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Review

Dimethyl Carbonate: Review of Synthesis Routes and Catalysts Used

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Abstract: This review summarizes the performance of potential catalysts for the synthesis of dimethyl carbonate (DMC) using CO_2 as a feedstock by two major processes—the direct route of carbonylation of alcohols and the indirect route of alcoholysis of urea. The reaction mechanisms and corresponding catalysts that were previously investigated are discussed. The major challenges associated with the conversion of CO_2 to DMC are the low yields, low DMC selectivity, and thermodynamic limitations (alcohol carbonylation) of reversible reactions with low equilibrium constants. This occurs mainly due to the highly stable carbon dioxide molecules. The development of novel catalysts with high yields and high selectivity needs to be studied to overcome these technical challenges. In addition, to enhance the DMC yield, the use of dehydrating agents for water removal from the reaction mixture is recommended and discussed in detail in this article. This review critically examines the different catalysts used by investigators, along with their respective operating conditions and suitability in applications for the commercial synthesis of CO_2-based DMC.

Keywords: dimethyl carbonate; direct conversion from CO_2; urea alcoholysis; heterogeneous catalysis; homogenous catalysis

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1. Introduction

The global demand for dimethyl carbonate (DMC) is increasing at a rate of 6.9% annually, for major applications such as a feedstock for manufacturing polycarbonates, as an electrolyte in lithium-ion batteries, as low-volatile organic compound (VOC) solvents, as chemical intermediate for polyurethane, and its potential use as a fuel additive for diesel to reduce pollution [1–4]. DMC is deemed a green chemical because of its low toxicity, ease of degradability, and miscibility with water. It can replace carcinogenic chemicals, such as dichloromethane and dimethyl sulfate, that are commonly used for carbonylation and transesterification reactions. This article reviews various potential catalysts used for the synthesis of dimethyl carbonate (DMC) utilizing carbon dioxide (CO_2) as a starting material.

To reduce the atmospheric CO_2 concentration, CO_2 capture and sequestration/storage (CCS), and chemical fixation of CO_2 into fuels and chemicals have gained widespread attention. In the CCS process, physical adsorption, absorption, and membrane separation technologies are mainly used to store CO_2 in adsorbents. CO_2 utilization as a green, abundant, and inexpensive chemical feedstock is a topic of immense research interest because of the environmental impact and economy of the process. Review articles dealing with CCS and CO_2 reduction processes are available in the open literature [5–9]. Modak et al. [5] reviewed the CO_2 reduction processes, mainly focused on the utility and challenges in achieving the activation of the CO_2 molecule. In another review article [6], the authors described CO_2 reduction using nanoporous materials such as porous organic polymers, covalent organic frameworks, and metal-organic frameworks as catalysts and catalytic supports. The favorable characteristics such as large surface area, high thermal stability, and tunability in the porous nanostructures play a significant role in synthesizing catalysts for CO_2 hydrogenation reactions. Ghosh et al. [7] reviewed the status of the CO_2 fixation and briefly discussed the various catalytic networks that are used for the synthesis of value-added chemicals from CO_2 utilization. The catalytic frameworks are needed based on their composition, surface area, porosity, and thermal stability. The activity of the catalysts is described mainly using their capacity, selectivity, recyclability, and product yield. Tamboli et al. [8] reviewed the DMC synthesis from CO_2 and methanol with emphasis mainly on the different catalysts such as metal carbonates, metal oxides, tin-based, organic, and polymer-based materials. CO_2 utilization for applications in the chemical and fuel industries, through reduction and carboxylation reactions, is summarized by Alper et al. [9]. The authors discussed the heterogeneously catalyzed hydrogenation, photocatalytic, and electrocatalytic CO_2 conversion to value-added chemicals. Significant research and development efforts have been reported in the literature for using CO_2 as a promising candidate reagent for organic synthesis and energy applications. However, huge challenges exist to use CO_2 as a starting material for producing high-value chemicals. It requires new synthetic routes including both advanced process technologies and catalysts.

DMC is a very useful fuel additive and organic synthesis intermediate. Two separate DMC synthesis processes are being developed for the DOE project: first, using ethylene oxide as a feedstock, and second, with ammonia as a chemical carrier. Ammonia-based DMC synthesis requires the conversion of captured CO_2 to methyl carbamate, which can be converted to DMC using suitable catalysts. The process was previously based on using urea as a feedstock [3,4]. There have been significant investigations of catalyst developments for direct conversion of CO_2 to DMC by reacting with methanol or an alcoholysis reaction with urea as a feedstock. The purpose of this review is to evaluate catalysts examined by previous investigators for direct conversion of CO_2 with methanol and urea-based DMC synthesis. Based on the critical review, candidate catalysts can be identified for the direct reaction of CO_2 with methanol and ammonia to synthesize methyl carbamate followed by conversion to DMC. This critical review provides a comprehensive outlook for developing catalysts for the conversion of captured CO_2, leading to an economic process to meet the global DMC demand.

The phosgene process is commercially used to manufacture polycarbonates [10]. However, considering the hazardous properties of phosgene, non-phosgene processes have been developed. A syngas-based process is being actively pursued to replace the phosgene process (ENIChem [11]). Other synthesis processes such as oxidative carbonylation of alcohol are being explored for DMC synthesis [12]. Investigators are exploring new, environmentally friendly, and economically viable processes for DMC synthesis. The two leading new generations of DMC synthesis routes that are reported in the literature are (i) the direct conversion of CO_2 by reacting with methanol and (ii) the indirect reaction of CO_2 and ammonia to urea, which can be converted to DMC by reacting with methanol, as presented by Figure 1.

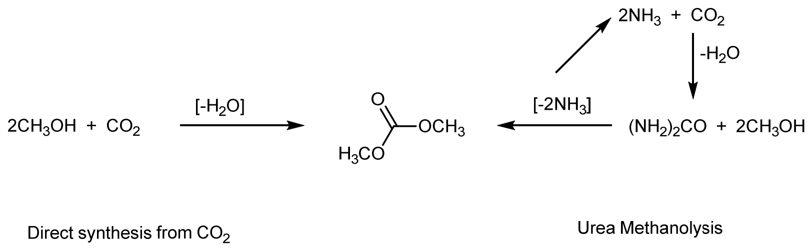


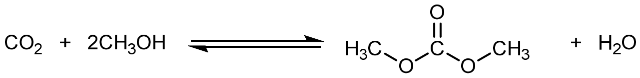
Figure 1. Synthetic routes for dimethyl carbonate (DMC) production (discussed in this review).

This critical review thoroughly discusses the catalysts that are investigated for these two DMC synthesis routes. The direct conversion of CO_2 and methanol to DMC is thermodynamically limited by a low equilibrium constant; therefore, in-situ removal of water would enhance DMC yields. For in-situ water removal, the use of dehydrating agents is discussed in detail. The use of ionic liquids as a catalyst for the direct conversion of methanol and CO_2 to DMC is presented. Another route, i.e., the indirect urea alcoholysis route, which is a low-cost, and the facile synthesis process is also covered in this review. The catalytic developments reported so far are summarized along with operating conditions. The last topic in this review summarizes the limitations associated with the discussed synthetic routes for DMC and possible solutions for their large-scale applications.

2. Carbon Dioxide (CO_2)-Based Synthesis of DMC

2.1. Direct Conversion of CO_2 to DMC

The direct conversion of CO_2 by reacting with methanol (CH_3OH) occurs at 493 K and 2.4 MPa by the oxidative carbonylation of methanol to form DMC (CH_3O-CO-OCH_3) with water (H_2O) as byproduct, as per Equation (1):



(1)

A low DMC yield has been generally reported in the literature [13–24]. The key factors that are responsible for low DMC yields include thermodynamic constraints, DMC hydrolysis, high CO_2 stability, and catalyst deactivation. Moreover, water removal from the reaction system is expected to shift the reaction equilibrium toward DMC synthesis. Therefore, the use of dehydrating agents has been reported extensively in the literature.

Table 1 summarizes the promising findings, including the catalysts and reaction conditions used for the direct conversion of CO_2 to DMC. Catalysts such as organometallic compounds [13,14], potassium carbonate [15], metal tetra-alkoxides [16], zirconia [17], and heteropolyacids, such as $H_3PW_{12}O_4/ZrO_2$ [18], H_3PO_4/V_2O_5 [19], Cu(Ni,V,O)/SiO_2 [20], and CuNi/V_2O_5-SiO_2 [21], have been reported for the conversion of methanol and CO_2 to DMC. However, DMC yields were observed to be very low, even in the presence of dehydrating agents such as $CaCl_2$ [18], 2,2-dimethylpropane (DMP) [22], molecular sieves [23], or light illuminations [24]. A few findings are explained in detail in the following section.

Zhao et al. [25] discussed the catalytic conversion reaction for DMC synthesis from CO_2 and methanol using nickel acetate at near supercritical conditions. The authors compared the results with non-supercritical conditions. At 305 K, 2 h, and 10.3 MPa conditions, 100% DMC selectivity was achieved, and the DMC yield was 350 mol%/mol-cat. Most importantly, the formation of the side product, methyl acetate, was not reported at near supercritical conditions. Thus, the study concluded that the supercritical conditions play a role in DMC formation in the presence of metal acetates as a catalyst.

Table 1. Literature review of the catalysts used for the direct conversion of CO_2 to DMC.

S. No	Catalysts	Dehydrating Agents Used	Reaction Conditions	MeOH Conversion, %	DMC Yield, %	DMC Selectivity, %	Source
1	Cu-Ni/TEG	-	T = 373 K; P = 1.2 MPa; MeOH:CO_2 ratio-2:1	4.97	-	89.3	[26]
2	20% Cu-Ni bimetal/0.4 mm molecular sieve	-	T = 393 K; P = 1.1 MPa; t = 5 h; n(CO_2/MeOH) = 10; Gas space velocity of 510/h		5	86	[27]
3a	Cs-DMP-HMS	-	T = 323 K; P = 15 MPa; t = 5 h; Catalyst = 7.21×10^{-3} g/cm^3; IL = 4.8×10^{-3} g/cm^3; n(CH_3OH/CO_2) = 2	5.8	-	17.2	[28]
3b	Cs-DMP-HMS + Phos-IL			8.1		23.6	
3c	Cs-DTP-HMS			10.1		24.4	
3d	Cs-DTP-HMS + Phos-IL			11.9		25.8	
3e	CHT-HMS + Phos-IL			9.1		68.5	
3f	CHT-HMS			9.2		82	
3g	Phos-IL			0		0	
4a	$Ce_{0.1}Ti_{0.9}O_2$	-	T = 443 K, CO_2/N_2 volumetric ratio 1/7	4.2	2.3	55	[29]
4b	$H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$			5.5	5	91.4	
5	DEG[Vim]$_2$[NTf$_2$]$_2$/MgO-CeO_2 nanofiber sponge	-	T = 393 K; P = 3 MPa; t = 3 h; MeOH = 437.5 mmol; IL = 0.85 mmol; Catalyst = 0.27 mmol	73.1[b]	-	98.9	[30]
6a	$Zn_{0.10}Ce_{0.90}O_2$/honeycomb ceramic (Monolithic)	-	T = 433 K; P = 2.4 MPa; MeOH = 0.145 mL/min; GHSV = 2880 mL gcat^{-1}h^{-1}	20.5	-	82.1	[31]
7a	CeO_2-nanorod	-	T = 413 K; P = 3 MPa; t = 3 h; MeOH = 35 mL; Catalyst = 0.5 g	-	1.5 [c]	-	[32]
7b	CoO_2/CeO_2				1.4 [c]		
7c	NiO/CeO_2				0.9 [c]		
7d	CaO/CeO_2				0.8 [c]		
7e	CuO/CeO_2				0.2 [c]		
8a	ZrO_2-HX-C (calcination of zirconia hydroxide)	-	T = 433 K; P = 4.8 MPa; t = 5 h	-	78 [a]	-	[33]
8b	ZrO_2-HT-(393 *)				163 [a]		
8c	ZrO_2-HT-(433 *)				140 [a]		
8d	ZrO_2-HT-(473 *)				116 [a]		
8e	ZrO_2-HT-(493 *)				115 [a]		
8f	ZrO_2-HT-(513 *)				90 [a]		
8g	meso-ZrO_2				83 [a]		
9	10% (*w*/*w*) Ce-Zr oxide/graphene nanocomposite	TMM	T = 383 K; P = 27.5 MPa; t = 16 h; 1:1 (*w*/*w*) TMM:MeOH	58	33	-	[34]

