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Synthesis of organic carbonates from alcoholysis of urea: A review

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ABSTRACT

Organic carbonates are green compounds with a wide range of applications. They are widely used for the synthesis of important industrial compounds including monomers, polymers, surfactants, plasticizers, and also used as fuel additives. They can be divided into two main classes: cyclic and linear carbonates. Dimethyl carbonate (DMC) and diethyl carbonate (DEC) are the important linear carbonates. Carbonyl and alkyl groups present in DMC and DEC make them reactive and versatile for synthesizing various other important compounds. Ethylene carbonate (EC), glycerol carbonate (GC) and propylene carbonate (PC) are well-known cyclic organic carbonates. Phosgenation of alcohols was widely used for synthesis of organic carbonates; however, toxicity of raw materials restricted use of phosgenation method. A number of new non-phosgene methods including alcoholysis of urea, carbonylation of alcohols using CO_2, oxy-carbonylation of alcohols, and trans-esterfication of alcohols and carbonates have been developed for synthesizing organic carbonates. Carbonylation of alcohols is preferred as it helps in utilization and sequestration of CO_2, however, poor thermodynamics due to high stability of CO_2 is the major obstacle in its large scale commercialization. Oxy-carbonylation of alcohols offers high selectivity but presence of oxygen poisons the catalyst. Recently, alcoholysis of urea has received more attention because of its inexpensive abundant raw materials, favorable thermodynamics, and no water-alcohol azeotrope formation. Also, ammonia evolved in this synthesis route can be recycled back to urea by reacting it with CO_2. In other words, this method is a step towards utilization of CO_2 as well. This article reviews synthesis of DMC, DEC, GC, PC, and EC from urea by critically examining various catalysts used and their performances. Mechanisms have been reviewed in order to give an insight of the synthesis routes. Research challenges along with future perspectives have also been discussed.

1. Introduction

Chemical industries largely depend on fossil based carbon resources for their growth. Considering continuous depletion of these resources, there is an

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urgent need to develop processes utilizing CO_2 as carbonaceous raw material (1–19). The utilization of CO_2 can be done in three major ways. It can be used as solvent, or as a feedstock or it can be used as a storage medium. Due to depletion in traditional fuels, other alternative fuels produced using CO_2 may fill the gap between the demand and the supply (20). Recently, many articles have been published on use of organic carbonates as alternative fuels. There are even environmental and economical reasons to set organic carbonates as synthetic targets for utilization of CO_2. The increasing use of polycarbonates is pressurizing the markets to synthesize more and more organic carbonates (21). Five important organic carbonates on which research have been highly recently focused include dimethyl carbonate (DMC), diethyl carbonate (DEC), glycerol carbonate (GC), propylene carbonate (PC), and ethylene carbonate (EC). Their wide applications are categorized in Fig. 1 (22–41).
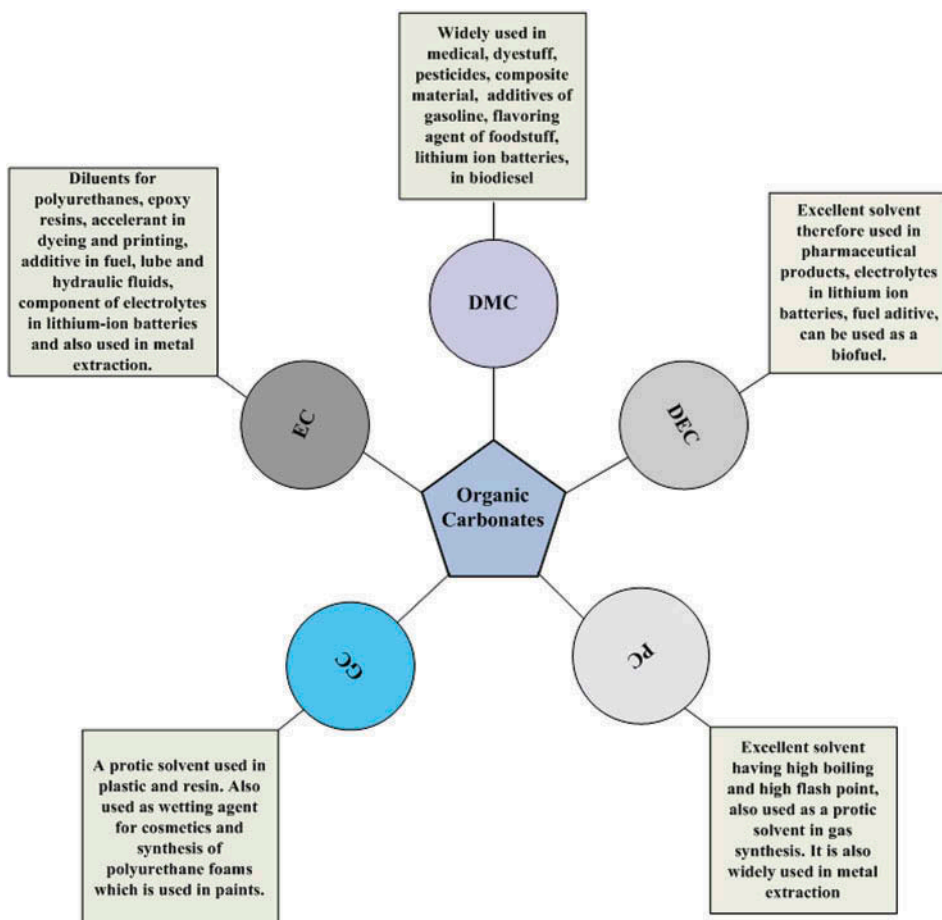

