

Recent progress in phosgene-free methods for synthesis of dimethyl carbonate*

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Abstract: Dimethyl carbonate (DMC) is considered as an environmentally benign chemical due to negligible ecotoxicity, low bioaccumulation, and low persistence. However, the traditional process of DMC synthesis via phosgene and methanol is limited in industry owing to the toxic raw material involved. Thus, environmentally friendly phosgene-free processes for DMC production have been proposed and developed in the past decades. Until now, the alternatives appear to be the oxidative carbonylation of methanol, the transesterification of propylene or ethylene carbonate (PC or EC), the methanolysis of urea, and the direct synthesis of DMC from CO₂ with methanol. In this review, we present some recent developments of these phosgene-free approaches and their prospects for industrialization.

Keywords: carbon dioxide; dimethyl carbonate synthesis; oxidative carbonylation; phosgene-free; transesterification; urea.

INTRODUCTION

Along with the global spread of sustainable development strategy, the chemical synthesis processes and materials endangering humans and the environment would be gradually restricted. The “clean production process” and “green chemicals” will be the developmental direction for the modern chemical industry, and the production and chemical utilization of dimethyl carbonate (DMC) are closely concerted by this trend.

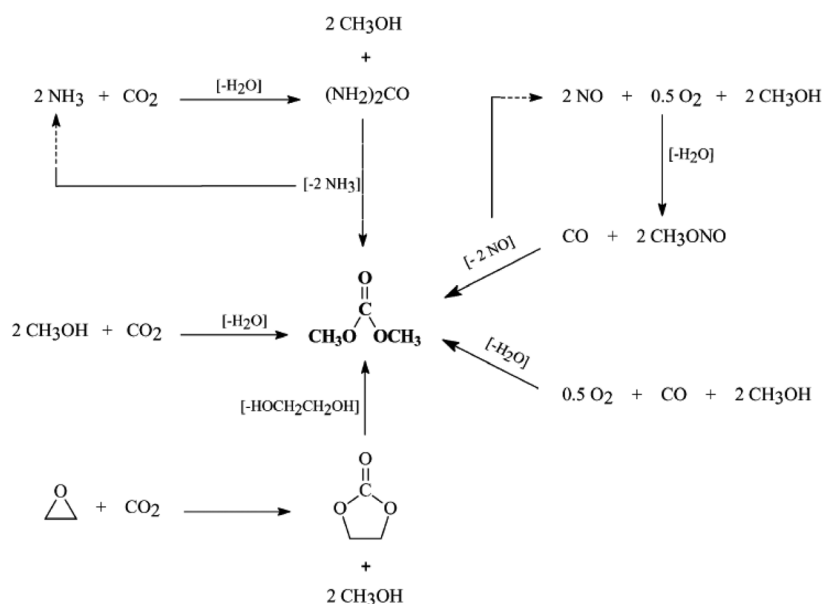
DMC is considered as an environmentally benign building block, due to its nontoxicity, good biodegradability, and excellent solubility [1]. It is an ideal additive for gasoline because of its outstanding oxygen content in the DMC molecule (53.3 wt %) combined with its good blending properties [2]. In addition, owing to its great reactivity toward nucleophilic molecules such as phenols or primary amines, DMC is used as an alternative to harmful phosgene for aromatic polycarbonate and isocyanate syntheses as a carbonylation agent, as well as for replacing dimethylsulfate and methylhalides, which are toxic and corrosive in methylation reactions [3]. Moreover, because of its versatile chemical properties, DMC is also used as electrolyte, foodstuff flavoring agent, and the solvent in the field of paints and adhesives in which it represents a viable alternative to ketones and ester acetates [4].

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The traditional industrial synthesis of DMC uses phosgene as reagent, which suffers from the shortcomings as corrosive gases of chlorine, treating with large amounts of pyridine and removing of the by-product NaCl salts. Considering the social and environmental effects of pollution, it is of the utmost importance to find phosgene-free routes for DMC synthesis, and, as a result, several non-phosgene approaches for DMC production have been explored and developed. Among them, the oxidative carbonylation of methanol, the transesterification of propylene or ethylene carbonate (PC or EC) and methanol, the urea methanolysis (synthesis of DMC from urea and methanol), and the direct synthesis of DMC from CO₂ with methanol are the most attractive and promising alternatives to the conventional process.

This review attempts to present some recent developments in the phosgene-free methods for DMC production, as depicted in Scheme 1. The reaction characteristics of the phosgene-free approaches and the catalysts involved in the reactions are reviewed, moreover, their advantages and disadvantages are discussed based on the experimental results obtained by us and other investigators.



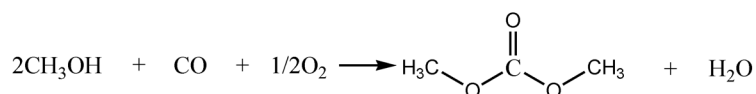
Scheme 1 Alternative synthesis routes of DMC.

OXIDATIVE CARBOXYLATION OF METHANOL

Up to now, besides the phosgenation process, which has been totally abandoned, the commercial processes for producing DMC include liquid-phase methanol oxycarbonylation (developed by Enichem) and methylnitrite carbonylation (developed by UBE). However, the methylnitrite carbonylation process has some drawbacks such as the risks of explosion related to the use of the Pd/NO/O₂ mixture, and the strong toxicity of the methylnitrite reactant. Thus, methanol oxycarbonylation, especially vapor-phase methanol oxycarbonylation (developed by Dow Chemical) has gained much attention in recent years [2].

Typically, the liquid-phase methanol oxycarbonylation process is carried out in a batch reactor at moderate pressure in the presence of a slurry catalytic system based on copper salts such as CuCl. The vapor-phase methanol oxycarbonylation process is investigated in a continuous-flow fixed bed reactor in vapor phase using CuCl₂ supported on activated carbon catalyst, which directly derives from the liquid-phase process [4].

At present, the study on the synthesis of DMC by oxidative carbonylation of methanol is mainly focused on supported CuCl catalysts in the liquid-phase process, as well as the catalytic materials consisting of active carbon-supported CuCl₂ catalysts and chloride-free zeolite-based catalysts in the vapor-phase process. Here, we only briefly discuss the catalytic DMC synthesis from oxidative carbonylation of methanol catalyzed by Cu-based catalysts, especially chlorine-free zeolite-based catalysts. For detailed information on this process, see the very recent review by Keller [4]. The oxidative carbonylation of methanol to DMC is described in Scheme 2.



Scheme 2 DMC synthesis by oxidative carbonylation of methanol.