Table 1. *Cont.*

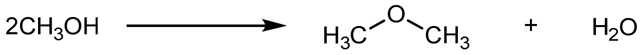
S. No	Catalysts	Dehydrating Agents Used	Reaction Conditions	MeOH Conversion, %	DMC Yield, %	DMC Selectivity, %	Source
10a	None	-	T = 383 K; P = 5 MPa (at room temp); t = 4 h; MeOH = 12 g; Cat = 1 g	-	0	0	[35]
10b	ZrO_2				0.12^{b}	100	
10c	$Fe_{0.3}Zr_{0.7}O_y$				0.24^{b}	100	
10d	$Fe_{0.5}Zr_{0.5}O_y$				0.35^{b}	100	
10e	$Fe_{0.7}Zr_{0.3}O_y$				0.44^{b}	100	
10f	$Fe_{0.9}Zr_{0.1}O_y$				0.28^{b}	100	
10g	Fe_2O_3				0.04^{b}	100	
11a	K_2CO_3 (0.0029 mol)	-	T = 353 K; P = 7.3 MPa; t = 6 h; MeOH = 0.85 mol, CH_3I = 0.048 mol	-	4.1	-	[36]
11b	KOH (0.054 mol)				8.5		
11c	NaOH (0.054 mol)				1.7		
11d	$KHCO_3$				0.5 (10 h)		
12a	CeO_2	2-picolinamide	T = 393 K; P = 20 MPa	17	-	>99	[37]
12b	CeO_2	2-cyanopyridine	T = 413 K; P = 20 MPa	92.4		>99	
12c	CeO_2	2-cyanopyridine	T = 353 K; P = 20 MPa	94		98	
13a	CH_3OK and CH_3I	Sieve/DMP	T = 353 K; P = 4 MPa; MeOH = 213 mmol; Catalyst = 10 mmol; Promoter = 20 mmol; Dehydrating agent = 10 mml; t = 24 h	48.6	42.8	88	[38]
13b	CH_3OK and CH_3I	Sieve/Na_2SO_4		14.8	14.8	100	
13c	CH_3OK and CH_3I	Sieve/butylene oxide		2.5	0.3	15	
13d	CH_3OK and CH_3I	Sieve/MgO		4.5	4.5	100	
14a	10 wt% Chitosan/$IL^{\#}$-NTF_2 (anion) + DBU	-	T = 373 K; P = 7.5 MPa; MeOH = 618 mmol; Catalyst = 3 g; DBU = 1 g	16.9	-	98.72	[39]
14b	10 wt% Chitosan/$IL^{\#}$-Cl (anion) +DBU			14.58		90.7	
14c	10 wt% Chitosan/$IL^{\#}$-PF_6 (anion) +DBU			14.89		94.87	
14d	10 wt% Chitosan/$IL^{\#}$ without DBU			10.21		98.12	
14e	Pure Chitosan			0.13		99.4	
15a	[bmim][Cl]	2,2-dimethoxypropane	T = 443 K; P = 4 MPa CO_2; t = 24 h; MeOH = 250 mmol; Dehydrant = 25 mmol; IL = 2.5 mmol	7.46	-	53.02	[40]
15b	[bmim][BF_4]			7.43		81.31	
15c	[bmim][PF_6]			7.19		46.9	
15d	[bmim][Tf_2N]			6.89		39.3	
15e	[emim][BF_4]			9.22		83.3	
15f	[emim][Tf_2N]			8.98		43.01	
15g	[mbmim][Tf_2N]			6.81		35.13	

Table 1. *Cont.*

S. No	Catalysts	Dehydrating Agents Used	Reaction Conditions	MeOH Conversion, %	DMC Yield, %	DMC Selectivity, %	Source
15h	$[dmbmim][Tf_2N]$	2,2-dimethoxypropane	T = 443 K; P = 4 MPa CO_2; t = 24 h; MeOH = 250 mmol; Dehydrant = 25 mmol; IL = 2.5 mmol	6.65		33.63	[40]
15i	[bpy][Cl]			7.73		53.44	
15j	$[bpy][BF_4]$			7.52		60.72	
15k	$[bpy][PF_6]$			7.57		41.4	
15l	$[bpy][Tf_2N]$			7.43		34.54	
15m	$[epy][BF_4]$			7.65		63.72	
15n	$[epy][Tf_2N]$			9.35		38.49	
15o	$[dmbpy][Tf_2N]$			6.78		28.81	
16a	$[C_1C_4Im][HCO_3]$, without base	DBU	T = RT; P = 1 MPa; t = 24 h; Base = 5 mmol	14	-	>99	[41]
16b	5 mmol $[C_1C_4Im][HCO_3]Na_2CO_3$			22		97	
16c	5 mmol $[C_1C_4Im][HCO_3]NaHCO_3$			24		>99	
16d	5 mmol $[C_1C_4Im][HCO_3]K_2CO_3$			61		54	
16e	5 mmol $[C1C_4Im][HCO_3]KHCO_3$			24		>99	
16f	5 mmol $[C_1C_4Im][HCO_3]Cs_2CO_3$			45		>99	
16g	0.25 mmol $[C_1C_4Im][HCO_3]Cs_2CO_3$			26		>99	
16h	2.5 mmol $[C_1C_4Im][HCO_3]Cs_2CO_3$			37		>99	
16i	20 mmol $[C_1C_4Im][HCO_3]Cs_2CO_3$			74		97	
16j	$[C_1C_4Im][HCO_3]Cs_2CO_3$		T = 323 K; P = 1 MPa; t = 24 h	54		>99	
16k	20 mmol $[C_1C_4Im][HCO_3]Cs_2CO_3$		T = 323 K; P = 1 MPa; t = 24 h	82		94	

DMC = Dimethyl carbonate; MeOH = Methanol; * = Reaction temperature; ^{a} = μmmol; ^{b} = mmol $gcat^{-1}$; ^{c} = mmol; TEG = Thermally expanded graphite; HMS = Hexagonal mesoporous silica; CHT = Calcined hydrotalcite; DMP = Dodecamolybdophosphoric acid; DTP = Dodecatungstophosphoric acid; Cs-DMP = Cesium substituted dodecamolybdophosphoric acid; Cs-DTP = Cesium substituted dodecatungstophosphoric acid; IL = Ionic liquids; Phos-IL = Phosphonium based ionic liquid; TMM = 1,11-trimethoxymethane; HT = Hydrothermal synthesis; $IL^{\#}$: 1-methyl-3-(methylsulfonyl)-1H-imidazol-3-ium chloride ([Msmim][Cl]); DBU = Diazabicycloundes-7-ene; [bmim][Cl] = 1-butyl-3-methylimidazolium chloride; $[bmim][BF_4]$ = 1-butyl-3-methylimidazolium tetrafluoroborate; $[bmim][PF_6]$ = 1-butyl-3-methylimidazolium hexaflurophosphate; $[bmim][Tf_2N]$ = 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[emim][BF_4]$ = 1-ethyl-3-methylimidazolium tetrafluoroborate; $[emim][Tf_2N]$ = 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[mbmim][Tf_2N]$ = 1-(3-methyl)butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[dmbmim][Tf_2N]$= 1-(3,3-dimethyl)butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [bpy][Cl] = N-butyl-pyridine chloride; $[bpy][BF_4]$ = N-butyl-pyridine tetrafluoroborate; $[bpy][PF_6]$ = N-butyl-pyridine hexaflurophosphate; $[bpy][Tf_2N]$ = N-butyl-pyridine bis(trifluoromethylsulfonyl)imide; $[epy][BF_4]$ = N-ethyl-pyridine tetrafluoroborate; $[epy][Tf_2N]$ = N-ethyl-pyridine bis(trifluoromethylsulfonyl)imide; $[dmbpy][Tf_2N]$ = 1-(3,3-dimethyl)butyl-pyridine bis(trifluoromethylsulfonyl)imide; and $[C_1C_4I_m]$ = 1-butyl-3-methylimidazolium.

Supported transition metal (TM)-based catalysts were found to have high catalytic effects on DMC yield [26,27,42]. Bian et al. [26] demonstrated the catalytic applications of bimetallic Cu-Ni catalysts supported on thermally expanded graphite (TEG) to synthesize DMC. The 5% methanol conversion with 89% DMC selectivity was reported at 373 K and 1.2 MPa in the presence of a Cu-Ni bimetallic catalyst. In addition, CO, formaldehyde (HCHO), and water were detected as byproducts of the reaction. The proposed reaction mechanism includes steps (i) methanol activation on the metal surface to generate methoxide anion CH_3O^-, (ii) CO_2 activation on the metal surface to form $-C{=}O$ species, and (iii) reaction between CH_3O^- and –C=O species, forming DMC and metal regeneration. The role of the support was described as the following: TEG support facilitates better dispersion of Cu and Ni atoms resulting in a higher surface area of catalysts. The electronic transporting properties and conductivity of graphite might change the electronic balance of the metal-support system, which in turn enhances the metal-support interactions, thereby affecting the selectivity and reactivity of the chemical reaction. Bian et al. [42] examined the activity of an activated carbon (AC)-supported $CuCl_2$ catalyst for a single-step DMC synthesis. The results demonstrated that the catalyst activity was greatly influenced by the metal loading amount and calcination temperature used. The investigators observed that for metal (Cu) loading greater than 7%, the catalyst activity did not increase. This behavior was attributed to the change in the morphology of the catalysts which could have been due to the blockage of active sites by the deposition of metal particles. The major side products reported were dimethyl ether (DME), CO, methyl formate (MF), and water. CO was formed by the cleavage of the C-O bond of CO^{2-} species; the formation of MF and formaldehyde (HCHO) can be explained by Equations (2) and (3).



(2)

$$CH_3OH \xrightarrow{+O} HCHO \xrightarrow{+O} HCOOH \xrightarrow{+CH_3OH} HCOOCH_3 \tag{3}$$

The results shown in Figure 2 present the effects of reaction temperature and reaction pressure on the rate of product formation. As the reaction temperature increased from 373 to 413 K, below 343 K no DMC yield and a very low amount of reaction products were formed. On the contrary, a large concentration of by-products such as DME and MF were formed above 423 K by the reaction of CH_3OH with HCHO and formic acid (HCOOH). Therefore, the authors concluded an optimum reaction temperature of 393 to 403 K for the DMC synthesis. The authors also studied the effect of reaction pressure 1.0–1.4 MPa at a constant temperature of 393 K. With an increasing reaction pressure, the production rate of DMC increased continuously. DMC selectivity was also markedly increased from 77 to 90% with a pressure of 1.0 to 1.4 MPa. The surface properties and morphology of the catalysts using ammonia-temperature programmed desorption (NH_3-TPD), X-ray diffraction (XRD), scanning electron microscopy energy dispersive X-ray (SEM-EDX), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) techniques showed that the co-existence of Cu^0, Cu^+, and Cu^{2+} species in the form of micro-crystallinity on the catalyst. The catalyst calcined at 673 K maximized the presence of Cu^{2+} species that was responsible for the higher DMC formation. Thus, creating an effective Cu structure on the AC surface could promote more selective DMC formation. Chen et al. [27] explored the catalytic application of a (Cu-Ni)/0.4 mm molecular sieve catalyst to synthesize DMC from CO_2 and methanol in a continuous-flow fixed-bed reactor. The highest DMC yield was 5% with a 20% loading of the catalyst system. Based on characterizations of the catalyst system using advanced techniques, the proposed mechanism for the reaction is that a large amount of basic sites facilitates methanol activation to methoxide anions and their subsequent reaction with $CO_2{}^-$ species, activated on acid sites.

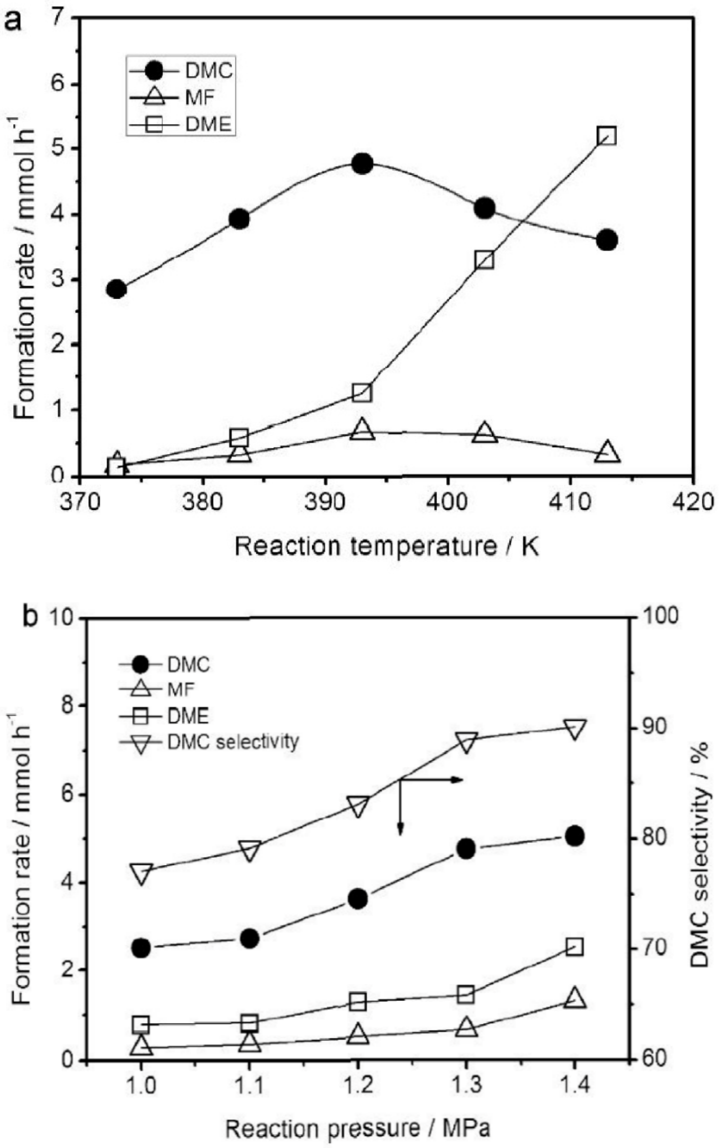


Figure 2. Effects of (**a**) reaction temperature and (**b**) pressure (at 393 K) on the DMC formation from CO_2 and methanol with a $CuCl_2$/AC catalyst [42]. (Adapted with permission from Ref. [42], 2010, Elsevier).