Figure 1. Various types of organic carbonates and their applications. DMC: dimethyl carbonate; DEC: diethyl carbonate; GC: glycerol carbonate; EC: ethylene carbonate; PC: propylene carbonate.

Patents have already been registered for use of DMC and DEC as a fuel additive in gasoline due to their excellent blending properties, high octane number, and oxygen content. Diesel engines are much more efficient than gasoline engines, however, they suffer from NO_x and particulate emissions. Many studies have already been reported on the reduction of hydrocarbons, CO, NO_x, and particulate emission from diesel engines because of the use of organic carbonates as oxygenate in the fuel (42–44). DMC and DEC are also considered as "green solvents" due to their environment friendliness and properties such as low vapor pressure. As the use of lithium ion batteries is growing exponentially, the use of organic carbonates as an electrolyte is also increasing proportionally. PC and EC are also good candidates for use as solvent due to their high potential to solubilize Li although their viscosities restrict their wide applications. DEC and DMC are other potential solvents, because of their low viscosity (45). Organic carbonates are also widely used for synthesizing important compounds such as polycarbonates, carbamates, unsymmetrical alkyl carbonates, ethylbenzene, 3-aryl-2-oxazolidinones, and imidazolindin-2-ones due to the presence of alkyl and carbonyl group. Moreover, they can substitute the toxic phosgene for the alkylation reaction.

Commonly used methods of synthesizing organic carbonates are shown in Fig. 2. These include phosgenation, oxidative carbonylation of alcohols (46), alcoholysis of urea, carbonylation of alcohol using CO_2, and trans-esterification of carbonates with alcohol.

Phosgenation of alcohol is the oldest technique used for the synthesis of organic carbonates. In this method, organic compounds containing solvent with an excess pyridine are phosgenated below room temperature. The type of organic compound formed, symmetrical, or asymmetrical carbonate, depends upon the hydroxyl group. Reactivity of a hydroxyl compound depends on its acidity. The more acidic the alcohol is, the less reactive it is.

Carbonylation of alcohols using CO_2 is a sustainable method as it involves sequestration of CO_2 (47–49). However, the thermodynamics of the reactions is not favorable, and hence, some modifications in the method are desired. The formation of dialkyl carbonates from oxidative carbonylation of alcohols is a well-known route. This method synthesizes the organic carbonates with very high selectivity, however the poisoning of catalyst, due to presence of CO and O_2, hampers the process.

Trans-esterification of carbonates with alcohols leading to an exchange of alcohol groups is also a method for synthesizing organic carbonates. The hydroxyl group is chosen accordingly to the targeted organic compound. This route proceeds with the formation of azeotrope, and thus, a complex design for separation of products.