As for the synthesis of DMC by the liquid-phase process, researchers have been devoted to developing a heterogeneous Cu-based catalyst system. Cao et al. reported a novel heterogeneous catalyst system based on CuCl immobilized on a diamide-modified mesoporous SBA-15 silica, which is air-stable and reusable, and exhibited excellent catalytic performance for the oxidative carbonylation of methanol to DMC. The dramatic increase in the reaction efficiency of the CuCl catalyst upon immobilization in the present case can be understood by a strong ligand interaction between the Cu species and the amide moieties in the SBA-15 material [5]. Mo et al. studied the influence of various N-donor ligands coordinating with Cu of CuCl/Schiff base in the synthesis of DMC by oxidative carbonylation of methanol, and they found that a homogeneous complex catalyst, CuCl/1,10-phenanthroline (CuCl/Phen), exhibited high catalytic activity and corrosion resistance [6]. In order to enhance the reusability of this catalytic system with high activity, the authors prepared a heterogeneous catalyst (CuCl/Phen-PS) by immobilizing CuCl on polystyrene-modified 1,10-phenanthroline (Phen-PS), which was also investigated in the oxidative carbonylation of methanol. The immobilized catalyst showed high catalytic activity, high stability in consecutive catalytic runs, easy separation from the reaction mixture, and less leaching of active metal species [7]. Ren et al. prepared CuCl/SiO₂-TiO₂ catalysts by microwave heating method and investigated the effect of support composition. It was suggested that the interaction between CuCl and the support of CuCl/SiO₂-TiO₂ catalysts favored the synthesis of DMC via the oxidative carbonylation of methanol. Moreover, the authors synthesized novel Cu-SiO₂-TiO₂ cogelled xerogel catalysts prepared by the sol-gel route. The structural features, catalytic performance, and corrosion effect of the catalyst were studied. It was found that the relatively inferior catalytic activity and reduced corrosion obtained on the catalyst with 12.5 mol % of Cu loading may be attributed to highly dispersed Cu⁺ active centers as well as lower chloride content [8]. Recently, Dong et al. has reported ionic liquids (ILs) as an efficient promoting medium by using Cu salt catalysts for the synthesis of DMC by the oxidative carbonylation of methanol. The *N*-butylpyridinium tetrafluoroborate-mediated CuCl catalyst system exhibited the best activity. Under the reaction conditions of 120 °C and 2.4 MPa of a 2:1 mixture of CO and O₂, 17.2 % conversion of methanol and 97.8 % selectivity of DMC were achieved [9]. In addition, they also found that the CuBr₂-PyIL/SBA-15 catalyst was more active and selective than CuBr₂ and CuBr₂/SBA-15 prepared by the conventional impregnation method [10]. Stricker et al. studied a number of ILs containing Cu in the anion or the cation or both. Of particular interest were the unique cupronium cuprate ILs [Cu(Im¹²)₂][CuX₂] (X = Cl, Br) forming crystalline laminate structures at ambient temperature, and [Cu(Im¹²)₂][CuBr₂] showed the best catalytic performance in the synthesis DMC by the oxidative carbonylation of methanol [11].

Compared to the liquid-phase process, the vapor-phase oxidative carbonylation of methanol has been considered as a more attractive way to produce DMC because it can avoid the drawbacks such as halide corrosion and product recovery. The catalysts used in this process mainly include supported

CuCl₂ catalysts [12], supported CuCl₂-PdCl₂ catalysts [13], and chlorine-free zeolite-based catalysts. Although they showed the high catalytic performance in synthesis of DMC, the CuCl₂- and CuCl₂-PdCl₂-supported catalysts employed in the process suffered from quick deactivation owing to the loss of chlorine. Compared to the CuCl₂- and CuCl₂-PdCl₂-supported catalysts, chlorine-free zeolite-based catalysts have gained much more interest in recent years.

King firstly reported that the Cu^IY catalyst made by the high-temperature solid-state ion exchange of CuCl with HY zeolite under flowing helium was active for synthesizing DMC by the vapor-phase methanol oxycarbonylation. Compared with the carbon-supported CuCl₂ catalyst, the Cu^IY catalyst showed more excellent activity to produce DMC without deactivation, which is due to the loss of chloride. The catalytic mechanism based on an in situ Fourier transform/infrared (FT/IR) study was also supposed [14]. Anderson and Root also prepared CuX and Cu-ZSM-5 catalysts by solid-state ion-exchange method. They found that the weaker adsorption of CO onto CuX compared to Cu-ZSM-5 is advantageous for DMC production because adsorbed CO blocks sites for methoxide formation but did not participate in DMC formation. Moreover, it has been proved that the insertion of gaseous CO into surface methoxide to form a carbomethoxide via an Eley-Rideal pathway is the rate-determining step for DMC production [15]. According to Richter et al., chloride-free Cu-impregnated zeolite Y catalysts (prepared by incipient wetness impregnation of zeolite Y with Cu^{II} nitrate solution) were the active catalysts for the oxidative carbonylation of methanol to DMC and Cu loading of 14–17 wt % gave the best performance. Furthermore, it could be seen that the formation of the main by-product dimethoxymethane (DMM) was affected by CO. Details of the reaction mechanism were reasoned from feed variation and transient response of the catalytic system. At the same time, the other chloride-free Cu/zeolite Y catalysts (prepared by precipitation from aqueous Cu^{II} acetate solutions) also exhibited good catalytic activity in this reaction. The characterization results revealed that the solid-state ion exchange during inert activation is accompanied by reduction of Cu²⁺ to Cu⁺ [16].

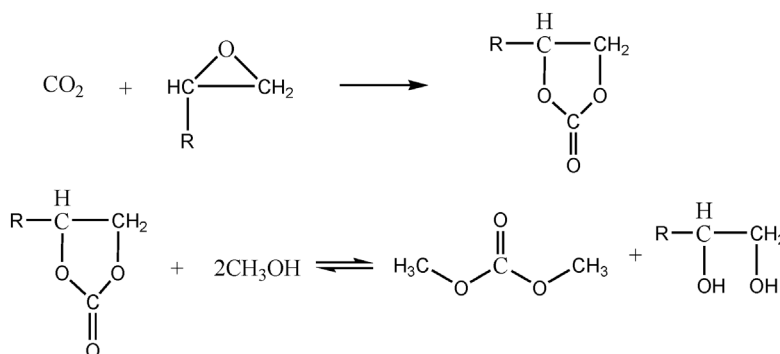
Bell et al. have studied in detail the effects of zeolite structure/chemical composition on the activity and selectivity of Cu-exchanged Y (Si/Al = 2.5), ZSM-5 (Si/Al = 12), and Mordenite (Si/Al = 10) for DMC synthesis by the oxidative carbonylation of methanol. DMC was observed as the primary product when a mixture of CH₃OH/CO/O₂ was passed over Cu-Y, whereas DMM was the primary product over Cu-ZSM-5 and Cu-MOR. The higher activity and selectivity of Cu-Y can be attributed to the weaker adsorption of CO on the Cu⁺ cations exchanged into Y zeolite. Furthermore, the authors investigated the mechanism of DMC synthesis from oxidative carbonylation of methanol over Cu-exchanged Y zeolite using in situ FT/IR and mass spectrometry under transient-response conditions. The proposed mechanism comprises as a first step the reaction of molecularly adsorbed methanol with oxygen to form mono- or di-methoxide species bound to the only present Cu^I cations. Then, the mono-methoxide species reacts with CO, forming monomethyl carbonate (MMC). The formation of DMC proceeds via CO addition to the di-methoxide species or the reaction of methanol with MMC [17]. In addition, the mechanism mentioned above is further confirmed by density functional theory (DFT) calculations, which are in very good agreement with the experimental observation [18].

