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One-pot synthesis of dimethyl carbonate from carbon dioxide, cyclohexene oxide, and methanol

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Abstract Dimethyl carbonate (DMC) and 1,2-cyclohexanediol (CHD) were directly synthesized by using K_2CO_3 from cyclohexane oxide (CHO), CO_2, and CH_3OH. K_2CO_3 and corresponding potassium-based catalysts were explored in the reaction system for the first time. The reaction was controlled by two mechanisms (the direct alkoxide and polymer dissociation mechanisms) under different reaction temperatures. The best catalytic performance with 95.7 % CHO conversion and a maximum of Y_{DMC} and Y_{CHD} were 55.4 and 63.4 %, respectively, which were obtained using K_2CO_3 as the catalyst under optimized reaction conditions. This approach is effective for producing DMC and CHD due to its easy operation, fewer hybrid ion introductions, and low cost of the catalyst.

Introduction

Dimethyl carbonate (DMC) is one of the important chemicals that exhibit numerous chemical reaction activities and unique physical properties such as low toxicity and excellent biodegradability. By 2013, the worldwide production capacities of DMC have been increased to more than 1 million tons. Besides its application in the

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synthesis of polycarbonate resin, DMC is a friendly green reagent that could be an alternative for dimethyl sulfate or phosgene in methylation and carbonylation, respectively [1–3]. DMC can also be used as a fuel additive and battery electrolyte [1]. To date, the potential method of DMC synthesis makes use of abundant, nontoxic, and renewable CO_2 as carbon resource, which is a prerequisite for green chemistry [4]. DMC has been directly synthesized from CO_2 and CH_3OH since the 1980s. This synthesis results in low yields (lower than 10 %) because of thermodynamic limitations [5]. Coupling reagents such as epoxides can change the reaction path to relax the thermodynamic limitation and improve the DMC yield. *Vic*-diol can also be generated, which can be extensively used as chemical intermediates. The reaction is accomplished by cycloaddition and transesterification. The integration of two processes into a one-pot reaction is preferred to avoid high intermediate investment and separation. Among the catalysts in the one-pot method, alkali metal salts are often dissolved in CH_3OH solvent and *vic*-diol to form a homogeneous system under reaction conditions. Although a homogeneous reaction causes difficulties in catalyst separation, the reaction rate of a homogeneous reaction is high and industrialization is more likely to be achieved with the low cost of the catalysts. K salts, such as K_2CO_3 and KI [6, 7] are ideal for this reaction. For example, the use of a KI/K_2CO_3 mixture for DMC synthesis from CO_2, CH_3OH, and ethylene oxide results in a DMC yield above 73 % at 100 % ethylene oxide conversion [8].

This study used cyclohexene oxide (CHO) as the coupling agent to generate both DMC and 1,2-cyclohexanediol (CHD). In addition to DMC, CHD is also an important chemical raw material for producing unsaturated polyester resin and pharmaceutical intermediates [9]. Especially, CHD can change into cyclohexanone catalyzed by Pd/C with high yields, which is the most important material for the synthesis of nylon-66 and Caprolactam [10]. CHO is the model compound of alicyclic epoxides published in previous studies, such as polyester by direct copolymerization and cyclohexene carbonate ester (CHC) by cycloaddition through CHO/CO_2 [11, 12]. Some recyclable catalysts, such as triazine-based covalent organic frameworks [13] or MCM-41 grafted quaternary ammonium salts [14], were used for the DMC synthesis, but the very low yield of DMC obtained via one-pot or two-step processes maybe due to the steric hindrance of the CHO. In addition, Li et al. [15] investigated the one-pot synthesis of DMC catalyzed by the ionic liquid [$N_{114,\ 6N11}$]Br via $CHO/CO_2/CH_3OH$ at 150 °C for 8 h, thus resulting in a DMC yield of 38.7 %. The high cost of the two-step reaction and the complex structure of the catalysts make K_2CO_3 a cheaper and more efficient catalyst for DMC synthesis. The purpose of this paper is to investigate DMC synthesis with $CO_2/CHO/CH_3OH$ catalyzed by using K_2CO_3. The experimental results provide further proposals on reaction mechanisms.