Trans-esterification of alcohols with urea is a widely used method for the synthesis of organic carbonates. Due to the high availability and low-cost nature of the raw materials, this route is economically viable. No azeotrope
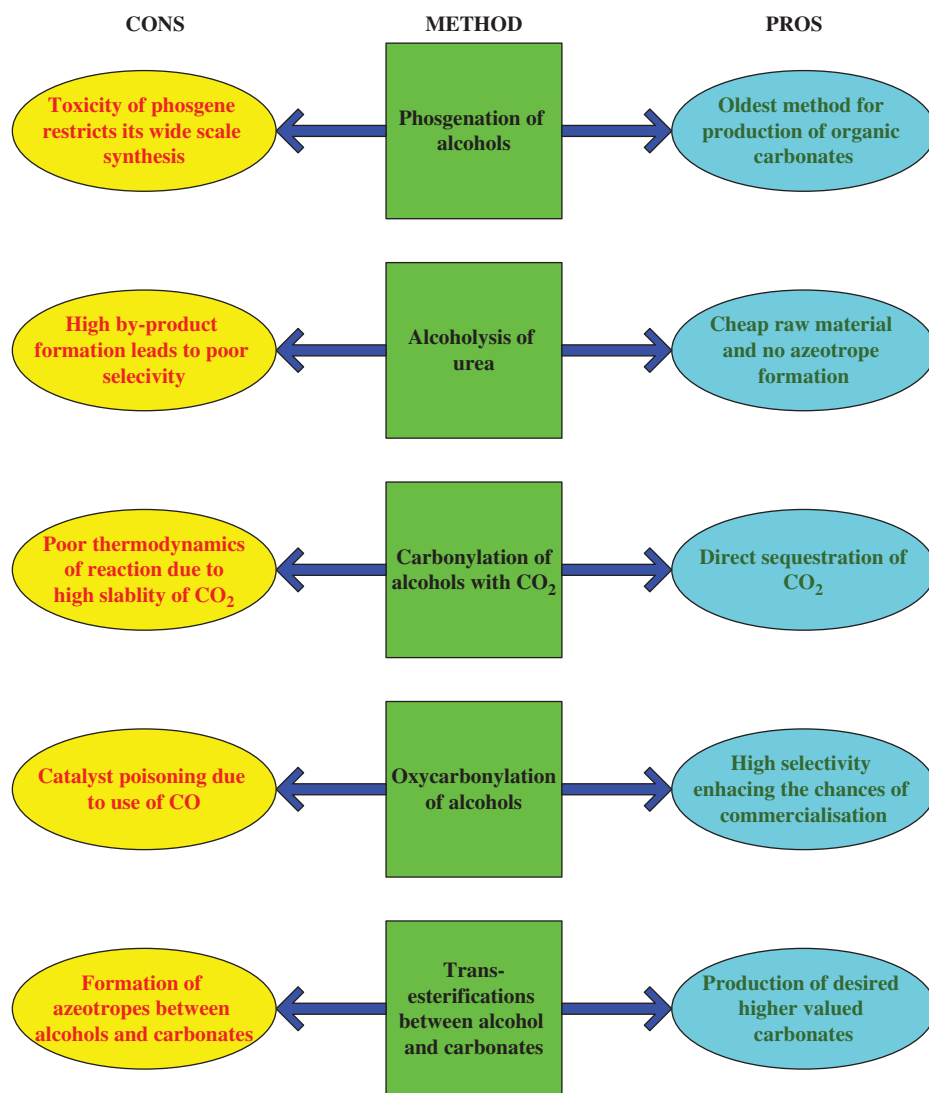
CONS	METHOD	PROS

Toxicity of phosgene restricts its wide scale synthesis ← **Phosgenation of alcohols** → Oldest method for production of organic carbonates

High by-product formation leads to poor selecivity ← **Alcoholysis of urea** → Cheap raw material and no azeotrope formation

Poor thermodynamics of reaction due to high slablity of CO_2 ← **Carbonylation of alcohols with CO_2** → Direct sequestration of CO_2

Catalyst poisoning due to use of CO ← **Oxycarbonylation of alcohols** → High selectivity enhacing the chances of commercialisation

Formation of azeotropes between alcohols and carbonates ← **Trans-esterifications between alcohol and carbonates** → Production of desired higher valued carbonates

Figure 2. Advantages and disadvantages of various methods for the synthesis of organic carbonates.

formation takes place in this pathway; hence separation of carbonates from the reaction mixture is quite simple. A number of articles have been reported on synthesis of organic carbonates using urea. These are summarized year wise in Fig. 3. The synthesis of DMC and GC has been extensively investigated over the years. DMC is the simplest organic carbonate; it is widely synthesized and utilized with glycerol for the production of GC. Table 1 lists the patents filed for the synthesis of mentioned five carbonates using urea alcoholysis reaction (50–69).