Hydrotalcites, commonly known as mixed oxides, are also promising catalysts that have been used in several industrially relevant applications [28]. These are the magnesium and aluminum oxide solid solutions that are mainly calcined at 773–1073 K. In particular, the calcined hydrotalcites (CHT) supported on hexagonal mesoporous silica (HMS) possess several basic and Lewis acid sites. Therefore, CHT can be used for carbonate synthesis. Kabra et al. [28] demonstrated the process using CHT supported on HMS as a catalyst and phosphonium-based ionic liquids (Phos-ILs) as a promoter. The process was conducted in a supercritical phase. The catalysts based on heteropolyacids, such as dodecatungstophosphoric acid (DTP) supported on HMS, are active, but selectivity for DMC was very low (~25%). The reason is the formation of byproducts, i.e., DME, MF, and dimethoxymethane (DMM) oxalate. However, when the CHT/HMS catalyst was used, DMC selectivity was much higher comparatively, and there was only one byproduct, DME. CHT/HMS catalysts are called dual-site catalysts due to the presence of both basic and acidic sites. These sites are required for activating methanol and CO_2 molecules. The researchers also proposed a reaction mechanism, which is shown in Figure 3. According to the mechanism, CHT/HMS, a bifunctional catalyst, contains S_1 acidic and S_2 basic sites. Methanol was adsorbed on the S_1 active sites and CO_2 on the S_2 sites. Then, these chemisorbed species had undergone a surface reaction to produce DMC. A low temperature favors the formation of DMC. The use of heteropolyacids such as $H_3PW_{12}O_{40}$-$Ce_xZr_{1-X}O_2$ [43,44] and $H_3PW_{12}O_{40}$-$Ce_xTi_{1-X}O_2$ [29,45,46] for the DMC synthesis has also been extensively reported. Chiang et al. [29] synthesized the $H_3PW_{12}O_{40}$-$Ce_{0.1}Ti_{0.9}O_2$ catalyst and compared its activity with $Ce_{0.1}Ti_{0.9}O_2$ for the catalytic conversion of methanol and CO_2 to DMC at different reaction temperatures (383, 443, and 493 K), 5 MPa, and 10 h. Acidic and basic sites of these bifunctional catalysts were responsible for the formation of DMC.

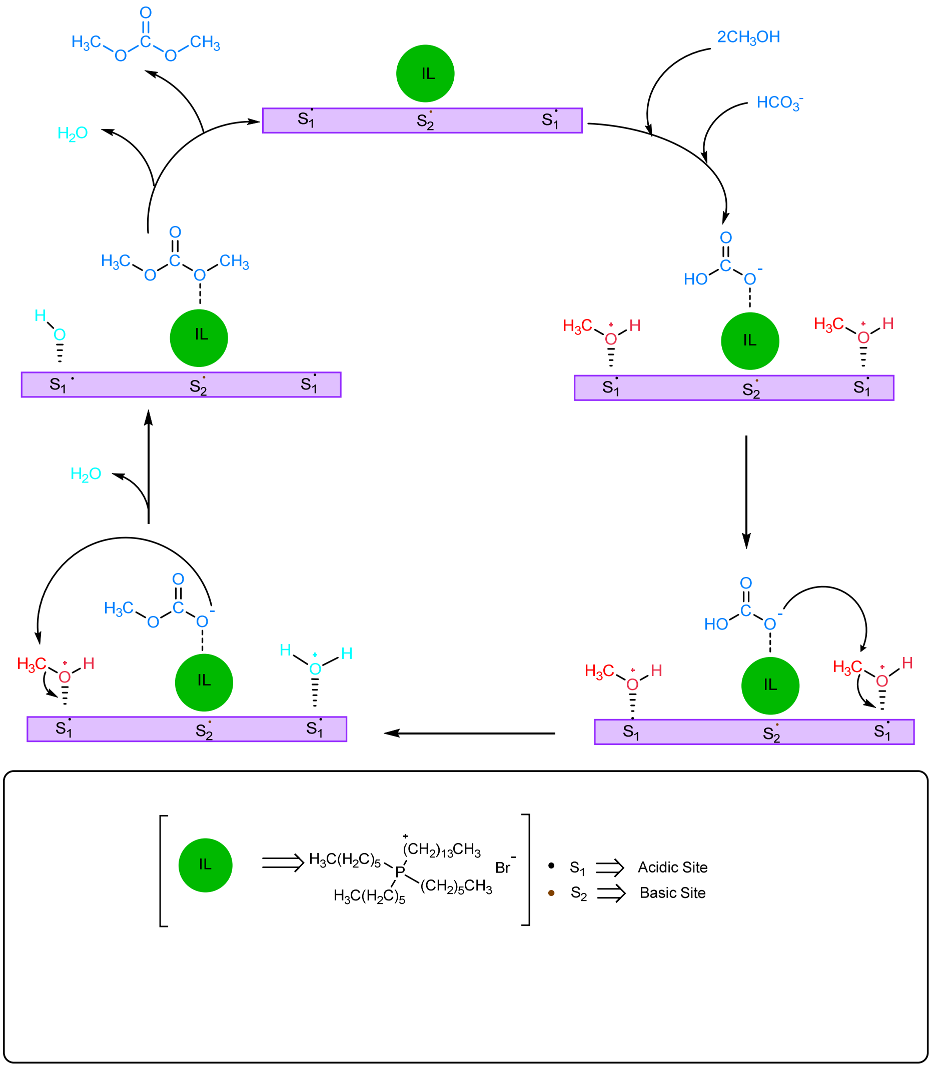


Figure 3. Reaction mechanism for the conversion of CO_2 and methanol to DMC proposed by Kabra et al. [28]. (Reprinted with permission from Ref. [28], 2016, Elsevier).

To study the effect of acidity and basicity of the transition metal oxide-based catalysts, Lee et al. [47] prepared various $MO/Ce_{0.6}Zr_{0.4}O_2$ catalysts, where MO = Ga_2O_3, Ni_2O_3, La_2O_3, Fe_2O_3, Co_3O_4, Y_2O_3, and Al_2O_3. The catalyst activity was investigated for the direct DMC synthesis from methanol and CO_2. NH_3-TPD and CO_2-TPD were carried out for determining the acidity and basicity of $MO/Ce_{0.6}Zr_{0.4}O_2$ catalysts. The acidity of the catalysts $Ce_{0.6}Zr_{0.4}O_2$, $Ga_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $La_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Ni_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Fe_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Y_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Co_3O_4/Ce_{0.6}Zr_{0.4}O_2$, and $Al_2O_3/Ce_{0.6}Zr_{0.4}O_2$, was 85.7, 226.3, 210.4, 188.6, 180.1, 164.5, 146.5, and 132.6 μmol-NH_3/g catalyst as determined by NH_3-TPD [47]. On the contrary, the basicity of the catalysts $Ce_{0.6}Zr_{0.4}O_2$, $Ga_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $La_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Ni_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Fe_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Y_2O_3/Ce_{0.6}Zr_{0.4}O_2$, $Co_3O_4/Ce_{0.6}Zr_{0.4}O_2$, and $Al_2O_3/Ce_{0.6}Zr_{0.4}O_2$, was 17, 121.8, 110.8, 94.2, 88, 84.6, 78.3, and 68.2 µmol-CO_2/g catalyst, as determined by CO_2-TPD [47]. The results showed that the amount of DMC produced using catalysts increased with the increasing acidity of the catalysts. Among the tested catalysts, $Ga_2O_3/Ce_{0.6}Zr_{0.4}O_2$ showed the largest acidity and best catalytic performance for the direct DMC synthesis from methanol and CO_2. The high acidity of the catalyst was favorable for the activation of methanol to methyl species leading to the facile DMC formation. A correlation between basic sites and catalytic performance of the catalysts showed that the amount of DMC formed over $MO/Ce_{0.6}Zr_{0.4}O_2$ increased with the increasing basicity of the catalysts. The $Ga_2O_3/Ce_{0.6}Zr_{0.4}O_2$ catalyst with the largest basicity showed the best catalytic performance for DMC synthesis. It has been reported that the basic sites of the catalysts are required for the formation of methoxy carbonate anion via the reaction of CO_2 and methoxy species. The methoxy carbonate anion formed on the basic sites of the catalyst reacts with methyl species on the acid sites of the catalyst to produce DMC. Thus, both the acidity and basicity of the catalysts served as crucial factors in determining the catalytic performance for the DMC synthesis from CO_2 and methanol.

Further, metal-oxide-based nanocrystals were also investigated for conversion reactions. These nanocrystals are interesting mainly because of their size, shape, crystallinity, and crystal structure, which can be tuned by varying reaction conditions. These nanocrystals possess large surface areas because of their smaller size and exposed crystal planes. Marin et al. [48] studied kinetics for the DMC synthesis using methanol and CO_2 and utilizing ceria nanorods as nanocrystals. The activation energy barrier for the nanorod ceria and non-nanostructured ceria catalysts (commercial) was found to be 65 ± 14 kJ/mol and ~110 kJ/mol, respectively. The authors concluded that the kinetics for the conversion process could best be improved by (i) maximizing the surface area of the catalyst; (ii) reducing the energy barrier required for CO_2 adsorption and the activation step; and (iii) performing the reaction with a low methanol to CO_2 ratio.

A sponge-type MgO-CeO_2 metal oxide nanostructure was developed using the electrospinning technique and the resulting nanostructure possesses characteristics such as high surface area, 3D matrix morphology, and hierarchical porous structure [30]. The catalytic activity of the synthesized metal oxide with different ionic liquids (ILs) combinations for DMC synthesis was evaluated. The synthesized metal oxide nanofiber sponge was found to be easily mixed into ILs resulting in the formation of a highly porous network that provides a huge surface-to-volume ratio which is helpful for CO_2 capture. The combination of metal oxide with IL showed a 73 mmol g^{-1} cat DMC yield with 98.9% selectivity. The reaction conditions used were 3 MPa CO_2 pressure, 393 K temperature, 3 h time, and a 1.12 mmol catalyst. The catalytic activity of the monolithic catalysts was also evaluated for the direct synthesis of DMC from CO_2 and methanol [31]. For the catalyst synthesis, Zn-Ce-based metal oxide nanoparticles were prepared using an aqueous-phase co-precipitation method. Further, synthesized nanoparticles were coated on honeycomb ceramics to obtain monolithic catalysts. The highest catalytic activity was observed with a monolithic $Zn_{0.10}Ce_{0.90}O_2$ catalyst, even in the absence of a dehydrating agent. The advantages associated with the monolithic catalysts are their large geometrical surface area, low-pressure drop, better mass and heat transfer, and easy catalyst separation. In addition, these catalysts possess regular channel structures, which make better contact between the catalyst surface and regular gas stream and remove water (by-product) in time.

Darwish et al. [32] discussed the role of a Ce-nanorod doped with metals such as Ni, Cu, and Co for the direct conversion of CO_2 into DMC. The ceria shape was found to affect the DMC yield. For instance, Ce-nanorods gave a 1.6 mmol DMC yield, which is higher compared to a Ce-nanooctahedra (1.5 mmol) and a Ce-nanocube (1.0 mmol). It was observed that Ce-nanorods having (110) and (100) facets showed the highest DMC yield compared to the cubes (100) and octahedra (111) nanostructures. Mixed-metal oxide exhibits the catalytic activity in the following order $CoO/CeO_2 > NiO/CeO_2 > CaO/CeO_2 > CuO/CeO_2$. The results proposed that high oxygen storage capacity catalyst samples can be designed and obtained by shape-selective synthesis strategies.

The use of a zirconia (Zr)- based catalyst is extensively reported in the literature for the CO_2-based DMC synthesis process. Akune et al. [33] reported DMC synthesis using ZrO_2 nanocrystals. The reported work used three different kinds of ZrO_2: (i) ZrO_2-HT (nanocrystal synthesized by hydrothermal treatment), (ii) ZrO_2-HX-C (prepared by calcination of zirconium hydroxide), and (iii) meso-ZrO_2 (mesoporous ZrO_2). The results showed that ZrO_2-HT and ZrO_2-HX-C catalysts exhibited much higher activity compared to meso-ZrO_2. The meso-ZrO_2 catalyst showed low activity because of its poor crystallinity. The authors also studied the relationship between the reaction rate and the amounts of surface species. CO_2-TPD and in-situ Fourier transform infrared (FT-IR) experiments were performed to determine the amount of surface species. The structures of some species detected are shown in Figure 4. The surface sites on which bidentate species (b-HCO_3^- and b-CO_3^{2-}) formed play a promising role in the rate-determining step. A b-HCO_3^- species forms an unsaturated Zr^{4+} site and OH group, and a b-CO_3^{2-} species forms a coordinately unsaturated Zr^{4+} site. Wang et al. [49] proposed that the amount and strength of Bronsted acid sites and the size of the band gap present in ZrO_2 strongly influenced the catalytic performance for the synthesis of DMC from CO_2 and methanol.