Experimental

Materials and equipment

CO_2 (>99 %) was purchased from Tianjin Ganda Gas (China). All other chemicals were of reagent grade and were directly used as purchased from Tianjin Jiangtian

Chemical Reagent Factory (China). The 100-ml autoclave was equipped with a constant temperature controller ($\pm$0.2 K), a pressure gauge ($\pm$0.02 MPa), and a magnetic stirrer.

General process

A typical procedure of DMC synthesis was as follows: CHO (50 mmol, 4.90 g), CH_3OH (250.0 mmol, 10.10 ml), and K_2CO_3 (2.0 mmol, 0.28 g) were mixed in the stainless steel autoclave. After using N_2 to replace the air, CO_2 was charged and adjusted to 2.60 MPa. The resulting suspension was stirred vigorously at 150 °C for 6 h. After completion of the reaction, the reactor was cooled to room temperature, and CO_2 was slowly released to the atmosphere. The products were determined by gas chromatography (GC) with a flame ionization detector and capillary column (PEG-20000). The conversion of CHO (C_{CHO}) and the selectivity and yield of DMC and CHD (Y_{DMC}, Y_{CHD}, S_{CHD}, and S_{DMC}) were calculated based on the CHO as a limited reactant.

Results and Discussion

Effects of different catalysts

Some products, such as DMC, *vic*-diol, alcoholysis products, cycloalkenyl carbonate esters, and copolymers, during DMC synthesis from $CH_3OH/CO_2/$ epoxides, have been reported in the numerous literature [12, 15–18]. Our experimental results show that the main substances in the reaction mixture were DMC, CHD, and 2-methoxycyclohexanol (MCH), in addition to small amounts of CHC and low polyether. These substances were determined by GC with authentic samples, GC/mass spectrometry, and [13] C NMR spectroscopy (see Supporting information S1) [15, 19].

K salts have many advantages such as low cost, good compatibility, and high catalytic efficiency. Table 1 lists some of the tested acidic, neutral, and alkali K salts at 150 °C under 2.60 MPa CO_2 for 6 h. C_{CHO}, Y_{DMC}, and Y_{CHD} were low without any catalyst but improved greatly with the addition of different K catalysts. The metholysis reaction is the main reaction in the absence of a K catalyst. The results show that the catalytic activity order of neutral halide K salts is KI > KBr > KCl. The byproduct MCH also increased with the same order. This order is in accordance with the halide ion solubility and nucleophilic and dissociated abilities [16]. Unfortunately, both neutral salt KNO_3 and weak acidic KHP also have poor CHD and DMC yields with rich metholyis of CHO. In addition, high Y_{MCH} (>20 %) takes place catalyzed by these above-mentioned salts, which indicates that the low yields of DMC might be due to a lack of basicity and the dissolved abilities in the CH_3OH solvent.

Compared with the former catalysts, the last four catalysts do not introduce hybrid ions into the reaction system and are inductive to the post-proceeding process. With the basicity increased from $KHCO_3$ and K_2CO_3 to CH_3OK, the

Table 1 DMC and CHD synthesis from CHO/CO$_2$/CH$_3$OH with different catalysts

Catalysts	C_{CHO} %	Y_{DMC} %	Y_{CHD} %	Y_{MCH} %
–	36.3	1.9	1.4	31.2
KCl	56.3	14.9	26.0	24.5
KBr	64.7	19.0	30.9	23.5
KI	88.4	21.3	29.1	20.7
KNO$_3$	63.3	14.2	13.9	38.5
KHP[a]	53.9	19.3	19.2	30.2
KHCO$_3$	56.2	36.7	38.4	10.1
K$_2$CO$_3$	81.0	38.7	41.5	12.9
CH$_3$OK[b]	84.5	54.4	64.4	17.9
KOH	73.0	28.6	33.6	21.8

50.0 mmol CHO, 250.0 mmol CH$_3$OH, 2.60 MPa CO$_2$, 1.0 mmol catalyst; 150 °C, 6 h