Rebmann et al. has used thermoconductive β-SiC supported Cu-Y zeolite composite as a catalyst for the vapor-phase oxidative carbonylation of methanol to DMC. The authors found that the space/time yields of DMC are improved and the influence of the temperature is limited, owing to the use of a thermoconductive material as support, which allows better control of the catalytic bed temperature and results in limited production of DME and CO₂ by-products even at high temperatures [19]. Engeldinger et al. discussed in situ FT/IR investigations of Cu-Y catalysts with varied Cu content to elucidate the specific role of the Cu species in the oxidative carbonylation of methanol. The results suggest that high Cu loadings exceeding the available cation sites caused the additional formation of CuO_x agglomerates, which favored oxidation and oxocarbonylation reactions of methanol and enhanced the formation of DMC [20]. Zhong et al. stated that CuCl₂ as a precursor was firstly used to prepare Cu^I catalyst supported on acidic Y zeolite by solid-state ion exchange. This Cu^IY catalyst proved to be a high catalytic activity in the oxidative carbonylation of methanol. The amount of ion-exchanged Cu^I in the Cu^IY cat-

alyst reached the maximum of 0.1 mol/g when the heating temperature was 650 °C, and the catalyst exhibited the best catalytic activity [21].

TRANSESTERIFICATION OF ETHYLENE (PROPYLENE) CARBONATE AND METHANOL

The synthesis of DMC by transesterification of cyclic carbonate and methanol is an excellent green process that turns the waste greenhouse gas CO₂ into the valuable chemicals with zero discharge and 100 % atom economy, as shown in Scheme 3. For example, in this reaction EC or PC are usually used as the materials, which can be synthesized by the reaction of CO₂ with EO or PO, respectively. Meanwhile, ethylene glycol (EG) or propylene glycol (PG) can be obtained as co-product.



Scheme 3 DMC synthesis by transesterification reaction.

A large number of base catalysts have been reported to be very effective in the transesterification reaction. However, homogeneous basic catalysts, such as alkali metal compounds [22] and quaternary ammonium salt [23], give rise to the problems of product separation and catalyst reuse. Consequently, heterogeneous basic catalysts such as composite metal oxide, alkali-treated zeolite, supported tertiary amino group, and silica-supported ILs have gained much more interest recently. Thus, in this section of the review, we will only focus on heterogeneous base catalysts in the transesterification reaction.

Feng et al. used amino-functionalized MCM-41 as a catalyst in the continuous transesterification of EC to DMC and obtained 44 mol % DMC yield. The catalyst exhibited excellent stability as well as good catalytic activity [24]. Zhao et al. investigated the catalytic activity of a quaternary ammonium salt functionalized chitosan for DMC synthesis through transesterification of PC with methanol, and 54 % DMC yield and 71 % PC conversion were obtained [25]. Dhuri and Mahajani found that the basic anion-exchange resin Amberlyst A-21 catalyst exhibited good catalytic performance for DMC synthesis of EC with methanol, and it gave more than 95 % selectivity toward DMC and EG [26]. Srivastava et al. employed Fe–Zn double-metal cyanide complexes as novel highly efficient solid catalysts for transesterification of PC with methanol, and DMC could be synthesized with 100 % selectivity and an isolated yield of >86 % [27]. Sankar et al. stated that the synthesis of DMC with 80 mol % yield was achieved through transesterification of EC with methanol at ambient conditions using alkali and alkaline-earth tungstates as solid catalysts. The results of Raman and IR spectra indicated the formation of a methoxide ion species adsorbed at the catalyst surface as one possible reaction intermediate [28]. Jagtap et al. reported the synthesis of DMC via transesterification of EC with methanol using poly-4-vinyl pyridine (PVP) as a novel, homogeneous, recyclable base catalyst with high yield [29]. The transesterification of EC with methanol to DMC has been investigated over Na-dawsonite derived aluminate catalyst by Stoica et al., it was suggested the basicity of the Na-containing oxides, attained by calcination of Na-dawsonite at 973 K, was required to obtain an active catalyst, which rendered a maximum

DMC yield ca. 65 % [30]. Williams et al. also found that verkade super bases (proazaphosphatranes) were especially effective at low catalyst loadings (0.5 %) for the rapid transesterification of PC with methanol under mild conditions and with high product selectivity (typically >99.5 %) [31].

Our work on the synthesis of DMC via transesterification mainly aims at highly effective and stable composite solid base catalysts, such as CaO/C and CaO/ZrO₂. Wei et al. investigated the effect of base strength and basicity on the synthesis of DMC from PC and methanol. It was found that the rise of base strength could reduce the temperature needed for this reaction remarkably. And then a CaO/C composite was prepared as a new solid base catalyst for this reaction. Compared with pure CaO, the CaO/C showed the same basic properties and a high performance, but could be reused with little deactivation [32].

Unfortunately, the activity of CaO-based catalyst gradually decayed with time-on stream due to leaching of Ca in the continuous synthesis of DMC. In order to improve the stability of solid base catalyst, Wang et al. designed and prepared a kind of highly active and stable CaO–ZrO₂ catalyst system by coprecipitation. Compared with the CaO/C catalyst, it showed greater catalytic performance as well as good stability in the reaction of PC and methanol. The characterization by X-ray diffraction (XRD) and Raman spectroscopy indicated that CaO is doped into the lattice of ZrO₂ to form CaO–ZrO₂ solid solution, and such a solid solution has strong base properties measured by CO₂-TPD. The high activity and stability in the transesterification reaction was attributed to the strong interaction of CaO and ZrO₂ in the solid solution. When the catalyst is subjected to the continuous reactive distillation, the conversion of PC remained at about 95 % even for 250 h, with no obvious loss of activity observed (Fig. 1). Further study indicated the activity and stability depend greatly on the Ca/(Ca + Zr) ratios. The activity of catalysts increased with the increase of CaO content, which is ascribed to the improvement of the base strength of catalysts. But the high stability is only obtained for the catalysts with Ca/(Ca + Zr) ratio from 0.1 to 0.3. This is due to the formation of homogeneous CaO–ZrO₂ solid solution [33].

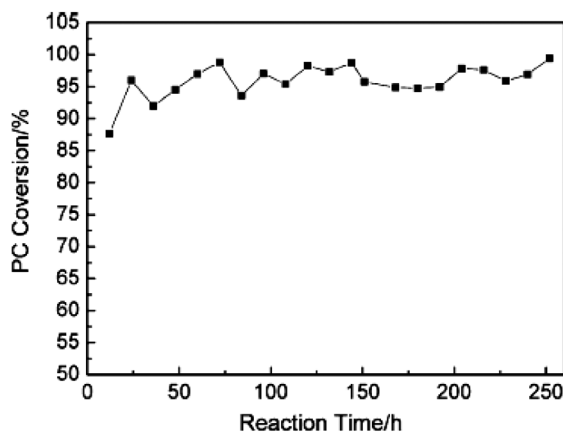


Fig. 1 Catalytic performance of CaO–ZrO₂ catalyst in catalytic distillation.