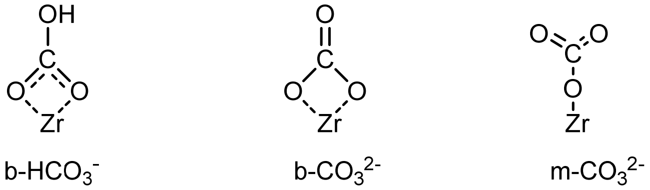


Figure 4. Reaction species involved using ZrO_2 catalyst for DMC synthesis, as proposed by Akune et al. [33]. (Reprinted/adapted with permission from Ref. [33], 2018, ACS).

Carbon nanotubes (CNTs) have various unique properties such as superior electronic conductivity and a high capacity for hydrogen uptake and are attracting increasing attention as a novel support for heterogenous catalysts. The major advantage of CNTs as support materials for catalysts is that they possess a high surface area and better electronic conductivity compared to conventional carbon materials such as graphite and activated carbon. The use of CNTs has been reported in heterogeneous catalysis, however, there are few reports on DMC synthesis. Bian et al. [50] reported the activity of the multi-walled carbon nanotube (MWCNT) supported Cu-Ni bimetallic catalysts for the direct DMC synthesis reaction. The Cu-Ni/MWCNT catalyst was found to be active for DMC production at 393 K and 1.2 MPa with 4.3% methanol conversion. The high activity of the catalyst was attributed to the synergistic effect of metals and the Cu-Ni alloy for the methanol and CO_2 activation. Later, Merza et al. [51] studied the DMC synthesis by oxidative carbonylation of methanol and CO_2 using chloride-free Cu-supported MWCNT catalysts. At the optimal reaction conditions, i.e., 393 K and atmospheric pressure, DMC yield was 1.2% and methanol conversion was 4% in the presence of Cu/MWCNT catalyst. XPS analysis of the catalyst showed that the DMC formation rate depends on the surface concentration of Cu^+ species.

Graphene-based inorganic nanocomposites as catalysts were also reported for the conversion of methanol and CO_2 to DMC at low-temperature and high-pressure conditions [34]. A unique, rapid, and innovative continuous hydrothermal flow synthesis approach was studied to synthesize an active and highly stable ceria-zirconia oxide/graphene. With a 10% (w/w) Ce-Zr oxide/graphene catalyst, the maximum 58% methanol conversion and 33% DMC yield was found at an optimized reaction condition of 383 K, 16 h, and 27.5 MPa. The authors concluded that Ce has the acid sites with the lowest strength, which increases on adding Zr to the catalyst; meanwhile, Ce-rich solid solutions possess a highly basic character. The weak acidity was favorable for the DMC synthesis because DME (side product) is mainly formed on strong acid sites. Ce-Zr mixed oxides prepared by the flame spray pyrolysis method exhibit higher activity compared to those prepared by the precipitation procedure [52]. The authors proposed that the flame spray pyrolysis method leads to a surface enrichment in CeO_2 in interaction with ZrO_2, which leads to a high concentration of adsorbed methanol at the catalytic surface. This method also generates high surface mixed oxides. In another study [35], the activity of FeZr-mixed metal oxide catalysts with different Fe contents showed better performance compared to pure Fe_2O_3 and ZrO_2 for DMC synthesis. The addition of iron to zirconia influenced the crystal structure of the ZrO_2, increasing the amount of surface acidic and basic sites. XRD and TPD results revealed that the presence of hexagonal Fe_2O_3 and cubic Fe_2O_3 favored the formation of moderate acidic and basic sites. These sites promoted methanol and CO_2 activation. The suggested mechanism was that methanol was activated to methoxy and methyl species on the basic and acidic sites of the catalyst, respectively. Then, methoxy species react with carbon dioxide, adsorbed on the basic sites of the catalyst, to form methoxy carbonate anion. Further, this anion reacts with methyl species to produce DMC.

Cai et al. [36] described the reaction of methanol and CO_2 to produce DMC using basic catalysts CH_3OK, KOH, and K_2CO_3. The activity order found was: $CH_3OK > KOH > K_2CO_3$, suggesting that the basicity of a catalyst in the reaction media is an important factor that affects catalytic activity. The reaction mechanism involved was:

$$\mathrm{Base} + \mathrm{CH_3OH} \leftrightarrow \mathrm{CH_3O^-} + \mathrm{H} --- \mathrm{Base} \tag{4}$$

$$\mathrm{CH_3O^-} + \mathrm{CO2} \leftrightarrow [\mathrm{CH_3OCOO}]^- \tag{5}$$

$$[\mathrm{CH_3OCOO}]^- + \mathrm{CH_3I} \leftrightarrow \mathrm{CH_3OCOOCH_3} + \mathrm{I^-} \tag{6}$$

$$\mathrm{I^-} + \mathrm{H} --- \mathrm{Base^+} \leftrightarrow \mathrm{HI} + \mathrm{Base} \tag{7}$$

$$\mathrm{HI} + \mathrm{CH_3OH} \leftrightarrow \mathrm{CH_3I} + \mathrm{H_2O} \tag{8}$$

This mechanism involves the methanol activation and CO_2 insertion, resulting in the formation of DMC. Reaction (4) is the rate-determining step because the formation of CH_3O^- is largely dependent on the basic nature of the solution, which also holds the potassium-rich catalysts. This means the stronger the basicity of the catalyst, the higher the concentration of CH_3OK formation. Further, the author recovered the CH_3OK catalyst after completing the synthesis reaction and used this catalyst for the reaction. Much lower activity was observed from the used catalyst compared to the fresh catalyst. This showed the deactivation of the catalyst occurs and from XRD analysis showing peaks for CH_3OK, KI, and $KHCO_3$ concluded that the following reaction occurs:

$$\mathrm{CH_3OK} + \mathrm{H_2O} + \mathrm{CO_2} \rightarrow \mathrm{KHCO_3} + \mathrm{CH_3OH} \tag{9}$$

Therefore, by removing water from the reaction system, catalyst deactivation could be decreased, making the synthesis reaction thermodynamically spontaneous using a coupling reaction. The authors suggested that designing a coupling reaction within the reaction system could be favorable as it decreases the occurrence of side reactions, subsequently increasing the DMC yield. The authors also performed thermodynamic estimations for the reaction and reported that the studied reaction is thermodynamically unfavorable ($G > 0$) at a finite temperature and pressure. The thermodynamic estimations suggest that an increase in reaction temperature is not good for DMC formation, while an increase in pressure leads to an increase in DMC yield. However, an increase in pressure is hard to achieve. Therefore, optimized reaction conditions are necessary for the direct DMC synthesis from methanol and CO_2.

2.1.1. Use of Dehydrating Agents

As stated above, the direct conversion of CO_2 and methanol to DMC is thermodynamically limited by a low equilibrium constant; therefore, in-situ removal of water would enhance DMC yields. Several studies have reported the use of different dehydrating agents for water removal from the reaction [36,53,54]. Physical drying agents can be used to absorb water in-situ that forms during the reaction. However, the use of physical drying adsorbents at a high temperature for water absorption from the reaction system is very difficult. Thus, various chemical dehydrating agents such as CH_3I [15], butylene oxide [55], acetonitrile [56], and 2-cyanopyridine [37,57–60] have been investigated for in-situ water removal. These agents have the advantage of performing well below 373 K. Bansode and Urakawa [37] used a fixed-bed reactor to synthesize DMC using CO_2 and methanol (as a reactant) and CeO_2 as a catalyst with 2-cyanopyridine and 2-picolinamide dehydrating agents. The authors used CO_2 at high pressure (20 MPa). The major drawback of the process was the blockage of the gaseous flow in the reactor system. Another drawback was the separation of the reaction products into pure forms that can be used directly for analytical systems. Other studies have reported that 2-cyanopyridine as a dehydrating agent can be easily hydrolyzed and regenerated by dehydration, particularly when the reaction is catalyzed by CeO_2 [57–60]. The DMC yield was also improved with 2-cyanopyridine as a dehydrating agent in the presence of a CeO_2 catalyst. Wang et al. [60] reported the effect of the derivatives of 2-cyanopyridine on DMC synthesis. The different dehydrating agents used were 2-cyanopyridine, 2-cyanofuran, 2-cyano-5-fluoropyridine, 5-bromo-2-cyanopyridine, and 5-chloro-2-cyanopyridine, and DMC yields reported were 351, 232, 334, 163, and 59 mmol/g catalyst, respectively. The highest DMC yield was obtained with 2-cyanopyridine. Tamura et al. [57] proposed the reaction mechanism for the 2-cyanopyridine hydrolysis (shown in Figure 5). In step 1, hydration occurs by dissociation of H_2O on the CeO_2 catalyst to produce $H^{\delta+}$ and $OH^{\delta-}$ ions. In step 2, a nitrile-CeO_2 adsorption complex forms and undergoes the addition of $H^{\delta-}$ to a nitrile carbon atom to generate an amide. In step 3, regeneration of the adsorption site on CeO_2 takes place. Step 2 and step 3 occur simultaneously. The last step is the rate-determining step in the proposed mechanism. This reaction mechanism suggests that the nitrogen/oxygen atom in the ring and the electronic charge of the carbon atom in the cyano group are important for the hydrolysis of cyano groups.

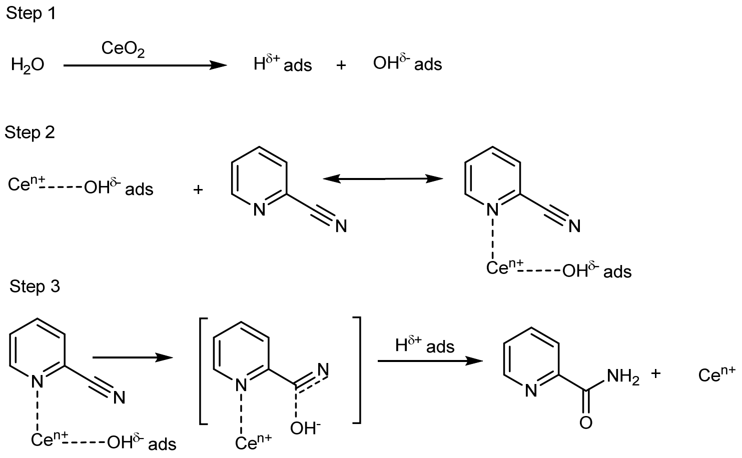


Figure 5. Reaction mechanism for the 2-cyanopyridine hydrolysis, as proposed by Tamura et al. [57]. (Reprinted/adapted with permission from Ref. [57], 2011, John Wiley and Sons).

Faria et al. [38] proposed a dehydration system for DMC synthesis by applying CH_3I as a promoter and CH_3OK as a catalyst. Various dehydrating agents such as 2,2-dimethoxypropane (2,2-DMP), magnesium oxide, sodium sulfate, and butylene oxide were used along with molecular sieves. This helps to minimize the reverse reaction. The optimized conditions proposed were 2 g of molecular sieve combined in the gas phase with 10 mmol of the dehydrating agent in the liquid phase. The proposed system was effective because, in this system, molecular sieves can be easily separated from the gas phase and the acetone formed from the 2,2-DMP can be recovered from the reaction medium using the distillation technique.

2.1.2. Use of Ionic Liquids (ILs)

It is a well-proven fact that the methanol and CO_2 conversion rates and DMC selectivity remain low because of the thermodynamic limitations of the conversion processes, even with dehydrating agents, as discussed. The reason for the low activity of the catalysts might be the hydrolysis of the catalysts. Further, investigations have been performed to enhance the CO_2, methanol conversions, and DMC selectivity by improving the catalyst activities or using ionic liquids (ILs) as catalysts. ILs are good solvents for CO_2 as they are basic and enhance the conversion and selectivity. In 2012, Du et al. [61] proposed the mechanism for the DMC synthesis from methanol and CO_2 using a K_2CO_3/CH_3I catalyst with imidazolium-based ILs under microwave conditions. Different ILs used for the study were 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6), and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4). Among these, [Bmim]Cl and [Bmim]BF_4 ILs increased the turnover frequency of methanol to DMC. The authors proposed (reaction mechanism shown in Figure 6) that ILs might act as a reaction medium, and regulate intermediate polarity, and dipole moment of the transition state, which enhances the selective absorption of microwave energy. Consequently, this reduces the interfacial reaction and activation energy and increases the solubility of CO_2. The number of reactive molecule collisions between CO_2 and CH_3OH increased, resulting in an improved catalyst activity. Bond distance and angle calculations, as reported in Table 2, showed that the CO_2 was activated by interaction with the ILs. The average distance of the O(1)-C(2) bond increased from 1.17 to 1.18 Å, and the bond angle of O(1)-C(2)-O(3) decreased from 176.73 to 174.21° in the IL-CO_2 system, compared to an isolated CO_2 molecule. This suggests that the CO_2 molecules adsorbed on ILs, promoting the activation of CO_2 for the favorable reaction.