[a] Potassium hydrogen phthalate

[b] Particle size of CH$_3$OK is below 200 mesh and the other catalysts are 50–100 mesh

catalytic reaction yields are gradually improved. This finding demonstrates that the catalyst basicity facilitates the generation of the desired products. Compared with these catalysts, KI exhibited high catalytic activity during the cycloaddition process but did not have an obvious effect on transesterification compared with K$_2$CO$_3$ or CH$_3$OK [20]. Thus, the conversion of CHO is high but the yields of DMC and CHD are poor. Transesterification from CHC to DMC is improved by using the strong alkali. In contrast to the former three catalysts with organic structures, KOH is a typical inorganic strong base with a weak catalytic effect. In summary, CH$_3$OK with 200 mesh has the best catalytic result with the highest DMC yield of 54.4 %, but it suffers many disadvantages, such as high cost, high corrosion, and moisture sensitivity, as well as high flammability. From the prospect of industrialization, K$_2$CO$_3$ is considered to be the best commercial catalyst in terms of catalytic efficiency, cost, safety, source, etc.

Effect of temperature

Generally, temperature has a significant influence on the reaction rate. The effect of reaction temperature was examined between 90 and 180 °C for 6 h at 2.60 MPa CO$_2$. The results, such as C_{CHO}, Y_{DMC}, Y_{CHD}, and S_{DMC}, are shown in Fig. 1. CHO conversion increases sharply with increasing temperature before a stabilizing platform was observed. The Y_{DMC} and Y_{CHD} initially increase and then decrease in parallel. Apparently, the curve of S_{DMC} is V-shaped. The lowest S_{DMC} occurs at a temperature of 130 °C. The selectivity of the two main products are similar (not give the curve of S_{CHD}). The yields of both DMC and CHD peak at 150 °C, and CHO conversion reaches as high as 95.7 %. K$_2$CO$_3$ reacted rapidly with CH$_3$OH to produce CH$_3$OK and KHCO$_3$ above 100 °C, thus rapidly increasing C_{CHO} above 120 °C. However, a significantly high temperature promotes the generation of a CHO polymer. The esterification of DMC with CHD by the base
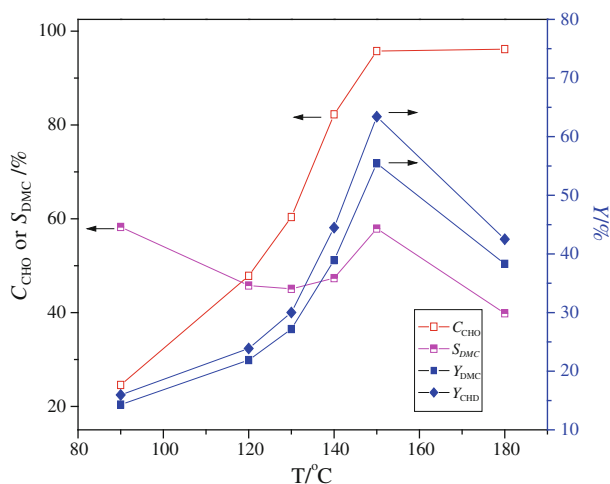
Fig. 1 C_{CHO}, Y_{DMC}, S_{DMC}, and Y_{CHD} under different temperatures (50.0 mmol CHO, 250.0 mmol CH$_3$OH, 2.60 MPa CO$_2$, 2.0 mmol K$_2$CO$_3$; 6 h)

catalyst results in the decrease of DMC and CHD yields. In addition, the preferred temperature is 150 °C.

A complicated and dynamic catalyst system exists in the whole process (Fig. 2). K$_2$CO$_3$ cannot be dissolved in CH$_3$OH solvent at room temperature. However, the reaction system becomes homogeneous at 150 °C. K$_2$CO$_3$ cannot return to its original form after the reaction, thus proving that K$_2$CO$_3$ is only a catalyst precursor. The dissolved mechanism of K$_2$CO$_3$ in this reaction might take place as follows: K$_2$CO$_3$ directly reacts with CH$_3$OH to form a dissolved CH$_3$OK and then it inserts CO$_2$ to obtain a stable CH$_3$OCO$_2$K. The former is endothermic and unspontaneous; the latter is exothermic and spontaneous. If the two reactions are coupling, K$_2$CO$_3$ spontaneously generates CH$_3$OCO$_2$K [21]. As for the partner KHCO$_3$, it could not directly react with CO$_2$ and CH$_3$OH due to a loss of the organized structure (monoclinic phase) of K$_2$CO$_3$. KHCO$_3$ could be decomposed into K$_2$CO$_3$ and H$_2$CO$_3$ which is decomposed into H$_2$O and CO$_2$ spontaneously at 100–200 °C [22]. On increasing along with CH$_3$OK from K$_2$CO$_3$ and CH$_3$OH, the corresponding products such as CHD or MCH reacted with CH$_3$OK to generate the corresponding K salt (CHDK and MCOK).