This article critically reviews synthesis of DMC, DEC, GC, PC, and EC from urea by examining the catalysts used and their performances, and the
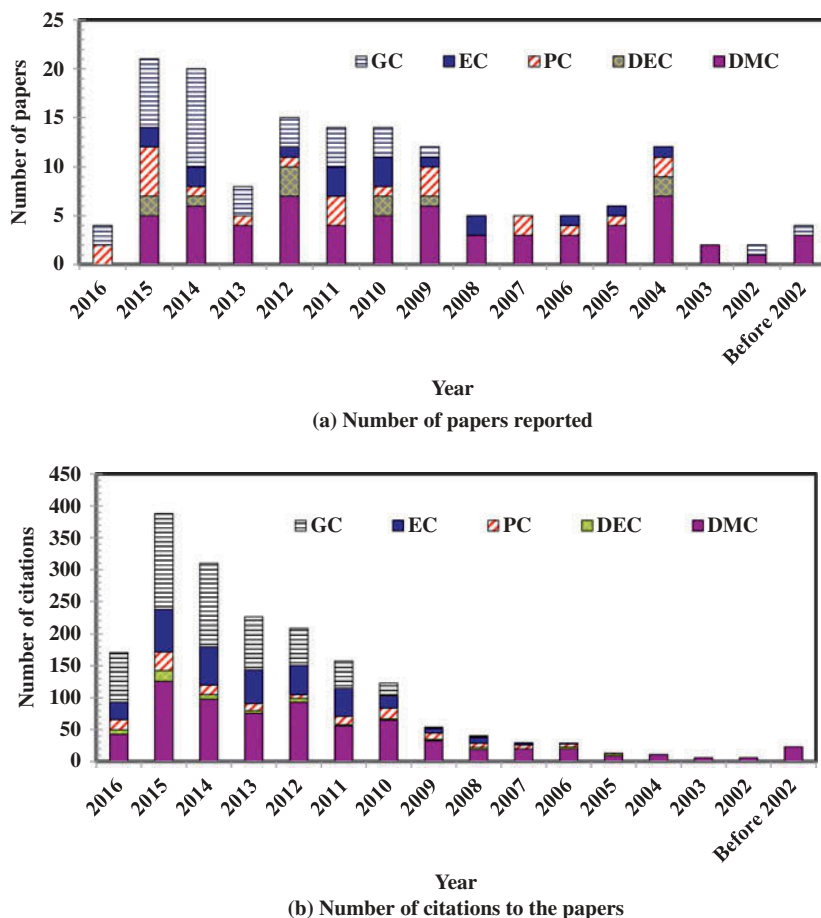
Figure 3. Number of research articles published and their corresponding citations for the synthesis of organic carbonates from urea. The data was obtained from Scopus on May 5, 2016 using the following strings: "dimethyl carbonate" AND "urea" AND "synthesis"; "diethyl carbonate" AND "urea" AND "synthesis"; "glycerol carbonate" AND "urea" AND "synthesis"; "propylene carbonate" AND "urea" AND "synthesis"; and "ethylene carbonate" AND "urea" AND "synthesis" for search in title-abstract-keywords; under the refinement of "physical science" AND subject area of "chemical engineering".

reaction mechanisms so as to identify the research challenges along with future perspectives.

2. Synthesis of dimethyl carbonate from urea with methanol

2.1. *General overview*

DMC containing both methyl and carbonyl groups, shows excellent reactivity and is also considered as a green chemical. DMC has replaced carcinogenic chemicals such as dimethyl sulfate, dichloro methane, etc., which are widely used for carbonylation and trans-esterification reactions. It is widely used in

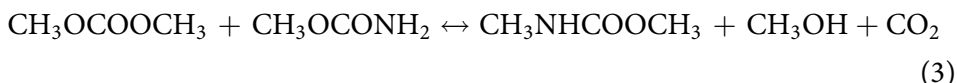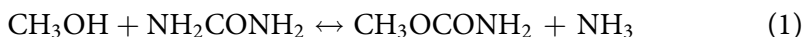**Table 1.** List of important patents filed on alcoholysis of urea for production of various carbonates.