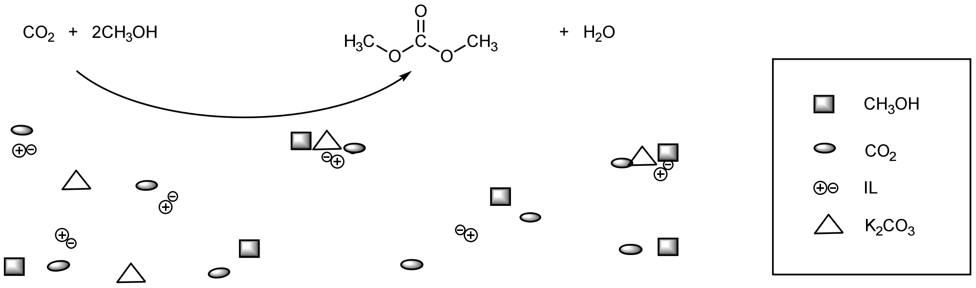


Figure 6. Scheme of ionic liquid (IL) promoted catalytic reaction process, as proposed by Du et al. [61]. (Reprinted with permission from Ref. [61], 2012, Elsevier).

Table 2. Effects of ionic liquids on bond distances and bond angles of CO_2 [61]. (Adapted with permission from Ref. [61], 2012, Elsevier).

Ionic Liquids	**Bond Distance, Å**		**Bond Angle, °**
	O(1)-C(2)	**C(2)-O(3)**	**O(1)-C(2)-O(3)**
CO_2 (gas phase)	1.169	1.692	180
[bmim][PF_6]	1.172	1.166	176.730
[bmim][BF_4]	1.173	1.165	175.462
[bmim][Cl]	1.175	1.166	174.207

[bmim][PF_6] = 1-butyl-3-methylimidazolium hexafluorophosphate; [bmim][BF_4] = 1-butyl-3-methylimidazolium tetrafluoroborate; and [bmim][Cl] = 1-butyl-3-methylimidazolium chloride.

A catalytic process was reported for the production of DMC from methanol and CO_2 using chitosan/IL at 7.5 MPa pressure without any dehydrating agent [39]. The ILs 1-methyl-3-(methylsulfonyl)-1H-imidazol-3-ium chloride ([Msmim][Cl]) with different anionic moieties (NTf_2, PF_6, Cl) were used for demonstration. The author reported that the 10 wt% chitosan/ILs catalyst, having an NTf_2 anion, showed a 17% methanol conversion with a DMC selectivity of 98%. The IL was shown to play a promising role as active sites of chitosan are more easily available for the reaction; the IL would increase the vapor pressure of the reaction system. Therefore, the large amount of CO_2 in the reaction system can affect product formation. The catalytic activity was found to be increased $NTf_2 > PF_6 > Cl$, suggesting that anions having fluoroalkyl groups provide the highest CO_2 solubility.

Vieira et al. [40] investigated the structural effect of ILs based on different cations (imidazolium and pyridine) and anions ($[PF_6^-]$, $[BF_4^-]$, $[Cl^-]$, $[Tf_2N^-]$) as catalysts for DMC production. The authors have used 2,2-DMP as a dehydrating agent. The $[bmim][Cl^-]$ and $[bmim][BF_4]$ gave a 7.5 and 7.4% methanol conversion at 4 MPa CO_2 pressure and 443 K in 24 h with 53 and 81% DMC selectivity, respectively. The results exhibited that the IL anion significantly affects DMC selectivity; however, it did not show much effect on methanol conversion. The DMC selectivity increases in the anion order of $[Tf_2N^-] < [PF_6{}^-] < [Cl^-] < [BF_4^-]$. The authors reported that the acidic nature of $[Cl^-]$ makes it an inferior candidate compared to $[BF_4^-]$ in terms of DMC selectivity. On the contrary, when the authors changed the imidazolium and pyridine cations, the methanol conversion was 7.6% and 7.7%, respectively. The imidazolium cations are 12% more selective than the pyridine ones, which could be credited to their higher basicity.

The catalytic application of bifunctional imidazolium hydrogen carbonate ionic liquids ($[C_nC_mIm][HCO_3]$) for DMC synthesis from CO_2 and methanol at room temperature was demonstrated by Zhao et al. [41]. Using different bases, such as K_2CO_3, $KHCO_3$, Cs_2CO_3, $NaHCO_3$, and Na_2CO_3, methanol conversion in the range of 22–74% was observed with 54–99% DMC selectivity. The author concluded that the IL system used for the conversion process acts as both a catalyst and dehydrant, as per the reaction mechanism shown in Figure 7. There is a transition in equilibrium from $C_nC_mIm\text{-}CO_2$ to $[C_nC_mIm][HCO_3]$ in the IL system. $C_nC_mIm\text{-}CO_2$ acts as a dehydrant that reacts with water formed during the reaction between methanol and CO_2 to produce DMC. As a result, the thermodynamic equilibrium shifts in the forward reaction, promoting higher product yield and consequently increasing methanol conversion. Thus, ILs contain a different equilibrium concentration of $C_nC_mIm\text{-}CO_2$ that has a catalytic and dehydrating ability.

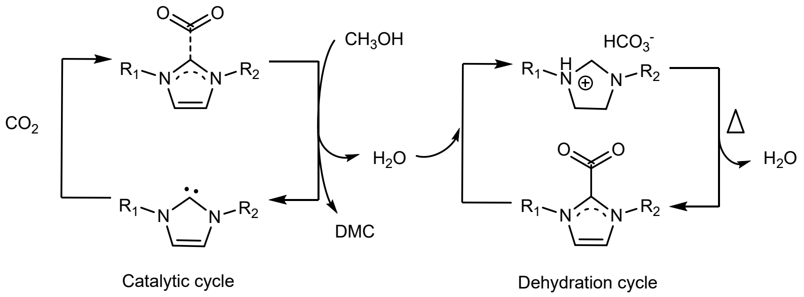


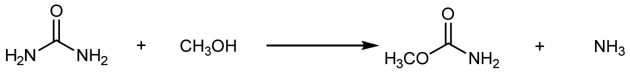
Figure 7. Catalytic and dehydration mechanism of $[C_nC_mIm][HCO_3]$ [41]. (Reprinted/adapted with permission from Ref. [41], 2017, John Wiley and Sons).

A new generation of green solvents i.e., deep eutectic solvents (DES) had shown potential applications such as CO_2 absorption [62–64], drug solubilization, biodiesel purification, and separation of azeotropic mixtures. DESs consisting of a hydrogen-bond acceptor and hydrogen-bond donor had the advantages of better CO_2 affinity, wide liquid range, and low volatility such as ILs. To the best of our knowledge, there is no report in the literature on the DMC synthesis from CO_2 and methanol using DES. However, these are reported as a new adsorbent in CO_2 separations [62,63]. The mass capacity of [monoethanolamine]Cl-ethylene diamine DES with a molar ratio of 1:3 was reported to be 0.337 g CO_2/g DES at 303 K temperature and 100 kPa pressure. Yan et al. [64] synthesized a three superbase IL, consisting of 1,8-diazabicyclo [5,4,0] undec-7-ene imidazole, 1,8-diazabicyclo [5,4,0] undec-7-ene indole, and 1,8-diazabicyclo [5,4,0] undec-7-ene 1,2,4-triazole, further combined with less viscous ethylene glycol (EG) for an efficient and reversible CO_2 capture. From the spectral studies and quantum chemistry calculation, the adsorption mechanism proposed that IL and EG simultaneously react with CO_2 to form carbamate and carbonate, respectively. In addition, the CO_2 adsorption performance of DES remained stable even after five cycles of adsorption and desorption. In addition, a liquid–liquid equilibrium for the system of DMC + methanol + DESs was reported. The researchers prepared two DESs with choline chloride and ethylene glycol/glycerol and tested for the separation of the mixture of DMC and methanol. Choline chloride/ethylene glycol DES provided a better extraction ability compared to the choline chloride/glycerol DES.

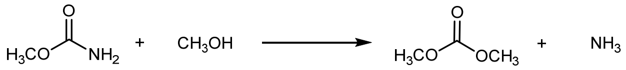
In summary, although various reports in the literature present the direct catalytic conversion of methanol and CO_2 to DMC, the reported shortcomings include (i) high thermodynamic stability of CO_2, (ii) kinetic inertia, (iii) catalyst deactivation, and (iv) DMC hydrolysis. These contribute to the lower DMC yield. Moreover, the catalyst should be highly selective for DMC synthesis to produce high-purity DMC. In addition, water removal from the reaction system is extremely necessary to shift the equilibrium toward DMC production. Because of the presence of water, catalyst deactivation is also a major concern. Therefore, novel catalysts that can activate CO_2 and can be effective in the presence of water are desirable. In addition, catalysts should have high DMC selectivity.

2.2. Conversion of Urea and Methanol to DMC

Urea alcoholysis [65–79] was considered an environmentally friendly and economically viable process to produce dialkyl carbonates. The coproduct, i.e., ammonia, can be recycled to synthesize urea by reacting with CO_2 or can be used for nitrile production. The synthesis of DMC from urea takes place as per Equations (10) and (11). In step I (Equation (10)), urea is converted into methylcarbamate (MC), and then in step II (Equation (11)), MC is converted into DMC in the presence of excess methanol. Step II is a rate-limiting step due to thermodynamic limitations. Because of the endothermic nature of the reaction (step II), the reaction equilibrium can be shifted in the direction of DMC formation by increasing the temperature or removing the ammonia from the reacting system. Interestingly, step I is thermodynamically favorable, while step II is not. As a result, DMC should be separated as it forms. DMC can react with MC to form a side product, i.e., N-methyl methylcarbamate (NMMC) because DMC is an active compound.



(10)



(11)

The heat of reaction (ΔHr°) of reactions shown in Equations (10) and (11) are −10.31 and 13.11 kJ/mol at normal temperature and pressure. Reaction (10) is exothermic, while the reaction as per Equation (11) is endothermic. Changes in the Gibbs free energy (ΔGr°) increase with an increase in temperature (for Reaction (10)) and decrease with an increase in temperature (for Reaction (11)). Thus, Reaction (10) is favorable, and Reaction (11) is unfavorable. The formation of NMMC is the major side reaction, and the activation energy of the side reaction is higher than the main reactions. Therefore, a high reaction temperature favors the side reaction. Overall, the first step is thermodynamically favorable, while the second step is not. Thus, DMC should be separated as soon as it is formed.

A detailed literature review that includes both homogeneous and heterogeneous catalysts is presented in Table 3.

2.2.1. Homogeneous Catalysts for DMC Production from Urea

In early investigations, organometallic compounds such as $Bu_2Sn(OCH_3)_2$ [66,67], metal (IV) tetra-alkoxides [16], potassium carbonate [15], and magnesium dialkoxide [68] have been investigated for the DMC synthesis from urea and methanol. However, the activity of the catalysts was very low, even in the presence of additives. In addition, these compounds were easily decomposed by water and considered to take place reaction in stoichiometric ratio. In addition, because of the organotin compounds' toxicity and the inconvenience involved in the recovery of the catalysts, researchers explored heterogenous catalysts.

Table 3. Literature review of the catalysts used for the synthesis of DMC based on the urea alcoholysis route.