The reaction catalyst system includes CH$_3$OK, MCOK, and CHDK, and their amounts change gradually along with the reaction time. CHC synthesis involves three main steps: ring-opening, CO$_2$ insertion, and ring-closing. This reaction follows two mechanisms: alkoxides and carbonate anions mechanisms (Fig. 3). The details are followed in S2 (Path A: alkoxides; Path B carbonate anions). These alkoxides come mainly in three ways: K$_2$CO$_3$ reacts with CH$_3$OH, CHO metholysis by CH$_3$OK, and carbonate releases CO$_2$ under high temperatures. They exhibit higher activities for *trans*-CHC synthesis and this is also conducive for DMC synthesis via transesterification. Poly(cyclohexene carbonate) (PCHC, molecular
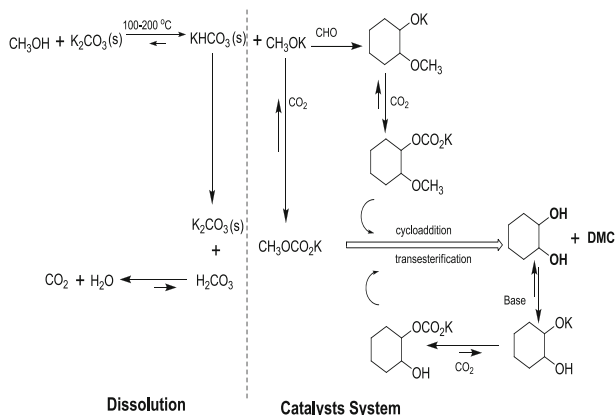
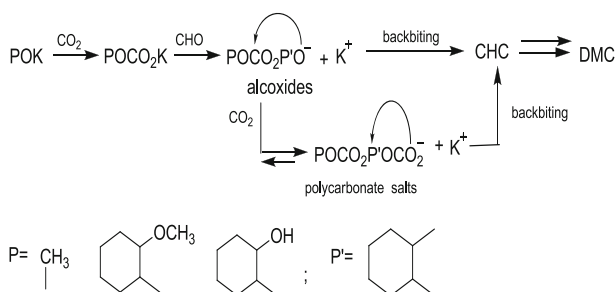Fig. 2 The catalyst system from K_2CO_3 in CH_3OH solvent

Fig. 3 The two cycloaddition mechanisms from alkoxides and carbonate anions

weight >500) comes from consecutive CHO ring-opening and CO_2 insertion without the ring-closing step. *Trans*-CHC can be formed directly from the alkoxide or PCHC. The ring-closing step from the former is called the direct alkoxide mechanism (path A-1) while that from the latter is called the polymer dissociation mechanism (path A-2). The final products are *trans*-CHD and DMC from the transesterification of *trans*-CHC. On the other hand, *cis*-CHC is generated via carbonate anions with low activity by the backbiting ways along the path B. The final products are *cis*-CHD and DMC via transesterification.

The Selectivity curve shows the product efficiency in the conversion of the feedstock. In general, the lower conversion will result in higher selectivity while the higher one causes low selectivity. The curve of S_{DMC} is V-shaped and is absolutely different from the general rules, indicating that the mechanism changes with temperature. Few papers have reported on this phenomenon. From the density functional theory calculation, the limited step in the direct alkoxide mechanism is the ring-opening process (see S2). It is the conformational transitions from a,a-type to e,e-type of different cyclohexane derivatives that brings the O atom of alkoxides and the carbonyl C atom closer and helps in the ring-closing process. The O atom of alkoxides with high activity can easily attack the carbonyl C atom of the carbonate.