Assignee	Description of patent	Reference
Union Oil Company of California	DMC when mixed with diesel reduces pollution levels	50
Bayer Aktiengesellschaft	DMC was synthesized using methanol and phosgene which was improved when reaction was conducted in presence of alkali metal hydroxide and organic solvent	51
Anic S.p.A.	DMC was synthesized from oxy-carbonylation of methanol using metal salts	52
Kuhlmann	Process to manufacture dialkyl carbonate from urea and alcohol	53
Catalytic Distillation Technologies	Process to synthesize dialkyl carbonate from primary alcohol with urea in presence of organo tin as a catalyst with electron donating compound	54
Robert C.	Manufacturing a catalyst by reacting dialkyltin oxide, alcohol and the corresponding dialkyl carbonate	55
Exxon Chemical Patents Inc	A process for making dialkyltin oxide with an alcohol and the corresponding alkyl carbamate	56
Moses Lake Industries	Synthesis of dialkyl carbonates from ethanol/methanol and either alkyl carbamate or urea	57
Catalytic Distillation Technologies	A process for synthesis of dialkyl carbonate from urea and primary alcohols in reactive distillation conditions	58
Sun, Yuhan	Synthesis of DMC was done in a catalytic rectification reactor rectifier	59
The Dow Chemical Company	Synthesis of alkylene carbonates from alkylene diol and alkyl trichloro acetate in presence of weak base	60
Montedison Fibre SPA	Direct synthesis of alkylene carbonates from olefins	61
Mitsui Petrochemical Industries, Ltd.	Synthesis of cyclic carbonates by reacting 1,3 diol with dialkyl carbonate with basic catalyst	62
Texaco Chemical Company	Synthesis of alkylene carbonate from alkylene glycol and urea in presence of organotin as the catalyst	63
Mitsubishi Gas Chemical Company Okamoto, Kenichi	Synthesis of alkylene carbonate from alkylene glycol and urea in presence of catalyst containing calcium, zinc, and magnesium at reduced pressure	64
Organisation Nationale Interprofessionnelle Des Oleagineux (ONID Ol.)	Synthesis of glycerol carbonate from glycerol ad urea in presence of catalyst bearing Lewis acid.	65
MontedisonFibre SPA	Synthesis of alkylene carbonate from olefins and carbon dioxide	66
Union Oil Company of California	Hydrocarbon fuels heavier than gasoline containing carbonates as additives reduce particulate emissions	67
Pittsburgh Plate Glass Co	Synthesis of carbonic acid ester is from hydroxyl compound and polyhaloformate	68
Bayer Aktiengesellschaft	Process of preparing dialkyl carbonate from glycerol carbonate and alcohol	69

the synthesis of medicines, pesticides, dyes, composite materials and fuel additives (23,70–72). It also acts as an ideal additive for gasoline because of its high oxygen number and good blending octane (72).

2.2. *Thermodynamics and kinetics of reaction*

DMC can be synthesized from methanol (CH_3OH) and urea (NH_2CONH_2) in two steps. Methanol reacts with urea to give methyl carbamate,

MC (CH$_3$OCONH$_2$) which then reacts with methanol to give DMC (CH$_3$OCOOCH$_3$). However, DMC being an active compound, can react with MC to form N-methyl methyl carbamate, N-MMC (CH$_3$NHCOOCH$_3$). The reactions are summarized below:

$$CH_3OH + NH_2CONH_2 \leftrightarrow CH_3OCONH_2 + NH_3 \qquad (1)$$

$$CH_3OCONH_2 + CH_3OH \leftrightarrow CH_3OCOOCH_3 + NH_3 \qquad (2)$$

$$CH_3OCOOCH_3 + CH_3OCONH_2 \leftrightarrow CH_3NHCOOCH_3 + CH_3OH + CO_2$$
$$(3)$$

Heat of reactions ($\Delta H_r°$) of first and second reactions are −10.31 and 13.11 kJmol^{-1} at normal temperature and pressure (NTP). Reaction 1 is exothermic while reaction 2 is endothermic. Change in the Gibbs free energy ($\Delta G_r°$) increases with an increase in temperature for reaction 1 and decreases with an increase in temperature for reaction 2. Hence, first reaction is favorable while the second is rather unfavorable in such conditions. Equation (3) is the main side reaction. The activation energy of this side reaction 3 is more than the main reactions; hence, high reaction temperature favors the side reaction. Therefore, first step is thermodynamically favorable while second is not. DMC should thus be separated as soon as it is formed (73–76).