The influence of preparation methods on the structure and performance of CaO–ZrO₂ catalyst was also performed by Wang et al., in which CaO–ZrO₂ catalysts were prepared by physical mixing, impregnation, and coprecipitation methods, respectively, and then were developed for the synthesis of DMC from PC and methanol. Both catalytic activity and stability are strongly influenced by the structure of CaO–ZrO₂. The aggregated CaO on the support as well as highly dispersed CaO shows poor catalytic stability, while Ca²⁺ ion substituted for Zr⁴⁺ ions in the host lattice to form homogeneous

CaO–ZrO₂ solid solution leads to the strong interaction between CaO and ZrO₂ and then high stability [34].

Nevertheless, although CaO–ZrO₂ solid base mentioned above exhibits remarkable stability, the specific surface area of this catalyst is only 10–50 m²/g. Thus, mesoporous Na–ZrO₂ and CaO–ZrO₂ catalysts were prepared via appropriate sol-gel process. The two mesoporous solid bases exhibited remarkable activity and durability in the synthesis of DMC from PC and methanol. Moreover, it was also found that the rate of the transesterification reactions over the mesoporous Na–ZrO₂ or CaO–ZrO₂ nano-oxide are much faster than that over CaO–ZrO₂ by coprecipitation, which may be interpreted to the relatively high specific area of mesoporous Na–ZrO₂ or CaO–ZrO₂ catalyst, which offers more basic sites and drove the reaction in a short time [35]. The Na⁺ or Ca²⁺ ions incorporate into the zirconia network, and the basic sites are firmly anchored to the substrate, which is similar to the results reported by Wang et al. [33b].

In recent years, ILs, used as catalysts for DMC synthesis via transesterification, have attracted significant attention because of their distinctive properties, such as high thermal stability, high loading capacity, or ease of recycling and environmental friendliness. Abimanyu et al. reported MgO–CeO₂ mixed oxide catalysts prepared and modified with various ILs exhibited good catalytic performance in transesterification of EC with methanol. The addition of ILs promoted the surface basicity, and the base strength distribution then enhanced the conversion of EC and the yield of DMC. It was also found that the catalyst prepared using [Bmim][BF₄] displayed the best performance [36]. Dharman et al. developed an energy-efficient route for the transesterification of EC with methanol using IL as a catalyst through microwave heating, and the coproduction of an equimolar amount of DMC was obtained in high yield and better selectivity [37]. Kim et al. found that the silica-supported ILs (BMImBr-AS and QCl-MS41) were effective heterogeneous catalysts for the synthesis of DMC from transesterification of EC with methanol. These catalysts can be reused for the reaction up to three consecutive runs with a slight decrease of their catalytic activities [38]. Yang et al. prepared DABCO-derived (1,4-diazobicyclo[2.2.2]octane) basic ILs, which were developed for the efficient synthesis of DMC via transesterification of EC with methanol. The catalyst [C₄DABCO]OH exhibited high catalytic activity, and 81 % DMC yield together with 90 % EC conversion was obtained. Moreover, a possible mechanism was also discussed [39].

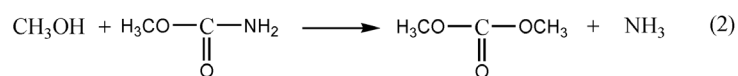
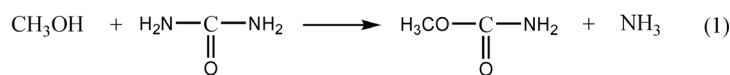
METHANOLYSIS OF UREA

Producing carbonates by alcoholysis of urea was first proposed by Peter Ball [40] in 1980. In this process, urea reacts with alcohols to form carbonates and ammonia, meanwhile the ammonia liberated in the carbonate synthesis can be recycled and only CO₂ and alcohol are consumed owing to the industrial synthesis of urea starts from CO₂ and ammonia (Scheme 4).



Scheme 4 Carbonate synthesis from urea and alcohol.

For this reason, producing DMC by urea alcoholysis is considered a green chemistry route to this important chemical and has attracted considerable attention in recent years. In fact, the reaction of urea and methanol can be divided into two steps as follows (Scheme 5):



Scheme 5 Two-step reactions of DMC synthesis by urea methanolysis.

In this approach, the intermediate methyl carbamate (MC) is first formed and further converted to DMC by reaction with methanol. A lot of catalysts such as organic tin, polyphosphoric acid (PPA), metal oxide, and zinc compounds have been tested in a batch reactor toward the reaction of urea and methanol. Lin et al. studied the kinetics parameters of DMC synthesis from urea and methanol using organotin as catalyst. The results showed that the activation energies of the secondary reactions are higher than those of the main reactions, and removing DMC and ammonia from the reaction system in time is vital to improving DMC yield [41]. Sun et al. reported that a good DMC yield can be obtained when using PPA as catalyst and absorbent for the ammonia in the reaction of urea and methanol, where ammonia becomes a starting material of a useful fertilizer [42]. Furthermore, they also investigated the continuously reactive rectifying process in laboratory scale, which gained a DMC concentration of more than 17 % in the overhead products [43]. At the same time, they reported that the producing DMC from urea and methanol was catalyzed by the metallic compounds using high boiling electron donor compounds (polyethylene glycol dimethyl ether, PGDE) as solvent at atmospheric pressure. Compared with other catalysts, zinc stearate ($\text{C}_{36}\text{H}_{70}\text{O}_4\text{Zn}$) was an optimal catalyst for its dissolubility and the amphoteric property that is favored by the forming of methoxyl [44]. Wu et al. found that both zinc powder and loaded Zn-based catalyst (supported by $\alpha\text{-Al}_2\text{O}_3$) showed preferable catalytic performance in the reaction of urea and methanol to DMC, under the selected reaction conditions, DMC yield reached 12.7 and 8.9 %, respectively. Treatment by H_2 could improve the catalytic activity of loaded Zn-based catalyst, which could be related to the change of chemical state of zinc atoms [45]. Recently, the synthesis of DMC from methanol and urea using ILs, such as $\text{Et}_3\text{NHCl}-\text{FeCl}_3$, $\text{Et}_3\text{NHCl}-\text{ZnCl}_2$, $\text{Et}_3\text{NHCl}-\text{CuCl}_2$, $\text{Et}_3\text{NHCl}-\text{SnCl}_2$, and $\text{emimBr}-\text{ZnCl}_2$, as catalysts has been investigated by Wang et al., it was found that $\text{Et}_3\text{NHCl}-\text{ZnCl}_2$ or $\text{emimBr}-\text{ZnCl}_2$ exhibited higher activity for the synthetic reaction and surprisingly high selectivity to DMC. The higher activity of the IL is due to its enhancing polarity and electrostatic field of the reaction medium and simultaneous activation of the two substrates. The reaction mechanism and the reasons to raise activity and high selectivity of the catalyst were also explored [46].

