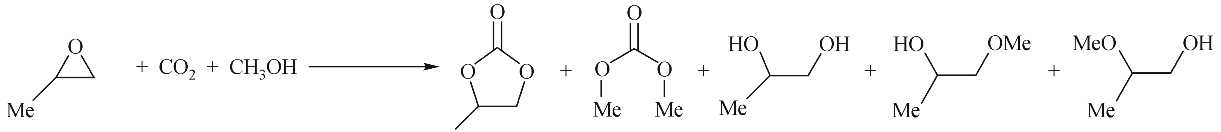


Figure 14 DMC synthesis from CO_2, propylene oxide, and methanol by a sequential route.

Table 5 Different reaction routes



1 2 3 4 5 6

entry[a)]	yields/%[b)]			
	PC	PG	DMC	5 + 6
1[c), d)]	94	0.3	0.4	3
2[c), e)]	93	1.3	1.1	3.4
3[c), f)]	90	2.5	2.6	3.5
4[c), g)]	89	5.0	5.5	3.7
5[c), h)]	70	17.3	15.3	9.8
6[c), i)]	71	22.4	21.3	4.4
7[j)]	85	10	9.8	3.3
8[k)]	40	57.6	57	0

a) All reactions were conducted under the conditions as follows: a stainless autoclave of 22 mL, 2.5 mol% K_2CO_3, 2.5 mol% KI, and CO_2 pressure 4 MPa.
b) Yields were determined by GC versus an internal standard.
c) The conditions used were 0.05 g MOF-5, reaction time 4 h, 10 mmol PO, and 100 mmol CH_3OH.
d) Reaction temperature was 90°C.
e) Reaction temperature was 100°C.
f) Reaction temperature was 110°C.
g) Reaction temperature was 120°C.
h) Reaction temperature was 130°C.
i) Reaction temperature was 140°C.
j) The conditions used were 0.05 g MOF-5, 10 mmol PO, 100 mmol CH_3OH, 2 h at 90°C, and then 2 h at 130°C.
k) The conditions used were 0.1 g MOF-5, 20 mmol PO and 2 h at 90°C, and after depressurization, 200 mmol CH_3OH was added into the autoclave and then reacted at 130°C for 2 h.

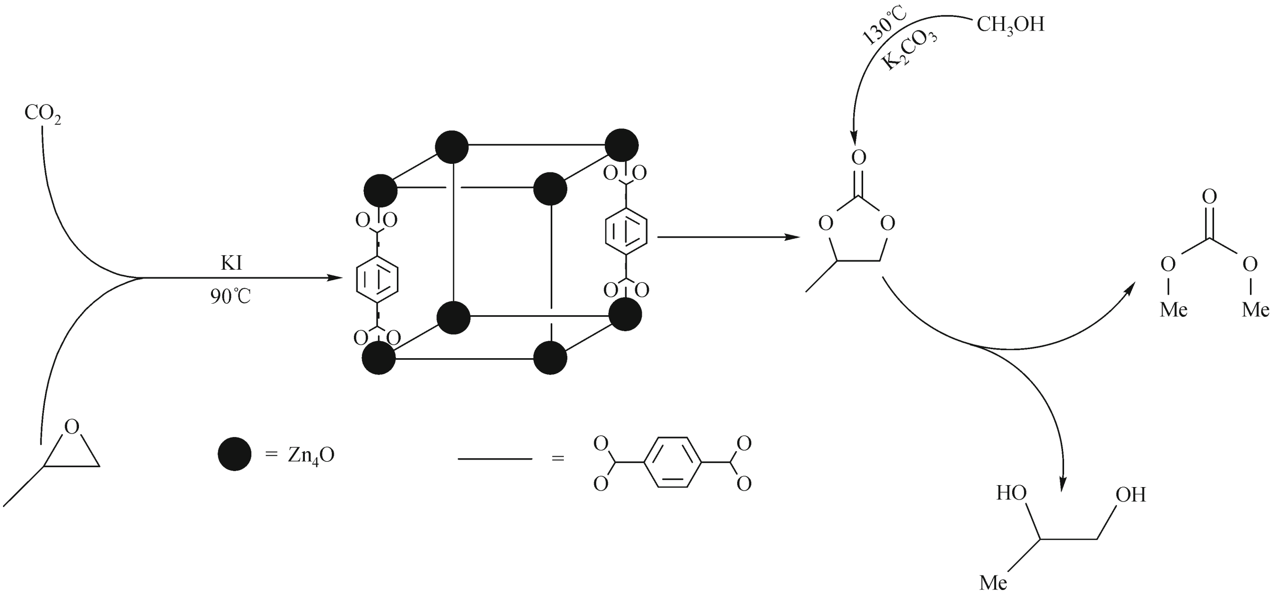


Figure 15 A plausible reaction mechanism by a sequential route.

potential application in the synthesis of the corresponding chemicals.

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