2.3. Catalysts used

Different catalytic studies performed for DMC synthesis from urea and methanol are summarized in Table 2. Zn-based catalysts have been widely used for the synthesis of DMC from urea or MC, whose performances are shown in Figs. 4a and 4b. Zn-CeO$_2$-La performed best among all the catalysts used for the synthesis of DMC through urea methanolysis, and La(NO$_3$)$_3$ performed best for the synthesis of DMC from MC. The alcoholysis of urea proceeds with the formation of an active component, isocyanic acid (HNCO), from urea decomposition (melting point of urea is 134°C) (75). The formation of MC doesn't require any catalyst while the formation of DMC requires a catalyst. The mechanism is shown in Fig. 5a. Ammonia produced in both the reactions (1 and 2) should be removed in order to shift the equilibrium towards the product side as the nucleophilicity of NH$_2$- is significantly higher than CH$_3$O$^-$. As DMC is a good methylating agent for oxide groups, it can react with MC to give NMMC. Also at high temperature, DMC can decompose to dimethyl ether and CO$_2$ (77).

Wu et al. (78) studied the activity of Zn and its oxide as catalyst. Zn as a metallic powder gave 1.65 times the yield obtained with ZnO, however the problem of sintering has to be dealt with when using it on a support. When

Table 2. Studies reported on the synthesis of dimethyl carbonate from methanolysis of urea or methyl carbamate.

Catalyst	Catalyst preparation method	Reactants	Reaction time (h)	Reaction temperature (K)	Reactor type	Molar yield DMC (%)	Reference
Dibutyl tin dimethyloxide	–	Methanol and urea	7	443	Autoclave	39	73
Zn- based catalysts, Zn powder*	Impregnation method	Methanol and urea	6	443	Autoclave	12.7	78
Zn and Pb based oxides, salts, carbonates, oxides of Ca, Mg, Zr (ZnO)*	Thermal decomposition/hydroxides by precipitation method	Methanol and urea	8	443	Autoclave	29	76
Polyphosphoric acid		Methanol and urea	4	413	Autoclave	67.4	80
Polyphosphoric acid		Methanol and urea	6	397	Reactive rectifying system	92.2	79
ZnO, CaO, TiO_2, $CaCl_2$, $C_{36}H_{70}O_4Zn$, $C_{36}H_{70}O_4Mg$, $C_{36}H_{70}O_4Ca$, organo tin, zinc stearate $(C_{36}H_{70}O_4Zn)^*$		Methanol and urea	10	423	Autoclave	22.4	91
CaO, La_2O_3, MgO, ZrO_2, MgO^*	Thermal decomposition/precipitation method	Methanol and urea	11	453, 473	Autoclave	2.88	81
CaO, La_2O_3, PbO, ZnO, ZnO-Al_2O_3, ZnO^*	Thermal decomposition of carbonates	Methanol and urea	8	453	Catalytic distillation	26	102
ZnO, $Zn(OH)_2$, $ZnSO_4$, $Zn(NO_3)_2$, $Zn(CH_3COO)_2$ $ZnCl_2^*$, $ZnBr_2$, $NaCl$, KCl, $Zn(NH_3)_2Cl_2$	Commercial reagents	Methyl Carbamate and methanol	10	463	Autoclave	33.6	82
ionic liquids, emimBr–$ZnCl_2^*$		Methanol and urea	8	433	Autoclave	25.5	94
$ZnAlO$, $ZnFeO^*$, $ZnCrO$, ZnO, Fe_2O_3, Al_2O_3, Cr_2O_3, ZnO-Fe_2O_3, $MgFeO$, $NiFeO$, $CuFeO$.	Precipitation method	Methyl carbamate and methanol	10	463	Autoclave	31.48	84
La_2O_3, $LaCl_3$, LaF_3, $La_2(CO_3)$, $LaPO_4$, $La(NO_3)_3^*$, $NaNO_3$, $Cu(NO_3)_2$	Evacuating the hydrated salts, thermal decomposition of carbonates	Methyl carbamate and methanol	8	453	Autoclave	53.7	85

(Continued)

Table 2. (Continued).

Catalyst	Catalyst preparation method	Reactants	Reaction time (h)	Reaction temperature (K)	Reactor type	Molar yield DMC (%)	Reference
ZnO, Fe_2O_3, ZnO-Fe_2O_3, ZFO-2,ZFO-4*, ZFO-8, ZFO-10, $ZnFe_2O_4$	Co-precipitation method	Methyl carbamate and methanol	10	463	Autoclave	30.7	87
ZnO(X)-CeO_2(1-X), ZnO(0.7)-CeO_2(0.3), ZnO(0.7)–CeO_2(0.3)*	Sol-gel method	Methanol and urea	4	443	Autoclave	28.9	88
ZnO-CeO_2-MO (MO: La_2O_3, Y_2O_3,Co_2O_3, Ga_2O_3, and ZrO_2), ZnO(0.64)–CeO_2(0.26)–La_2O_3(0.1)*	Sol-gel method	Methanol and urea	4	443	Autoclave	50.4	89
CaO, ZnO, ZCO-10, ZCO-4, ZCO-2, ZCO-0.85, ZCO-0.25, ZCO-4*	Urea precipitation method	Methanol and urea	10	453	Autoclave	41.2	90
		Methanol and urea	2	538	Autoclave	98	92
SO_3H-MCM-41		Methyl carbamate and methanol	6	433	Autoclave	16.7	101