At our lab, work on synthesis of DMC by methanolysis of urea is mainly focused on catalysts of metal oxides and Zn compounds and the catalytic mechanism. Wang et al. found that ZnO was superior to other catalysts for the synthesis of DMC from urea and methanol in a batch reactor in which the highest DMC yield was about 30 %, and the excellent activity of ZnO was considered to be related to its acidic and basic properties [47]. Moreover, a series of solid bases (metal oxides) was used as catalyst in the urea alcoholysis reaction, it was indicated that based on CO_2 -TPD (as shown in Fig. 2), the basic strength of solid bases follows this order: $\text{CaO} > \text{La}_2\text{O}_3 > \text{MgO} > \text{ZrO}_2$, which is in accordance with their activity order for the synthesis of DMC. Solid bases were found to be effective catalysts for the synthesis of DMC from MC and methanol, and the function of basic catalysts can be attributed to the activation of CH_3OH via the abstraction of $\text{H}^\delta+$ by base sites. The possible reaction mechanism over basic catalyst was also proposed [48]. In addition, major side reactions in the DMC synthesis included the thermal decomposition of DMC and reaction between MC and DMC, which reduced the DMC yield in the batch process, thus a catalytic distillation technique was performed to minimize the side reactions and shift the equilibrium for DMC synthesis. The DMC yield reached 60–70 % in the catalytic distillation reactor over the Zn-based catalyst [49].

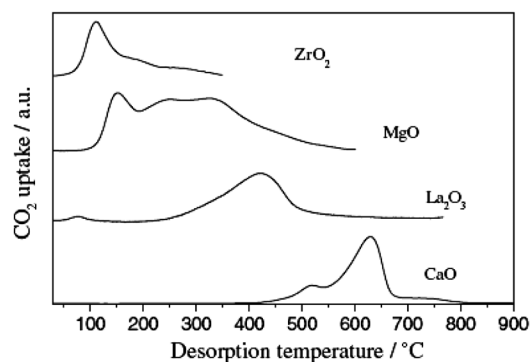


Fig. 2 CO₂-TPD profiles of solid catalysts.

Recently, further study on catalytic performance and reaction mechanism of dialkyl carbonate synthesis over ZnO by urea alcoholysis has been carried out [50]. Interestingly, ZnO was evidently found to be the precursor of homogenous catalyst Zn(NH₃)₂(NCO)₂ in the reaction. At first, a comprehensive study was conducted on DMC synthesized from urea and that from MC over ZnO and other catalysts. Surprisingly, it was found that ZnO was hardly active toward the reaction of MC and methanol, though it was highly active in the synthesis of DMC from urea and methanol. The yield of DMC from urea reached 34.0 %, while that from MC was only 4.2 % (see Table 1). The same performance was also observed for the synthesis of diethyl carbonate (DEC) over ZnO, which was the most active catalyst among a lot of metal oxides for the reaction of urea and ethanol in the previous work [51], and the yield of DEC from urea was 32.5 %, while that from ethyl carbamate (EC) was only 1.8 % (Table 2). This led to our interest in the role of ZnO in these two reactions.

Table 1 Yield comparison of DMC synthesized from urea and that from MC (reprinted with permission from ref. [50], copyright © 2009, Elsevier B.V.).

Entry	Catalyst	Reaction temp. (°C)	Reaction time (h)	DMC yield (%)
1	None ^a	180	10	0.8
2	None ^b	190	10	2.6
3	PbO ^a	180	8	22.0
4	PbO ^b	190	10	23.8
5	Zn(CH ₃ COO) ₂ ^a	190	10	24.0
6	Zn(CH ₃ COO) ₂ ^b	190	10	21.1
7	MgO ^a	200	10	16.9
8	MgO ^b	200	10	17.5
9	CaO ^a	180	11	15.8
10	CaO ^b	190	10	18.2
11	ZnO ^a	180	12	34.0
12	ZnO ^b	190	10	4.2

^aReaction condition: 0.1 mol urea, 64 g methanol, and catalyst amount 1 g. DMC yields based on urea.

^bReaction condition: 0.1 mol MC, 64 g methanol, and catalyst amount 1 g. DMC yields based on MC.

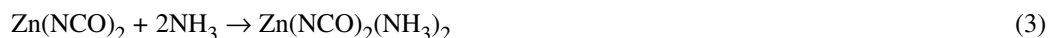
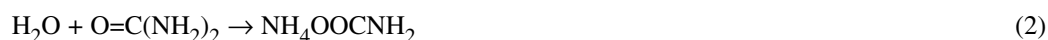
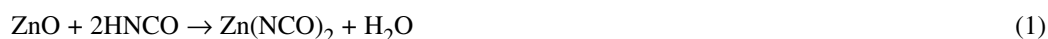
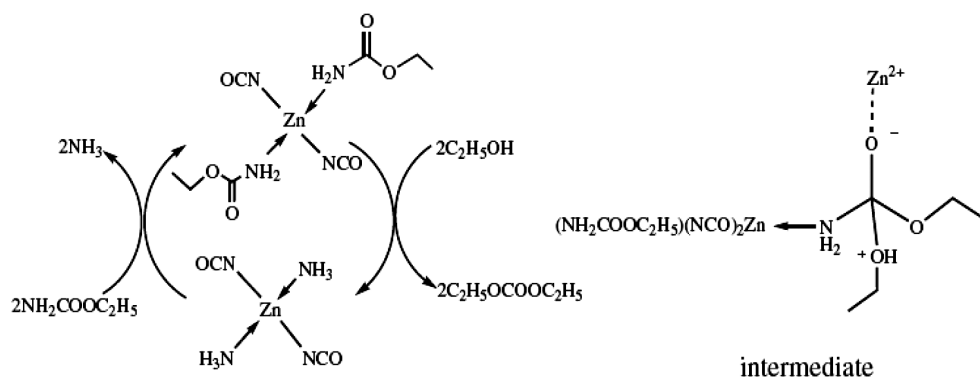
Table 2 Yield comparison of DEC synthesized from urea and that from EC (reprinted with permission from ref. [50], copyright © 2009, Elsevier B.V.).

Entry	Catalyst	Reaction temp. (°C)	Reaction time (h)	DEC yield (%)
1	CaO ^a	180	8	12.9
2	CaO ^b	180	8	10.8
3	ZnO ^a	180	8	32.5
4	ZnO ^b	180	8	1.8
5	Precipitate ^b	180	8	40.6

^aReaction condition: 0.1 mol urea, 46 g ethanol, and catalyst amount 1 g. DEC yields based on urea.