Kinetically, the above conformational transition and the ring-closing step would happen at a low temperature. Therefore, the ring-closing reaction is controlled mainly by the direct alkoxides mechanism below 90 °C. Meanwhile, CHO metholysis increases and the chains of PCHC grow with increasing temperature above 90 °C. The conformational transition from a,a type to e,e type of PCHC or CHC transesterification cannot take place under low temperatures, thus DMC cannot be formed between 90 and 130 °C. This is the reason why S_{DMC} is decreasing with the increase of temperature between 90 and 130 °C. When the temperature is up to 130 °C, PCHC begins to dissociate via the polymer dissociation mechanism and DMC can be formed via *trans*-CHC transesterification. Meanwhile, CHO metholysis is increasing slowly because of the decrease of liquid CH_3OH. Thus, the high S_{DMC} is obtained at 150 °C. At the same time, a small amount of *cis*-CHC is generated via overwhelming the higher activity barriers. Too high a temperature causes low S_{DMC} due to more side-reactions or DMC decomposition.

Effect of time

This reaction is a reversible equilibrium reaction. The results of different times are listed in Fig. 4. C_{CHO}, Y_{DMC}, and Y_{CHD} initially increase in parallel with increasing reaction time before stabilizing. C_{CHO} obviously changes with reaction time from 1 to 3 h, thus indicating that the ring-opening process occurs mainly in the first 3 h and that the rate is faster than the latter 3 h. After 6 h, C_{CHO} reaches more than 90 %. C_{CHO} is almost unchanged after another 6 h. Y_{DMC} also slightly decreases with increasing time because of the polymerization process of DMC and other by-products at very high reaction temperatures.

The curve of S_{DMC} is different from the others and is V-shaped. At the beginning of the reaction, the generated CH_3OK is on the surface of the solid K_2CO_3. At this
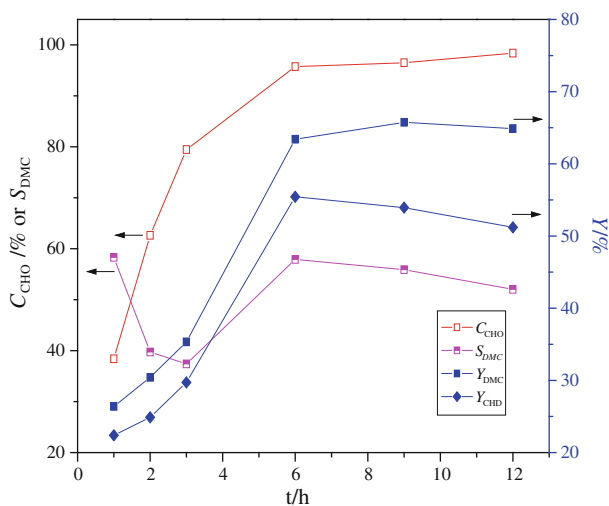

Fig. 4 C_{CHO}, Y_{DMC}, S_{DMC}, and Y_{CHD} with different reaction times (50.0 mmol CHO, 250.0 mmol CH_3OH, 2.60 MPa CO_2, 2.0 mmol K_2CO_3, 150 °C)

time, the CH_3OK concentration is higher near the surface and the ring-closing reaction is controlled mainly by the alkoxides mechanism. DMC is formed easily along path A-1 according to DFT calculation results. With CH_3OK dissolved in the CH_3OH solvent, high CO_2 insertion formed large-chain PCHC, which caused the low S_{DMC} under the higher pressure of CO_2 between 1 and 3 h. After C_{CHO} had reached more than 80 %, DMC was formed mainly via the polymer dissociation and transesterification processes from 3 to 6 h under a low concentration of CO_2. From these data, the reaction equilibrium is achieved for 6 h under 150 °C at 2.60 MPa CO_2 pressure.