S. No	Catalysts	Reaction Conditions	Urea/MC $^{\#}$ Conversion, %	DMC/DEC * Yield, %	Source
1a	Zn powder	T = 443 K; P = 1.6 MPa; t = 6 h; Urea:MeOH = 1:46; Zn = 2.4 wt%	-	12.7 ^{x}	[69]
1b	ZnO/Al_2O_3	T = 443 K; P = 1.6 MPa; t = 6 h; Urea:MeOH = 1:46; Zn = 10 wt%		8.9 ^{x}	
2a	None	T = 453–473 K; t = 8–10 h; Urea/MC = 0.1 mol; MeOH = 64 g; Catalyst = 1 g	-	0.8 ^{x}, 2.6 ^{y}	[71]
2b	PbO			22 ^{x}, 23.8 ^{y}	
2c	$Zn(CH_3COO)_2$			24 ^{x}, 21.1 ^{y}	
2d	MgO			16.9 ^{x}, 17.5 ^{y}	
2e	CaO			15.8 ^{x}, 18.2 ^{y}	
2f	ZnO			34 ^{x}, 4.2 ^{y}	
3a	None	T = 453 K; t = 10 h; Urea/MC = 0.2 mol; MeOH = 4 mol; Catalyst = 2 g	-	0.8 ^{x}, 1.0 ^{y}	[72]
3b	ZnO-I from $Zn(CO_3)_2$			29 ^{x}, 4.3 ^{y}	
3c	ZnO-II (CMR)			29 ^{x}, 5.5 ^{y}	
3d	CaO from $(CaCO_3)_2$			16 ^{x}, 15 ^{y}	
4a	None	T = 453 K; t = 8 h; MC = 7.5 g; MeOH = 64 g; Catalyst = 1 g	4.00 $^{\#}$	2.1 ^{y}	[73]
4b	La_2O_3		10.2 $^{\#}$	5.9 ^{y}	
4c	$LaCl_3$		73.9 $^{\#}$	28.1 ^{y}	
4d	LaF_3		20.0 $^{\#}$	6.1 ^{y}	
4e	$La_2(CO_3)_3$		12.4 $^{\#}$	8.2 ^{y}	
4f	$LaPO_4$		12.2 $^{\#}$	7.6 ^{y}	
4g	$La(NO_3)_3$		84.8 $^{\#}$	53.7 ^{y}	
4h	$NaNO_3$		9.90 $^{\#}$	4.5 ^{y}	
4i	$Cu(NO_3)_2$		11.4 $^{\#}$	5.2 ^{y}	
5a	None	T = 473 K; t = 3 h; Urea:EtOH = 1:10; Catalyst = 17 wt%	-	3.00 *	[74]
5b	La_2O_3-calcination temp. 773 K			29.2 *	
5c	Al_2O_3			5.30 *	
5d	MgO			3.60 *	
5e	TiO_2			4.50 *	
5f	CaO			8.40 *	
5g	ZnO			30.6 *	
6a	None	T = 453 K; t = 10 h; MC = 7.5 g; MeOH = 64 g; Catalyst = 2 g	4.10 $^{\#}$	2.6	[77]
6b	ZnO		5.30 $^{\#}$	3.5	
6c	Al_2O_3		5.90 $^{\#}$	3.3	
6d	ZnO-Al_2O_3, physically mixed		5.40 $^{\#}$	3.1	
6e	ZnO-Cr_2O_3		36.8 $^{\#}$	23.5	
6f	ZnO-Fe_2O_3		47.6 $^{\#}$	30.4	
6g	ZnO-Al_2O_3		56.4 $^{\#}$	34.6	
6h	$ZnAl_2O_4$		9.30 $^{\#}$	4.2	

Table 3. *Cont.*

S. No	Catalysts	Reaction Conditions	Urea/MC $^{\#}$ Conversion, %	DMC/DEC * Yield, %	Source
7a	ZnO(0.7)-CeO_2(0.3)	T = 443 K; t = 4 h; P = 2 MPa CO_2; Urea = 3 g; MeOH = 40 mL; Catalyst = 0.75 g	100	39.2^{x}, 49.1^{z}, 7.1^{NM}	[78]
7b	ZnO(0.64)-CeO_2(0.26)-La_2O_3(0.1)		100	50.4^{x}, 40.2^{z}, 6.7^{NM}	
7c	ZnO(0.64)-CeO_2(0.26)-Y_2O_3(0.1)		100	45.6^{x}, 44.4^{z}, 6.8^{NM}	
7d	ZnO(0.64)-CeO_2(0.26)-Co_2O_3(0.1)		100	41.8^{x}, 49.6^{z}, 4.9^{NM}	
7e	ZnO(0.64)-CeO_2(0.26)-Ga_2O_3(0.1)		100	29.9^{x}, 65.6^{z}, 2.4^{NM}	
7f	ZnO(0.64)-CeO_2(0.26)-ZrO_2(0.1)		100	34.9^{x}, 57.4^{z}, 6.3^{NM}	
8a	ZnO(0.64)-TiO_2 (0.36)	T = 413 K; t = 4 h; Urea = 16.6 mmol; MeOH = 333 mmol; Catalyst = 200 mg;	39.2	24.5^{x}	[79]
8b	ZnO(0.64)-Nb_2O_5 (0.10) TiO_2 (0.26)		52.8	33^{x}	
8c	ZnO(0.60)-Nb_2O_5 (0.14)-TiO_2 (0.26)		58.2	36.4^{x}	
8d	ZnO(0.54)-Nb_2O_5(0.20)-TiO_2 (0.26)		62.5	39.1^{x}	
8e	ZnO(0.50)-Nb_2O_5(0.24)-TiO_2 (0.26)		59.3	37.1^{x}	
8f	Nb_2O_5(0.64)-TiO_2 (0.36)		44.6	27.9^{x}	
9a	SBA-15	T = 453 K; t = 8 h; Urea = 0.0105 mol; MeOH = 1.68 mol; Catalyst = 0.3 g	-	0	[80]
9b	MCM-49			3.7	
9c	HMCM-49			4.1	
9d	Fe_2O_3			2.4	
9e	Fe_2O_3/SBA-15			10	
9f	Fe_2O_3/MCM-49			14.7	
9g	Fe_2O_3/HMCM-49			20.5	
9h	Fe_2O_3/HY			7	
9i	Fe_2O_3/HZSM-5			3.2	
10a	None	T = 453 K; t = 10 h; Urea = 0.1 mol; MeOH = 64 g; Catalyst = 0.5 g	-	6.50, 84.8^{z}	[81]
10b	ZnO			29.5, 84.8^{z}	
10c	Zn/Al hydrotalcites (Zn/Al 2.47 mol ratio)			36.5, 55.1^{z}	
11a	ZnO	T = 453 K; t = 10 h; Urea = 0.1 mol; MeOH = 64 g; Cat = 0.4 g; Zn/Ca = 2.72 molar ratio	-	30.8, 59.0^{z}	[82]
11b	ZnO + CaO Physically mixed			22.9, 70.9^{z}	
11c	ZnO + CaO Calcined at 1073 K			41.2, 50.5^{z}	
12a	ZnO	T = 453 K; t = 7 h; Urea:EtOH = 1:10; Urea:Cat = 7:1	-	17.0^{*}	[83]
12b	CuO/ZnO			10.3^{*}	
12c	In_2O_3/ZnO			7.40^{*}	
12d	SiO_2/ZnO			1.20^{*}	
12e	ZIF-8			15.20^{*} at 15 h	
12f	Tethered $Zn(NCO)_2$			1.01^{*}	
12g	Tethered $ZnCl_2$			0.71^{*}	
13a	$Zn(NO_3)_2.6H_2O$	T = 443 K; t = 4 h; Urea:MeOH = 1:15; Catalyst = 2 wt%	-	3.5, 45.7^{z}	[84]
13b	$Zn(AC)_2.2H_2O$			3.0, 48.8^{z}	
13c	$Ce(NO_3)_2.6H_2O$			3.2, 45.9^{z}	

Table 3. *Cont.*

S. No	Catalysts	Reaction Conditions	Urea/MC $^{\#}$ Conversion, %	DMC/DEC * Yield, %	Source
13d	$CeCl_3.7H_2O$	T = 443 K; t = 4 h; Urea:MeOH = 1:15; Catalyst = 2 wt%	-	3.4, 50.1 ^{z}	[84]
13e	$ZnBr_2$			2.4, 57.9 ^{z}	
13f	$ZnCl_2$			2.4, 59.2 ^{z}	
13g	$Zr(NO_3)_2$			1.6, 51.2 ^{z}	
13h	CaO			1.3, 44.9 ^{z}	
13i	ZnO			2.8, 51.2 ^{z}	
13j	$ZnO-CeO_2$			3.1, 55.7 ^{z}	
13k	$ZnO-CeCl_3.7H_2O$			3.1, 44.7 ^{z}	
13l	$ZnO-Ce(NO_3)_3.6H_2O$			2.6, 47.8 ^{z}	
13m	$Zn(OH)_2$; SiO_2; $Al(OH)_3$			0	
13n	$Zn(NO_3)_2-Al(OH)_3$			2.7	
13o	$Zn(NO_3)_2-Zn(OH)_3$			4.05	
14a	Y_2O_3	T = 423 K; t = 3 h; Urea = 6 g; EG = 9.3 g; Catalyst = 0.3 g	27		[85]
14b	ZnO		75		
14c	Zn/Y = 3:1 673 K		92		
15a	Ca-Zn-Al oxide	T = 443 K; t = 8 h; Urea:PG = 2, Cat = 2.7 wt%		82.4	[86]
16a	$ZnO-SrO_2$ molar ratio 3:1	T = 443 K; t = 6 h; Urea:MeOH = 1:15; Catalyst = 2.6 wt%	-	16 ^{x}, 72 ^{z}, 12 ^{NM}	[87]
16b	$ZnO-SrO_2$ molar ratio 2:1			18 ^{x}, 63 ^{z}, 19 ^{NM}	
16c	$ZnO-SrO_2$ molar ratio 1:1			35 ^{x}, 42 ^{z}, 23 ^{NM}	
16d	$ZnO-SrO_2$ molar ratio 1:2			24 ^{x}, 45 ^{z}, 31 ^{NM}	
16e	$ZnO-SrO_2$ molar ratio 1:3			19 ^{x}, 44 ^{z}, 37 ^{NM}	

DMC = Dimethyl carbonate; MC = Methyl carbamate; MeOH = Methanol; ^{x} = DMC yield based on urea; ^{y} = DMC yield based on MC; ^{z} = MC yield %; ^{NM} = NMMC yield %; EG = Ethylene glycol; Zn/Y = Catalyst made using zinc nitrate and yttrium nitrate; PG = Propylene carbonate; $^{\#}$ = MC yield; and * = DEC yield.

2.2.2. Heterogeneous Catalysts Used for DMC Production from Urea

In 2005, Wu et al. [69] compared the activities of ZnO and Zn powder-based catalysts. The Zn used was in a powder form and showed 1.65 times the DMC yield compared to that of the ZnO catalyst. However, when ZnO was loaded on the alumina, 8.9% of the DMC yield was obtained. The reason was that the doping of alumina in a ZnO lattice created electronegative vacancies. Later, many studies demonstrated that ZnO was quite active in the reaction. Wang et al. [70] concluded that ZnO- and Pb-based catalysts provided 29% and 24% DMC yields, respectively. The drawback was that the product DMC was impure and contaminated with ammonia.

Typically, ZnO is a heterogeneous catalyst; however, it has been shown to be soluble in the reaction media above a certain temperature. Therefore, the reaction would generally occur in a homogeneous phase. The ZnO acts as a precursor to the homogeneous catalyst for DMC production from alcohol and urea. To prove this, Wang et al. [72] recovered some precipitates from the reaction solution while reducing the reaction temperature, and the authors characterized these precipitates using FT-IR, TG-DSC, and XRD. Surprisingly, they found the structure of the complex $Zn(NH_3)_2(NCO)_2$ and proposed the reaction mechanism, as shown in Figure 8.

The reaction mechanism was explained as the following: The NH_3 of the $Zn(NH_3)_2$ $(NCO)_2$ complex was substituted by ethylene carbonate to generate a complex $Zn(NH_2COO$ $C_2H_5)_2(NCO)_2$; ethylene carbonate was activated via co-ordination with a Zn^{2+} ion. Later, the alcohol attacked the complex to produce a Zwitterion intermediate, and then molecular rearrangements took place to yield diethylene carbonate (DEC) [71,72]. Wang et al. [73] demonstrated various lanthanum (La)-based catalysts for DMC synthesis using MC and methanol as feedstocks. La_2O_3, LaF_3, $LaPO_4$, and $La_2(CO_3)_3$ produced DMC in the range of 6 to 8% (much less). On the contrary, $La(NO_3)_3$ displayed superior activity with a 54% DMC yield at 453 K and 3 h. The authors suggested that La^{3+} catalyzed the reaction. The mechanism involved (shown in Figure 9) was as follows: La^{3+} was bound to the MC molecule via the coordination with O-atoms of the carbonyl group and NO^{3-} species co-ordinates with La^{3+}. The catalytic activity was influenced by anion groups present in the catalysts and the solubility in methanol. La_2O_3, LaF_3, $LaPO_4$, and $La_2(CO_3)_3$ were almost inactive for DMC formation because they were insoluble in methanol. Although $LaCl_3$ is soluble in methanol, Cl^- might not co-ordinate effectively with trivalent La cations as it does with $NO_3{}^-$. As a result, $La(NO_3)_3$ produced the highest amount of DMC compared to the other La compounds. To further investigate, the authors used $NaNO_3$ and $Cu(NO_3)_2$ to learn whether this effect was due to a $NO_3{}^-$ ion. Although these two catalysts could be completely dissolved in methanol, the catalytic activity observed was low. Thus, La^{3+} ions were crucial for producing the maximum DMC yield. Further, Xin et al. [74] evaluated the activity of the La_2O_3 catalyst (prepared at different calcination temperatures) for DEC synthesis from ethanol and urea. The prepared catalyst showed the highest catalytic activity with 43% EC and 29% DEC yields. The research suggests that if the calcination temperature was more than 873 K, the DEC yields decreased. Although a Zn-oxide-based catalyst was used frequently and found to be effective for the alcoholysis of urea to synthesize DMC/DEC, La_2O_3 can also be used as a solid base for these reactions. For large-scale applications, lanthanum could be used as an inexpensive catalyst for DMC/DEC synthesis because it is naturally in abundance.