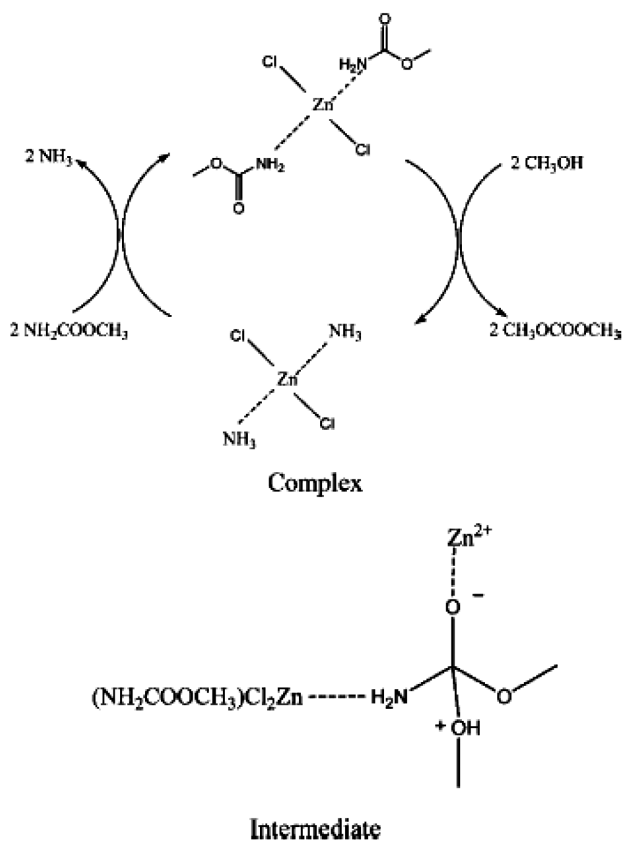
^bReaction condition: 0.1 mol EC, 46 g ethanol, and catalyst amount 1 g. DEC yields based on EC.

Fortunately, an interesting and significant phenomenon on the reaction of urea with ethanol was observed. That is, ZnO, which cannot dissolve in alcohol even at extremely high temperature, dissolved in the reaction solution, which was visually observed to be in the uniform phase at 70 °C, but some precipitate appeared in a few minutes with the further decrease in the temperature after the reaction. And then, this precipitate from the solution was filtered off, washed with ethanol, and determined by XRD, FT/IR, element analysis, and thermogravimetry/differential scanning calorimetry (TG/DSC). According to all the characterizations, the precipitate was suggested to be a pseudohalogen compound $\text{Zn}(\text{NH}_3)_2(\text{NCO})_2$, and such a species could be formed via the coordination of NH_3 to $\text{Zn}(\text{NCO})_2$, which originated from the reaction of ZnO with HNCO; the latter was the product of urea thermal decomposition (Scheme 6). More importantly, the precipitate ($\text{Zn}(\text{NH}_3)_2(\text{NCO})_2$) from the reaction of urea and ethanol showed high activity for the reaction of EC and ethanol, yielding 40.6 % of DEC (Table 2, entry 5). Thus, ZnO could be considered as the precursor of homogenous catalyst, which would be closely related to the conversion of urea in the synthesis process of DEC. The possible reaction mechanism was also proposed based on reaction results, FT/IR and XRD characterization, as described in Scheme 7.

**Scheme 6** Formation of $\text{Zn}(\text{NH}_3)_2(\text{NCO})_2$.**Scheme 7** Possible reaction mechanism in the reaction of EC with ethanol.

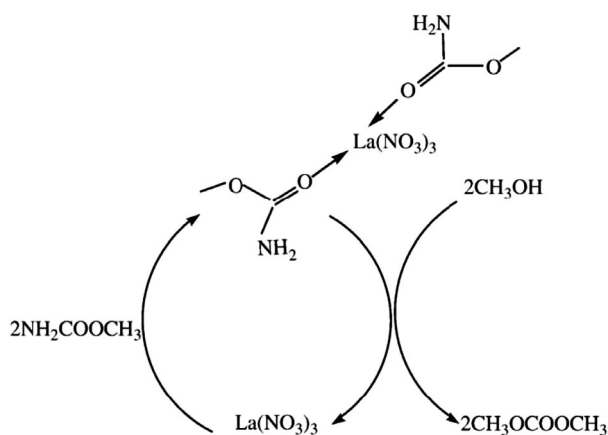
Although no precipitate was obtained in the synthesis of DMC from urea and methanol over ZnO owing to the different solubility of $\text{Zn}(\text{NH}_3)_2(\text{NCO})_2$ in methanol and ethanol, it could be easily concluded that $\text{Zn}(\text{NH}_3)_2(\text{NCO})_2$ might be the effective catalyst for the second step by the activation of MC to promote the formation of DMC in the urea methanolysis reaction, in which the reaction mechanism was similar to that in the reaction of urea with ethanol. In fact, $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ was also found in the reaction solution of synthesis DMC from MC and methanol over ZnCl_2 catalyst [52], such a Zn-complex, which was confirmed to be the same structure and analogous property as $\text{Zn}(\text{NH}_3)_2(\text{NCO})_2$, exhibited excellent catalytic performance in the reaction of MC with methanol.

As far as we know, the reaction of the urea methanolysis is a two-step process. The first step is fast and produces MC with high selectivity even without catalysts by urea monomethanolysis; however, the second step (MC to DMC), which is considered as the key and rate-control step for this approach, is more difficult than the first because ammonia accumulated in the first step will restrict the shift of the reaction equilibrium to DMC. Hence, dividing this reaction into two isolated steps will be a more efficient and promising method toward the synthesis of DMC, owing to the key to improve the production of DMC is to effectively promote the second reaction. Recently, Zhao et al. has investigated the reaction of MC and methanol using various zinc compounds as a catalyst in a batch reactor. Among them, ZnCl_2 showed the highest catalytic activity and led to the DMC yield of 33.6 % under the optimal conditions. FT/IR spectra and XRD characterization indicated that MC is activated by Zn^{2+} through the coordination of the nitrogen atom with $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ as an intermediate in catalytic circle after the reaction. Based on these, a possible reaction mechanism for catalyst ZnCl_2 was proposed as shown in Scheme 8 [52].



Scheme 8 Reaction mechanism in the reaction of MC with methanol.

Though ZnCl_2 exhibited high catalytic activity in the reaction of MC and methanol, it is a chlorine-containing homogeneous catalyst that is toxic and suffered from separation of productions. In order to overcome the corresponding shortcomings, other highly efficient heterogeneous chlorine-free catalytic materials for the production of DMC from MC and methanol were explored. Wang et al. prepared a series of zinc/iron mixed oxides (calcined by hydrotalcite-like compounds) as catalysts in the synthesis of DMC by MC with methanol. The MC conversion and DMC yield at the optimal reaction conditions were 46.1 and 30.7 %, respectively. Zinc/iron mixed oxide still showed high catalytic performance, and its structure was not changed at all after being used three times. This means that a heterogeneous catalyst with high catalytic performance and stability for this reaction was successfully developed [53]. Moreover, the authors exploited various lanthanum compounds as novel catalysts in the reaction of MC with methanol. Among them, $\text{La}(\text{NO}_3)_3$ presented the best catalytic performance with the DMC yield of 53.7 % under suitable reaction conditions. A possible reaction mechanism over $\text{La}(\text{NO}_3)_3$ was also proposed for this reaction on the basis of XRD, FT/IR, and element analysis, which revealed that MC is activated by La^{3+} via the coordination of the oxygen atom in carbonyl group, as described in Scheme 9 [54].