Effect of CH_3OH amount

K_2CO_3 cannot be completely dissolved under low polar aprotic solvents, such as 1,2-dichloroethane, ethyl acetate, and tetrahydrofuran, to form a homogeneous system at 150 °C (not listed). An inhomogeneous system is only catalyzed by the solid surface of K_2CO_3. C_{CHO} does not exceed 30 % in these solvents. CH_3OH is a polar protic solvent and it can generate CH_3OK to form a homogeneous system under high temperatures, thus catalyzing cycloaddition and transesterification. The reactions resulting from different amounts of CH_3OH are shown in Fig. 5. The molar ratio of CH_3OH and CHO varies from 1:1 to 10:1 under 2.60 MPa CO_2 for 6 h.

C_{CHO} initially increases before stabilizing with increasing CH_3OH, whereas Y_{DMC} and Y_{CHD} initially increase and then decrease. The molar amount of CH_3OH causes low product yield and selectivity but results in the formation of by-products such as polyether, polycarbonate, and CHC under high CHO conversion, similar to the solvent-free polyester reaction [23]. A significantly high CH_3OH concentration
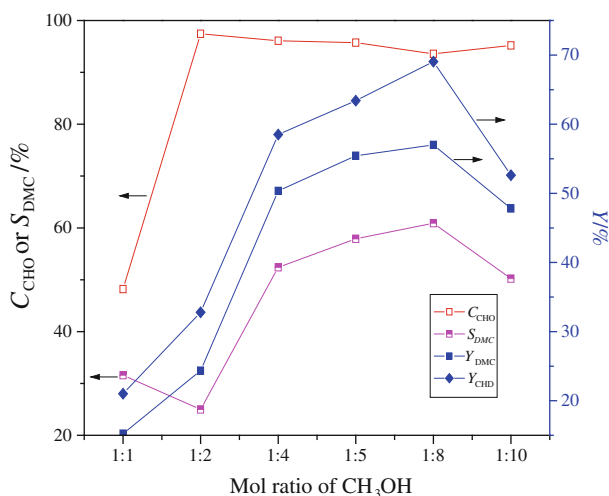

Fig. 5 C_{CHO}, Y_{DMC}, S_{DMC} and Y_{CHD} with different CH_3OH molar ratios (50.0 mmol CHO, 2.60 MPa CO_2, 2.0 mmol K_2CO_3, 150 °C, 6 h)
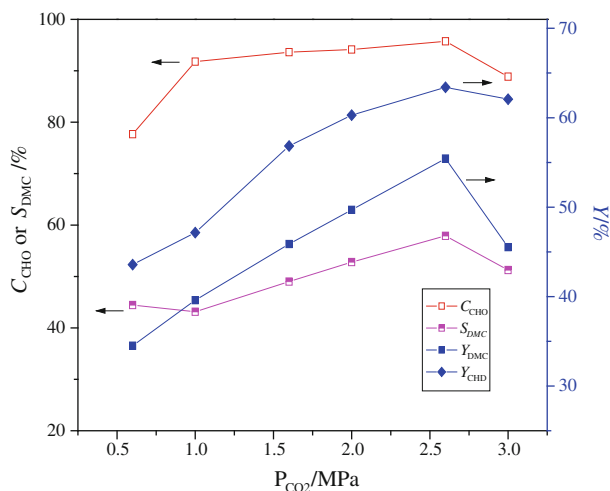
Fig. 6 C_{CHO}, Y_{DMC}, S_{DMC}, and Y_{CHD} with different CO_2 pressure (50.0 mmol CHO, 250.0 mmol CH_3OH, 2.0 mmol K_2CO_3; 150 °C, 6 h)

causes the dilution of the reactants and increases the occurrence of methanolysis. This phenomenon results in the decrease of Y_{DMC} and Y_{CHD} and the increase of separation costs.