No.	Catalyst	Ref
1	Zn powder	78
2	CaO	81
3	La_2O_3	81
4	MgO	81
5	ZrO_2	81
6	$ZnO(0.7)-CeO_2(0.3)$	89
7	$ZnO(0.7)-CeO_2(0.3)$	89
8	$ZnO(0.64)-CeO_2(0.26)-La_2O_3(0.1)$	89
9	$ZnO(0.64)-CeO_2-(0.26)-Y_2O_3(0.1)$	89
10	$ZnO(0.64)-CeO_2-(0.26)-Co_2O_3(0.1)$	89
11	$ZnO(0.64)-CeO_2-(0.26)-Ga_2O_3(0.1)$	89
12	$ZnO(0.64)-CeO_2-(0.26)-ZrO_2(0.1)$	89
13	ZnO-CaO (1:1)	90
14	ZnO-CaO (4:1)	90

(a)

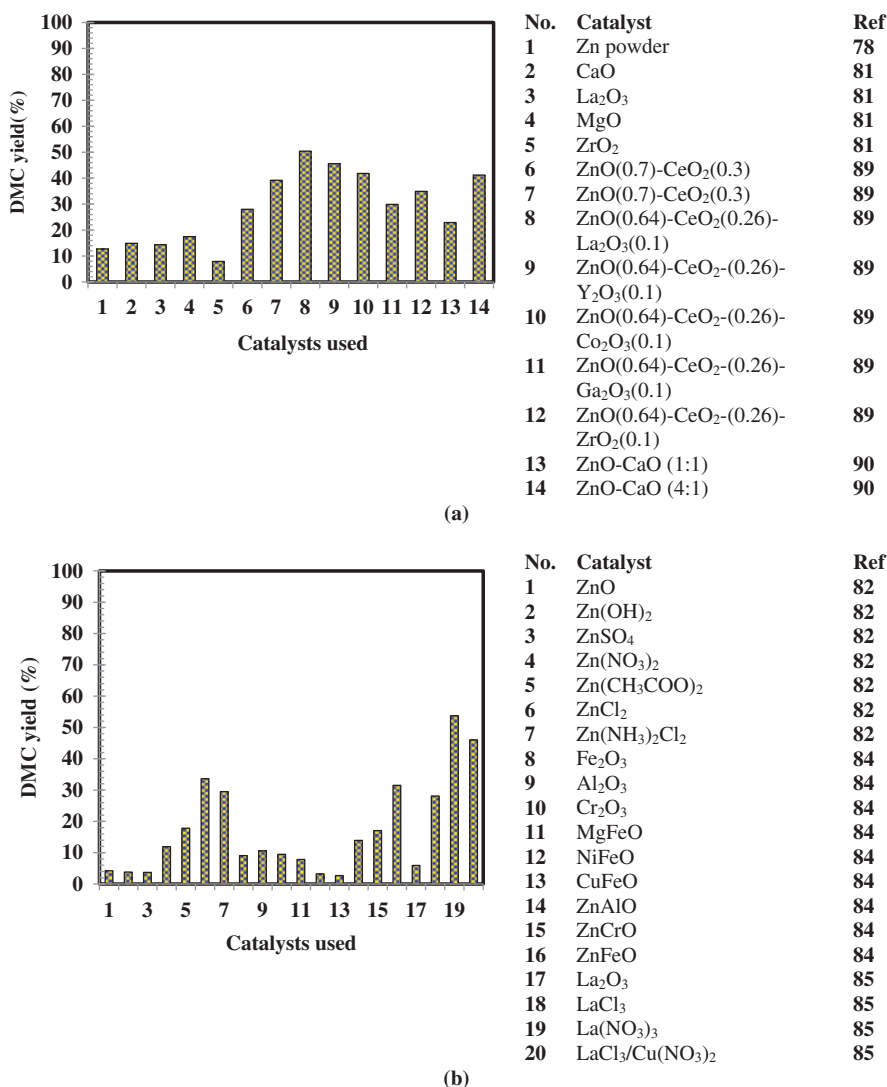| No.	Catalyst	Ref
1	ZnO	82
2	$Zn(OH)_2$	82
3	$ZnSO_4$	82
4	$Zn(NO_3)_2$	82
5	$Zn(CH_3COO)_2$	82
6	$ZnCl_2$	82
7	$Zn(NH_3)_2Cl_2$	82
8	Fe_2O_3	84
9	Al_2O_3	84
10	Cr_2O_3	84
11	MgFeO	84
12	NiFeO	84
13	CuFeO	84
14	ZnAlO	84
15	ZnCrO	84
16	ZnFeO	84
17	La_2O_3	85
18	$LaCl_3$	85
19	$La(NO_3)_3$	85
20	$LaCl_3/Cu(NO_3)_2$	85