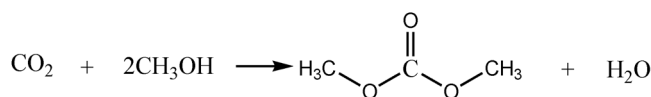
Scheme 9 Possible reaction mechanism.

Besides the work on catalytic performance and reaction mechanism, modeling of the catalytic distillation process and kinetic studies of DMC synthesis from urea and methanol were also studied at our lab, which make us more understanding of the whole process for DMC synthesis via urea methanolysis. Wang et al. developed a nonequilibrium model of the catalytic distillation for the DMC synthesis via urea methanolysis over a solid base catalyst at the bench scale. The Wilson model was used to account for the non-ideality of the liquid phase, and the influence of pressure, temperature, and reactive sensitivity was discussed. The results indicated that as the process includes the formation of a binary azeotrope and the removal of the noncondenser component of ammonia, the catalytic distillation is appropriate for the process of DMC synthesis and product separation [55]. Zhang et al. carried out a kinetic experiment on the synthesis of DMC by urea and methanol over ZnO catalyst in an isothermal fixed-bed reactor. A kinetic model based on the mole fraction was proposed, and the kinetic parameters were estimated from the experimental results. The experimental and simulated results indicated that the reaction from MC to DMC is the rate-controlling step in the DMC synthesis process from urea and methanol. It seems necessary to remove the DMC and by-product ammonia to achieve a high selectivity of DMC. This implied that reactive distillation might be used in the synthesis of DMC on an industrial scale to achieve a higher selectivity of DMC [56].

DIRECT SYNTHESIS OF DMC FROM CO₂ WITH METHANOL

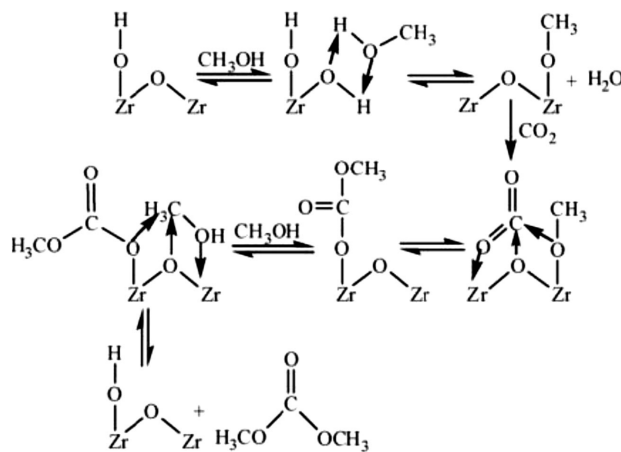
Chemical fixation of CO₂ may be very important in the future as a solution for the problem of increased atmospheric CO₂ level. In recent years, various chemical processes have been tried to convert CO₂ into valuable chemical compounds [57]. One of the most important methods of CO₂ chemical fixation is direct synthesis of DMC from CO₂ and methanol, which is favorable not only for reduction of greenhouse gas emissions but also for development of a new carbon resource. Hence, the direct synthesis of DMC from CO₂ and methanol is a much more attractive method since such an approach is environmentally benign, although the conversion (based on methanol) is still far from satisfaction at present because of the reaction equilibrium limitation and chemical inertness of CO₂. The direct synthesis of DMC from CO₂ and methanol is shown in Scheme 10.

So far, several studies have been devoted to the development of various catalyst systems for the direct synthesis of DMC from CO₂ and methanol. Generally, the synthesis of DMC directly from CO₂ and methanol was carried out in an autoclave reactor. Fang et al. reported that MCO₃ (here, M = alkaline metal) was superior for DMC formation from CO₂ with methanol, moreover, CH₃I played a key role in the reaction [58]. Toshiyasu et al. indicated that the yield and selectivity of DMC enhanced by the increase of CO₂ pressure, taking R₂Sn(OMe)₂ as the homogenous catalyst under the critic condition. However, R₂Sn(OMe)₂ is unstable in the moist environment, which can hydrolyze with the by-product water. Thus, some typical dehydrating agents, such as dimethyl acetal and trimethyl ortho ester, to consume the water were used in this reaction system and the DMC yield could reach as high as 70 % [59].



Scheme 10 DMC synthesis direct from CO₂ with methanol.

Bell et al. deduced the adsorption configuration of CO₂, DMC, and methanol through Raman spectra over ZrO₂-based catalysts. In addition, the mechanism for the reaction of methanol and CO₂ was elucidated in Scheme 11. Moreover, the study also confirmed that the effectiveness of ZrO₂ as a catalyst in this reaction is due to the presence of both Brønsted basic hydroxyl group (Zr–OH) and coordinately unsaturated Zr⁴⁺O²⁻ [60].



Scheme 11 Mechanism for the reaction of methanol and CO₂.

Jiang et al. found that the zirconia-supported Keggin unit 12-tungstophosphoric acid/zirconia ($\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$), which was prepared via a sol-gel technique, promoted the formation of DMC from CO_2 and methanol effectively under mild conditions. The results showed that with the amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on the catalysts in the range of 0–50 mg the DMC formation increased almost linearly. And the mechanistic studies indicated that acid–base bifunctional catalysis is essential in selective DMC synthesis. Compared with ZrO_2 , the $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$ catalyst has weak Brønsted acid sites, uniquely, which are more effective than Lewis acid sites for CH_3OH activation [61]. La et al. also reported that $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ catalysts prepared via sol-gel method were superior to the corresponding $\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$. The catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ showed a volcano-shaped curve with respect to cerium content. Moreover, it was found that the catalytic activity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ increased with increasing acidity (acid amount) and with increasing basicity (base amount) of the catalyst, which suggested that the acid–base bifunctional property of the catalyst is beneficial to the reaction [62]. Aouissi et al. investigated the catalytic properties of the prepared 12-heteropolytungstates ($\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$, $\text{Fe}_{1.5}\text{PW}_{12}\text{O}_{40}$) and 12-heteropolymolybdates ($\text{Co}_{1.5}\text{PMo}_{12}\text{O}_{40}$, $\text{Fe}_{1.5}\text{PMo}_{12}\text{O}_{40}$) for the direct synthesis of DMC from CO_2 and methanol. It was found that $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ was the most active and selective catalyst in the reaction, which could be attributed to the synergetic effect between Co and Fe. The direct conversion of the methanol in DMC could be enhanced if the 12-tungstophosphate cobalt salt was supported on a support (such as Al_2O_3) that is adequately basic [63].