Effect of CO_2 pressure

CO_2 can easily insert O–M bonds and generate organic carbonates. Higher CO_2 pressure in the gas phase results in higher CO_2 concentrations in the liquid phase [23]. The initial CO_2 pressure varies from 0.6 to 3.0 MPa and the reaction results are shown in Fig. 6. C_{CHO} increases to 2.60 MPa and then slightly decreases with increasing CO_2 pressure. The curves of Y_{DMC} and Y_{CHD} are similar to those of C_{CHO}. Below the theoretical molar amount, CO_2 conversion is almost equivalent to that of C_{CHO}, thus showing that CO_2 easily reacts with the active species in the reactions. Although higher CO_2 pressure helps form DMC and CHD, a considerably high CO_2 pressure is unfavorable. CO_2 is able to penetrate into the epoxides and polymers, resulting in a swelling of the epoxide or polymers phase. The swelling effect of CO_2 increases when CO_2 pressure is at 3.0 MPa, thus reducing the CHO concentration and reaction mixture polarity [8, 24]. The preferred pressure of CO_2 is 2.60 MPa.

Effect of catalyst concentration

If the K_2CO_3/CHO molar ratio increases from 1.0 to 10.0 %, the DMC yield increases from 27.2 to 54.3 %, as shown in Fig. 7. The quantity of K_2CO_3 directly influences the CH_3OK concentration in the liquid phase. The curves of C_{CHO}, Y_{DMC}, S_{DMC}, and Y_{CHD} change with increasing K_2CO_3, which is similar to the curves of CO_2 pressure and reaction time. A significantly high CH_3OK concentration
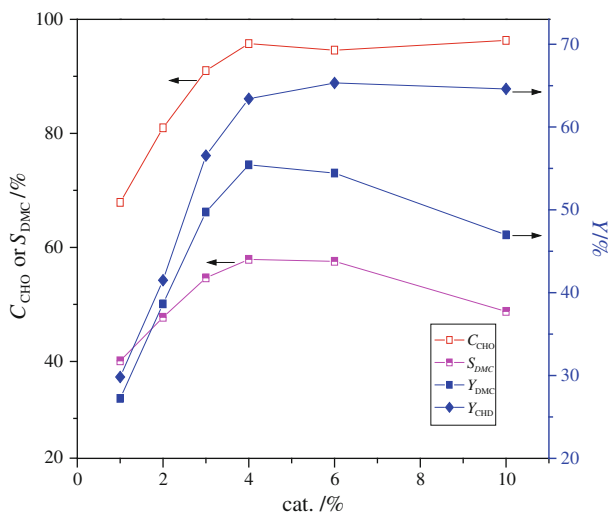
Fig. 7 C_{CHO}, Y_{DMC}, S_{DMC}, and Y_{CHD} with different catalyst dosages (50.0 mmol CHO, 250.0 mmol CH_3OH, 2.60 MPa CO_2; 150 °C, 6 h)

promotes the methanolysis of CHO and accelerates DMC decomposition [25]. When the catalyst mole ratio is more than 4 %, no obvious influence on C_{CHO} is observed. However, Y_{DMC} and S_{DMC} are reduced because of DMC decomposition. The figure implies that the 4 % K_2CO_3 catalyst obtains the best result.

Conclusions

1. K_2CO_3 is a catalytically efficient and cost-effective catalyst precursor that exhibits fewer hybrid ion introductions for DMC and CHD formation via one-pot reaction. The best conditions are as follows: $CHO:CH_3OH = 1:5$, 2.60 MPa CO_2, and 4.0 % catalyst for 6 h at 150 °C. C_{CHO} reaches ~ 90 %, and Y_{DMC} and Y_{CHD} are 55.4 and 63.4 %, respectively.
2. The reaction catalyst system is a complicated and dynamic catalyst system. CH_3OK formed initially by K_2CO_3 catalyzes the homogeneous reaction. Thereafter, MCOK from CHO methanolysis gradually increases and becomes a co-catalyst with CH_3OK.
3. At different temperatures, the title reaction is controlled, respectively, by the direct alkoxide and polymer dissociation mechanisms.

The present results have provided more deep insight into DMC synthesis via alicyclic epoxides. It also helps in understanding the intrinsic properties of the important reaction sequence including DMC and epoxides. Cyclopentene oxide and cycloheptene oxide can give similar results. Other alcohols can be used as raw materials instead of CH_3OH. However, it is under high temperature that alcoholysis of epoxides and K_2CO_3 are greatly influenced on the yield of DMC. Low reaction

temperature, higher catalytic activity, and inhibition of alcoholysis should be focused on in future.

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