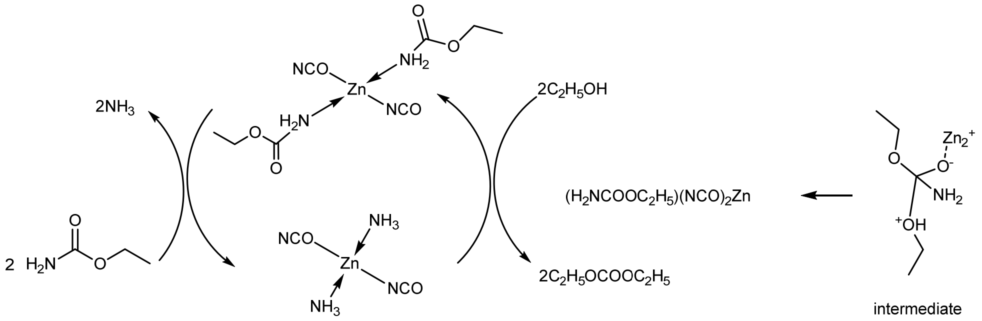


Figure 8. The reaction mechanism of diethyl carbonate (DEC) production, as proposed by Wang et al. [72]. (Reprinted with permission from Ref. [72], 2010, Springer Nature).

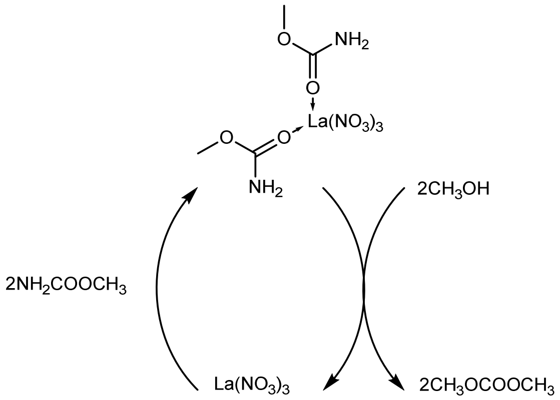


Figure 9. The reaction mechanism for DMC production, as proposed by Wang et al. [73]. (Reprinted with permission from Ref. [73], 2010, Elsevier).

Despite several experimental studies reported in the literature, the mechanism involved in urea methanolysis used to produce DMC is still uncertain. Gao et al. [75] proposed the coordination of EC to the Zn-metal center via an N-moiety with the N-donor atom.

Later, Wang et al. [72,73] conducted a density-functional theory (DFT) study to compare various proposed reaction mechanisms. The most favorable proposed approach was the interaction of NCO in the $Zn(NH_3)_2(NCO)_2$ complex with methanol, which leads to the formation of an active complex $Zn(NH_3)_2(NCO)(NHCOOCH_3)$. In their most recent study, Dibenedetto et al. [76] described the reaction mechanism for the DEC synthesis through an integrated experimental/theoretical approach. With basic chemistry concepts, EC/MC should follow a similar trend as urea coordinates to the Zn-metal center by an (i) O-atom of the carbonyl, and an (ii) N- and an (iii) O-atom of the ester moiety (shown in Figure 10). Based on the approach used, the authors concluded that the coordination of EC/MC occurs through the carbonyl O-atom to the metal center. Then, there is a concerted addition of two molecules of ethanol/methanol to the complex system. The same mechanism was proven to be applicable for DMC synthesis as well.

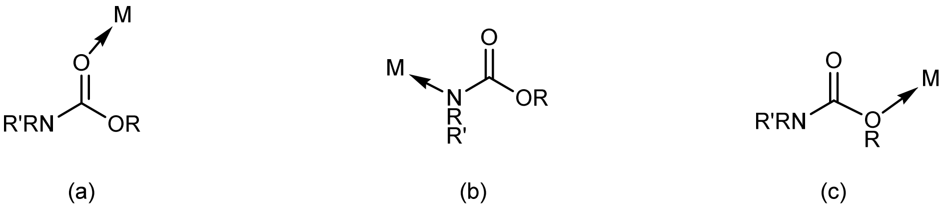


Figure 10. Co-ordination of urea to metal centers through (**a**) O-atom of the carbonyl, and (**b**) N-atom and (**c**) O-atom of ester moiety. (Reprinted with permission from Ref. [76], 2014, Elsevier).

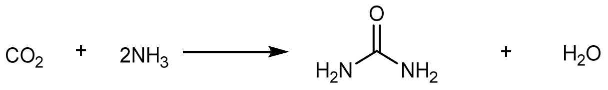
Due to the solubility of ZnO in the reaction media as a $Zn(NCO)_2(NH_3)_2$ active species, recovery of the catalyst becomes difficult, preventing the use of ZnO in continuous reactor systems and making its recovery in the batch systems challenging. Therefore, the use of Zn-based heterogeneous catalytic materials is widely reported in the literature. Wang et al. [77] prepared Zn-containing mixed oxides to produce DMC from MC and methanol. The researchers obtained the DMC yield of 35% and 56% MC conversion with a ZnO-Al_2O_3 catalyst. X-ray diffraction analysis of the ZnO-Al_2O_3 catalyst demonstrated the presence of two phases, ZnO and $ZnAl_2O_4$. However, $ZnAl_2O_4$ alone produces only 4% DMC (low activity), suggesting that there is a synergism between $ZnAl_2O_4$ and ZnO, resulting in a high DMC yield. Joe et al. [78] synthesized a series of ZnO-CeO_2-Mx (Mx: Y_2O_3, La_2O_3, Ga_2O_3, ZrO_2, and Co_2O_3) mixed oxides and studied their performance in the conversion of urea and methanol to DMC. The results showed that ZnO(0.64)-CeO_2(0.26)-La_2O_3(0.1) produces 50% DMC. The researchers also studied the effect of acidity and the basicity of the tested catalysts on the DMC yield. It was observed that the DMC yield depends on the basicity of the ZnO(0.64)-CeO_2(0.26)-MO(0.1) catalyst, and yields increased with an increase in the basicity of the tested catalysts. Basicity decreased in the order of ZnO(0.64)-CeO_2(0.26)-La_2O_3(0.1) > ZnO(0.64)-CeO_2(0.26)-Y_2O_3(0.1) > ZnO(0.64)-CeO_2(0.26)-Co_2O_3(0.1) > ZnO(0.7)-CeO_2(0.3) > ZnO(0.64)-CeO_2(0.26)-ZrO_2 (0.1) > ZnO(0.64)-CeO_2(0.26)-Ga_2O_3(0.1). On the contrary, DMC yield was observed to be independent of the acidity of the tested catalysts.

The ZnO-Nb_2O_5-TiO_2 catalysts were synthesized using the sol-gel method, in which ZnO was effectively dispersed in the TiO_2 matrix [79]. The synthesized catalyst showed better performance (DMC yield 39%), even at low temperatures and reaction time. The results suggested that Nb_2O_5 and ZnO in the TiO_2 matrix promote the DMC formation and the TiO_2 matrix prevented the leaching of metals into the reaction medium.

Zhang et al. [80] screened the catalyst activities of the Fe-based supported catalysts using supports SBA-15, HY, HZSM-9, HMCM-49, and MCM for DMC synthesis, using urea and methanol as reactants. The results were also compared with only the supports, and SBA-15 (mesoporous) was found to be inactive for the DMC synthesis process. The Fe_2O_3/HMCM-49 catalyst was found to be highly active with a 21% DMC yield and 98% selectivity compared to the rest of the screened catalysts. The results demonstrated that the catalyst possessing medium acidity promotes the activation of urea and methanol and interacts with the ammonia that was released during the reaction. This whole process shifts the reaction equilibrium to form DMC.

Zhao et al. [81] demonstrated the use of Zn/Al mixed oxides (ZAO) to synthesize DMC. The authors synthesized the different ZAO catalysts with varying Zn/Al molar ratios (0.21–2.47) and at different calcination temperatures (623–1273 K). The results indicated that catalysts with a low Zn/Al molar ratio (<0.5) showed inferior activity for DMC synthesis because of the formation of $ZnAl_2O_4$. On the contrary, with the catalysts that have high Zn/Al molar ratios, there is a synergism between ZnO and $ZnAl_2O_3$, leading to the maximum DMC yield (37%). Another reason for high activity was the presence of weak basic and acidic sites on the catalyst that promoted the synthesis of DMC. Later, the same authors tested ZnO-CaO bifunctional catalysts to synthesize DMC from urea and methanol [82]. With Zn/Ca (molar ratio of 2.72) calcined at 1073 K, 41% of DMC was produced and was attributed to the interaction between ZnO and CaO with sufficient acidic and basic sites. The authors proposed that metal isocyanate was formed because of the decomposition of urea on the acidic sites with a subsequent nucleophilic attack by activated methanol on the basic sites, leading to the formation of DMC. Dibenedetto et al. [84] investigated three different kinds of Zn-based heterogeneous catalysts mixed oxides (CuO/ZnO, In_2O_3/ZnO, and SiO_2/ZnO) to synthesize DEC by the ethanolysis of urea. Among these, the CuO/ZnO catalyst showed the maximum DEC yield (10%). In addition, the leaching of metals from the active catalyst was much less, as the XPS analysis determined that Cu was homogeneously distributed between the surface and bulk, which stabilizes the Zn centers. This helps in reducing metal leaching from the catalyst. The same authors also studied the activity of the Zn-imidazolate frameworks (ZIF-8) and Zn-tethered catalysts for DEC synthesis by urea ethanolysis. ZIF-8 frameworks were the organic-inorganic compounds with Zn-centers, in which coordination occurs by N-atoms of 5-membered imidazolate (IM) units. This catalyst produced 15% DEC at 15 h and 473 K. However, the yield was lower at 23% compared to ZnO. The authors explained that the accessibility of Zn centers in crystalline ZIF-8 was more difficult compared to the homogeneous Zn catalyst. Tethered $ZnCl_2$ and $Zn(NCO)_2$ showed a low DEC yield, which was because accessibility to the Zn center was influenced by bidentate N-N ligands. The authors also revealed that the acid and base properties of the catalysts direct a higher DEC yield than the BET surface area. ZIF-8 possesses a higher number of strong acid sites as well as basic sites; therefore, the ZIF-8 catalyst showed higher activity. In another study [85], the metallic salts with hydrates displayed higher activity compared to the ones without hydrates. It has been suggested that metallic salts with hydrates (such as $Zn(NO_3)_2 \cdot 6H_2O$, $Zn(Ac)_2 \cdot 2H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $CeCl_3 \cdot 7H_2O$; entry 13a-d; Table 3) partially transformed into metal oxides because of the presence of an alkaline environment (provided by urea). Consequently, these catalysts act as a mixture of an oxide and a salt. Based on these observations, the authors also tested hydroxyl-containing compounds such as $Zn(OH)_2$ and $Al(OH)_3$; however, no DMC was formed. The researchers revealed that the hydroxyl-containing compounds were active when combined with a $Zn(NO_3)_2$ catalyst, active metallic species. A $Zn(NO_3)_2$-$Zn(OH)_2$ catalyst having a weight ratio of 6 produced a maximum of 4% DMC, which was even higher than that from $Zn(NO_3)_2$. The strength of hydrogen bonding in the hydroxyl-containing compounds is responsible for the activity of the catalysts. The strong hydrogen bonding between MC (formed by urea methanolysis) and hydroxyl-containing species might weaken the C-N bond in MC and promotes the DMC formation.

Two-step DMC synthesis using urea, methanol, and ethylene glycol (EG) feeds was reported by using zinc–yttrium mixed oxides [85]. The reaction scheme involved the following Reactions (12)–(15):



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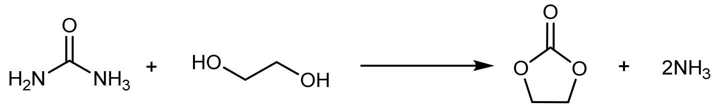

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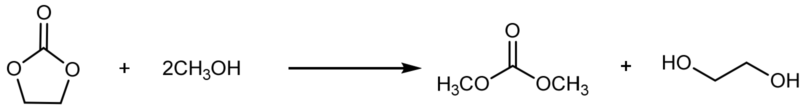

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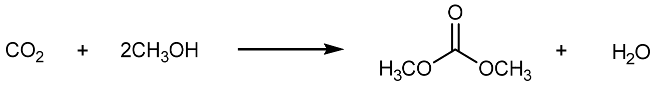

(15)

Urea reacts with diols to form cyclic carbonates (Equation (13)), and in the next step, transesterification of cyclic carbonate takes place with methanol to form DMC (Equation (14)). In the process, EG is recycled for cyclic carbonate (Equation (13)), while ammonia is recycled for urea (Equation (12)) production, which is a commercial process. Thus, the net reaction can be considered a reaction between methanol and CO_2 (Equation (15)). The pure Y_2O_3 catalyst showed poor catalytic activity, with a 63% EC selectivity and a 27% urea conversion. ZnO exhibits a high urea conversion and EC selectivity compared to the Y_2O_3 catalyst. The results indicated that the Zn/Y = 3:1 (calcined at 673 K) as the catalyst showed the highest activity for EC synthesis. The Ca-Zn-Al mixed oxide catalyst was prepared by incorporating calcium hydroxide into the ZnAl hydroxide system, and the prepared catalyst was tested for the single-step reaction of urea, propylene carbonate, and methanol to produce DMC [86]. With the Ca/Al molar ratio of 1.6:1, the maximum DMC yield obtained was 82%. The catalyst activity testing and XRD analysis of the catalyst showed that new crystalline phases $Ca_3Al_4ZnO_{10}$ and/or $ZnAl_2O_4$ created a reactive medium between CaO and ZnO, which leads to a better catalytic activity. The ZnO-SrO mixed-oxide catalyst, having different molar Zn-to-Sr ratios, was also tested for the urea alcoholysis [87], as reported in Table 3. The results indicated that the mixed oxides showed a higher conversion to DMC compared to the pure oxides. The catalyst having a high Sr content produces more side product (NMMC), while the catalyst having a high Zn content showed a maximum MC yield. The difference in the catalytic activities was found to be dependent on the acid and base properties of the tested catalysts. The high activity with catalyst ZnO-SrO (1:1) calcined at 773 K was due to the presence of acid or base sites per unit surface area. In addition, these mixed oxides possess ZnO and SrO/$SrCO_3$ phases that were well dispersed, which leads to higher conversions.