Wu et al. has investigated the catalytic properties of modified V_2O_5 catalysts (such as $\text{H}_3\text{PO}_4/\text{V}_2\text{O}_5$ and $\text{Cu-Ni}/\text{V}_2\text{O}_5\text{-SiO}_2$) for the direct synthesis of DMC from gaseous methanol and CO_2 . In the $\text{H}_3\text{PO}_4/\text{V}_2\text{O}_5$ catalysts, the direct interaction between V and P forms weak Brønsted acid sites, which are more effective for the CH_3OH activation [64]. Fan et al. prepared highly stable heterogeneous organotin catalysts by in situ tethering $(\text{MeO})_2\text{ClSi}(\text{CH}_2)_3\text{SnCl}_3$ on the mesoporous silica (SBA-15) and successively replacing Cl^- bonded to Sn with CH_3O^- groups. This material showed much higher activity than the sample prepared by the grafting method for the synthesis of DMC from CO_2 and CH_3OH owing to the formation of organotin clusters with different structures and possessing a larger surface area. Further studies implied that the structure, surface property, and crystal size of mesoporous silicas have strong influences on the catalytic properties, and SBA-15 as a host was superior to SBA-16 and large-pore Ia3d [65].

Aymes et al. explored the catalytic properties of SnO_2 in the coupling of CO_2 with methanol to afford DMC. The SnO_2 catalysts prepared by the sol-gel route from $\text{Sn}(\text{OtBu})_4$ were much more active than a commercial one in this reaction owing to their higher surface areas. However, comparison with ZrO_2 , prepared and tested under the same conditions, it was shown that zirconia-based catalysts were the most selective among the heterogeneous catalysts already studied [66].

More recently, Bian et al. have studied a series of Cu-based catalysts for one-step catalytic synthesis of DMC directly from CO_2 and CH_3OH . The effects of preparation and reaction conditions on the catalyst performance were intensively investigated in terms of DMC formation rate and DMC selectivity. Cu^0 , Cu^+ , and Cu^{2+} coexist in the form of microcrystallinity on the catalyst, and they are the active species in the formation of DMC [67]. Moreover, the authors systemically investigated the influence of carbon material supports on the performance of Cu–Ni bimetallic catalysts. The carbon materials included graphite [68], thermally expanded graphite (TEG) [69], multiwalled carbon nanotubes (MWCNTs) [70], and V-doped activated carbon [71]. The results showed that the highly catalytic activity of the carbon material supported Cu–Ni bimetallic catalysts can be attributed to the synergetic effects of metal Cu, Ni and Cu–Ni alloy in the activation of CH_3OH and CO_2 , the unique structure of the carbon materials, and the interaction between the metal particles and the supports. Besides, possible catalytic mechanism for the direct synthesis of DMC from CH_3OH and CO_2 over the Cu–Ni bimetallic catalysts was also proposed. Zhang et al. discussed the solid solution series $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0$) with a bimodal pore structure prepared by the citric acid sol-gel

method, which was used in the synthesis of DMC from CO_2 and methanol. Results indicated that the Ce/Zr molar ratio in $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ is the key factor in determining the catalytic activity for the synthesis of DMC. For example, $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ calcined at 1273 K was confirmed to have a bimodal pore structure with both meso and macropores, and showed the highest catalytic performance in the reaction. In addition, 1,1,1-trimethoxymethane (TMM) was used to remove residual H_2O in situ, and was found to increase the methanol conversion in the process [72].

At our lab, direct synthesis of DMC from CO_2 and methanol was carried out at near supercritical conditions using nickel acetate as the catalyst. It was demonstrated that DMC could be produced as the unique product at such a low temperature as 305 K, and the yield was 12 times higher than that at non-supercritical conditions. The synthesis was sensitive to the reaction pressure and showed a maximum for DMC yield at the pressure of 9.3 MPa. Nickel acetate appeared to be the precursor of the catalyst. The formation mechanism of DMC in supercritical phase was proposed [73].

CONCLUSIONS AND PERSPECTIVES

As an environmentally friendly “green” chemical product, DMC has been widely used in many fields of chemical industry, but the production of DMC is still related to the toxic phosgene. Thus, the exploitation of “clean” routes for DMC syntheses becomes urgent and significant.

In recent years, many efforts have been dedicated to the development of phosgene-free synthesis methods for DMC. Up to now, producing DMC by non-phosgene routes via the oxidative carbonylation of methanol (both EniChem liquid-phase methanol oxycarbonylation and UBE methylnitrite carbonylation processes) and the transesterification method (Texaco process) have already been transferred to the industrial scale. However, the EniChem process and the UBE process have succeeded in avoiding phosgene but still employ a chlorinated derivative (CuCl or PdCl_2) as the catalyst and suffer from the use of poisonous or corrosive gases of CO_2 , hydrogen chloride and methyl nitrate and bearing the possibility of explosion. In addition, a significant portion of the capital employed in the EniChem system has to be devoted to the separation issues associated with breaking up the azeotropes between DMC, water, and methanol. In order to overcome all these drawbacks, producing DMC by a vapor-phase process of the oxycarbonylation of methanol over chlorine-free zeolite-based catalysts is considered as the most potential replacement for the EniChem process in the commercial production of DMC, although the production of DMC is unfortunately still low when compared to chlorine-containing activated charcoal-based catalysts.

Another promising approach for the synthesis of DMC is based on the transesterification of cyclic carbonates (PC or EC) with methanol. The transesterification is considered an excellent green chemical process in DMC production, using CO_2 and ethylene epoxide to produce an intermediate EC, and CH_3OH by transesterification to coproduce useful EG without producing any toxic reagent or pollution. However, the present commercial production process via transesterification employs homogeneous catalyst such as NaOCH_3 , which gives rise to the problems of the product separation and the catalyst recycle. In addition, the transesterification method is limited by the thermodynamic equilibrium conversion, which leads to low production of DMC. In the near future, the heterogeneous solid base catalyst will become a promising alternative to homogeneous catalyst in the industrial process of DMC production via transesterification, yet the yield of DMC over them is less than those over the industrial homogeneous catalyst at the present time.

In fact, producing DMC by urea methanolysis is a really ideal green chemistry route. This process uses urea and methanol, which have abundant resources and are low-priced, as raw materials, facilitated by non-toxicity catalysts such as Zn-based catalysts. As there is no water formed during this process, the ternary azeotrope, methanol-water-DMC, is not formed, the subsequent separation and purification of DMC thus being simplified. If ammonia, the only by-product, is connected with the urea production line, it is subjected to the duty cycle operation. This route is, therefore, considered to have an alluring foreground in industry application. In our group, lots of work has been done to actualize industry appli-

cation of DMC production via methanolysis of urea for about 10 years, and the pilot of this process has already been successfully achieved so far. We believe that the first set of industrial plants for urea methanolysis to DMC will be built somewhere in the world during the rest of this year.

The synthesis of DMC direct from CO₂ and methanol is still far from large-scale commercialization because of its poor conversions and low yields of DMC resulting from the thermodynamic stability and kinetic inertness of CO₂. However, it still attracted much attention in very recent years due to its importance in CO₂ chemical fixation, which is favorable for reduction of greenhouse gas emissions. Of course, it should be pointed out that the design of new catalysts and/or the use of efficient dehydrating agent are the key to achieve high yield and selectivity in this reaction. This synthetic route, if it could be successfully managed first at the laboratory scale and further at the industrial one, is believed to be the most economic one.

In conclusion, both transesterification and urea methanolysis are the most promising phosgene-free routes for DMC synthesis and will be the main direction of the industrialization for “clean” production of DMC in the future.

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