The reaction of the DMC synthesis from methanol and urea was also reported under supercritical conditions. The advantages associated with the supercritical fluids include: (i) they are environmentally friendly, (ii) they have a low reaction time and higher product yields, and (iii) they have less severe requirements for better material qualities [88]. Similarly, supercritical methanol is one of the most promising supercritical fluids due to its milder reaction conditions (Tc = 513 K), high ionic product, and higher solubility. Besides, supercritical processes are also simpler and easier in product separation. The use of supercritical methanol for the alcoholysis of urea was reported by Hou et al. [89]. The authors reported the influence of the reaction temperature (518–558 K), methanol/urea ratio (12–31), time (1–3 h), and the reactor loading (265–315 μL) to analyze the effect on the DMC yield (shown in Figure 11). The optimized reaction conditions included a 538 K reaction temperature, 2 h reaction time, 14 methanol/urea ratio, and 285 L volume of the reaction solution. The maximum DMC yield obtained was 93% at 2 h and 538 K. The study showed that when the reaction temperature exceeded 548 K, DMC yield gradually decreased. This might be due to the rate of side product formation that increased with a higher reaction temperature.

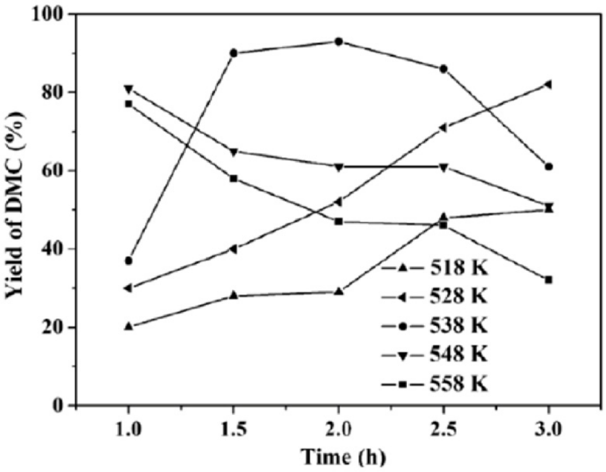

Figure 11. Effect of temperature and time on DMC yield during alcoholysis of urea in the presence of supercritical methanol. [Reaction conditions used: molar ratio methanol/urea = 25, reactor loading = 285 µL, reaction pressure = 6.4 MPa (518 K), 8.0 MPa (528 K), 9.2 MPa (538 K), 10.0 MPa (548 K), and 10.8 MPa (558 K)]. (Reprinted/adapted with permission from Ref. [89], 2014, Elsevier).

Based on the discussion here and the literature review, Figure 12 shows the reaction mechanism involved in the catalytic conversion of methanol and urea to DMC. According to this mechanism, at a temperature higher than 407 K, an intermediate isocyanic acid was formed by the decomposition of urea. The reactive intermediate can be converted into MC, even without a catalyst. The conversion of MC to DMC is challenging, and a catalyst is required to enhance the DMC formation. It is well proven that the conversion of MC to DMC takes place by a typical nucleophilic substitution on the acidic/basic sites of the catalyst. MC and methanol are first activated by adsorption on the catalytic acid and base sites, respectively. Further, the activated methoxide (OCH_3^-) anion attacked the carbonyl carbon of the adsorbed MC, resulting in the formation of DMC and ammonia.

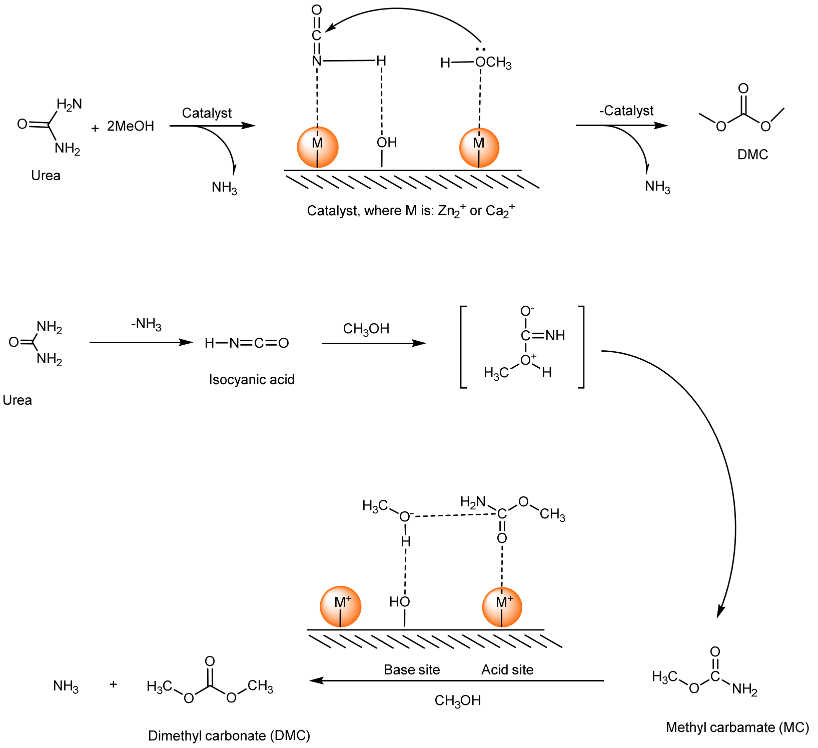

Figure 12. Most common reaction mechanism for the conversion of urea and methanol to DMC.

3. Outlook and Future Perspectives

In summary, this review discussed the DMC synthesis by two routes i.e., direct carbonylation of methanol using CO_2 and indirect urea alcoholysis. The direct conversion route has thermodynamic limitations, and catalysts used for the processes have low DMC yields (~4–10%) with catalyst deactivation because of the water formed during the reaction. The technical challenges of low conversion rates and low yield have not been fundamentally solved, preventing large-scale application. Research work has been reported to improve the methanol conversion and DMC selectivity through various ways, such as (a) water removal; (b) base additive reactions; (c) and catalyst modifications. Among these, modifying catalysts is proven to be an effective approach. We have discussed the development of various catalytic systems such as supported transition-metal, metal-oxides, mixed metal-oxides, and functional carbon support-based catalysts. The catalytic frameworks are needed based on their composition, surface area, porosity, and thermal stability.

The most popular catalysts are transition metal oxides, and many reports are available for DMC production. In general, these catalysts showed low activity with stable performance. $Ce_xZr_{1-X}O_2$ catalysts have excellent stability and recyclability because oxide is an active component in the catalysts and the catalytic deactivation (oxidative) is significantly less. The challenge is the preparation of these catalysts with tunable properties to improve the catalytic activity. Therefore, designing efficient metal oxides is still a challenge for large-scale applications.

Heteropolyacids as catalysts have attracted much attention nowadays. The beauty of this type of catalyst lies in the complex pore structures of heteropolyacid roots. However, the specific surface area and catalytic activity of these catalysts are highly inconsistent. These catalysts still need more investigations, such as the "quasi-liquid phase" behavior of these catalysts and the reaction mechanism involved were not explored.

The utilization of supported catalysts is also investigated, and these were found to be highly efficient. In general, the use of support can increase the catalytic efficiency by more than 10 times. These can also help in absorbing water which can promote the forward movement of chemical equilibrium. This leads to high catalytic efficiency.

The catalytic activities of ionic liquids for the direct conversion of CO_2 and methanol to DMC are also explained in detail. These catalysts are relatively clean and presented a high methanol conversion of ~72–74%. The reaction mechanism related to these catalytic systems is still unknown. It is necessary to study the reaction mechanism involved for DMC production's easiest and least energy-consuming process.

The use of dehydrating agents for in-situ water removal showed a better result for the direct DMC synthesis from CO_2 and methanol. Dehydrating agents can significantly improve the catalyst stability because water present during the reaction deactivates the catalysts. Ceria-based catalysts with dehydrants were reported showing 20–30 times improved DMC yield. Thus, these need to be considered for large-scale applications.

DMC synthesis using urea and methanol as feedstocks is a low-cost and facile production process because of the cheap and non-toxic materials used. In this reaction, water was not produced to form a methanol–water–DMC ternary azeotrope. To increase DMC yield, several methods have been evaluated. These methods involve removing one of the products to shift the reaction equilibrium towards the product side. Ammonia absorption may lead to the reaction toward the product side. The removal of DMC during the reaction also increases the DMC yield. Distillation methods such as catalytic distillation and reactive distillation can be used to increase the DMC yields by several folds.

For this route, zinc-based catalysts were considered promising catalysts due to their high conversion and selectivity. Mixed metal-oxides showed higher DMC yield, and metal leaching from these catalysts was significantly less. Although different catalysts have enhanced the DMC yield and selectivity, further catalyst developments are required for the commercialization of the DMC synthesis process. The use of ionic liquids has been widely reported as catalysts or co-catalysts for different reactions but is not qualified for the conversion of urea to DMC. The homogeneous catalysts, other than ionic liquids, were found to be effective compared to the heterogeneous catalysts but the difficulty in separation needs to be considered for the large-scale application. Kinetic studies reported are few and, hence, there is a lack of insight on the catalyst activity, which includes calculation of activation energy and frequency factor.

The catalytic activities are described mainly using their capacity, selectivity, recyclability, and product yield. Most of the catalyst studies were conducted in batch reactors, with very few tested in continuous flow conditions. However, it is highly demanding to study reaction under continuous flow to develop a commercial benefit and cost-effective, time and energy-saving process. In continuous flow conditions, catalyst stability and evaluation of intermediate species and active sites are major issues. These need to be addressed. Particularly, catalysts having a high surface area with hierarchical porosity, optimized acid–base properties, surface composition, and nanostructure need to be designed.

Although several catalysts have been reported for DMC synthesis by direct carbonylation of methanol using CO_2 and indirect urea alcoholysis, issues are still there for large-scale application. For instance, to solve the problem of scale-up economics, it is required to explore the new synthesis routes using cheap metal precursors and easy process synthesis steps. Since CO_2 conversion at low pressure is more important than at high pressure, catalysts with multiple functional sites should be designed for better interaction with CO_2. Structural features of the synthesized catalyst need to be analyzed for a better understanding of their actual structure and to study the reaction mechanism involved. Other aspects such as cost of catalyst preparation and regeneration (after usage), large-scale synthesis, stability, and energy input need to be evaluated, in addition to the DMC yield and selectivity, before considering these catalysts for real application.

4. Concluding Remarks

Dimethyl carbonate could play an important role in the development of more sustainable chemical methods, as it is environmentally friendly and has versatile applications, for instance, as a solvent, fuel additive, or reactant. However, its large-scale synthesis limits its application as a commodity, which could be significantly reduced by using carbon dioxide as a cheap and abundant feedstock. The direct DMC synthesis from carbon dioxide and methanol is the most desirable route since it promotes carbon dioxide capture and utilization and uses fewer toxic reactants. However, this route is unfavorable due to thermodynamic limitations. Although progress has been made in catalyst developments, DMC yield is still incredibly low. It is still challenging to find a catalyst with a high surface area, a large number of active sites, and moderate acidic and basic sites that can provide high DMC yield with good selectivity. For the direct reaction of methanol and CO_2 for DMC synthesis, the effect of water produced, and thermodynamic limitations should be carefully evaluated during the catalytic designing process. An appropriate dehydrating agent needs to be introduced in order to shift the equilibrium to the products.

An indirect urea alcoholysis route is a low-cost and facile DMC synthesis process; however, novel catalytic systems are required for the commercialization. As homogeneous catalysts have shown promising results, catalyst recycling studies need to be considered for large-scale applications. In conclusion, developments reached so far are fundamental for carbon dioxide utilization for DMC synthesis.

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