(b)

Figure 4. Performances of various catalysts studied for the synthesis of DMC from urea or MC.

zinc powder was used as the catalyst, 12.7% yield was obtained, however, only 8.9% yield was obtained when it was loaded to alumina. This was attributed to the doping of Al_2O_3 in ZnO lattice thereby creating electro-negative vacancy. When PbO along with ZnO was used as catalyst, the electron cloud around Zn increased, which in turn increased its binding energy (78).

Wang et al. (79) screened the catalysts for DMC synthesis and ZnO performed best giving 29% DMC yield. Pb-based catalyst also performed better giving 22 and 24% DMC yield. Since DMC acts as a N-methylating agent, the main by-product formed was N-MMC (71). However, the DMC produced by this method is of low quality since it is contaminated with
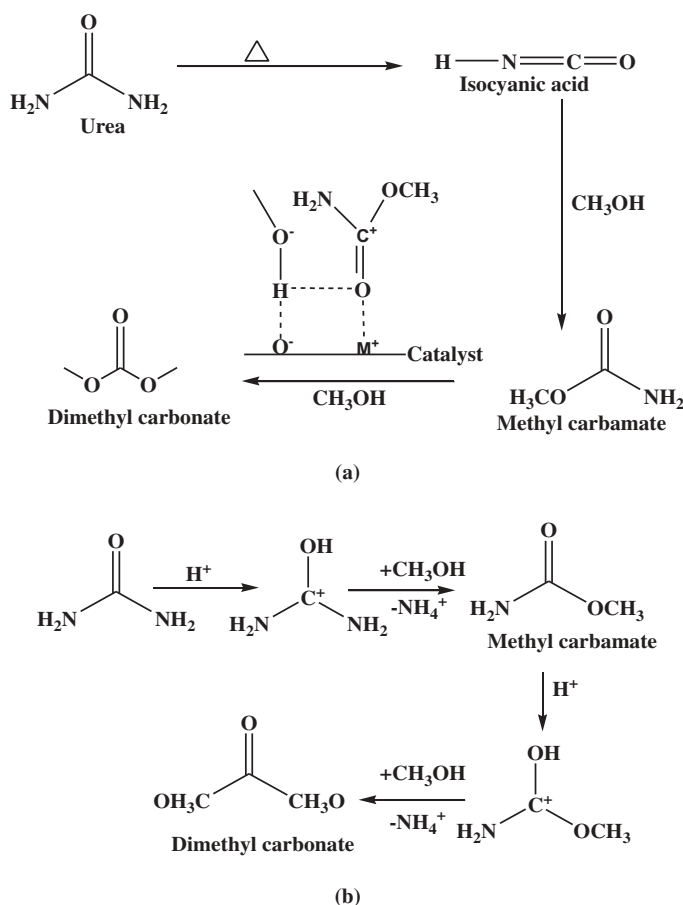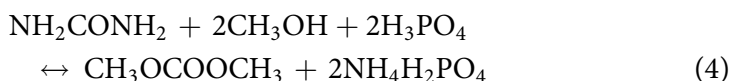
Figure 5. Reaction mechanisms for the synthesis of DMC from urea and methanol (a) over metal oxides (proposed by Wang et al. ([76])) and (b) in acidic medium (as proposed by Sun et al. ([80])).

ammonia. Hence, Sun et al. ([80]) used polyphosphoric acid (PPA) which reacted with ammonia to form ammonium polyphosphate (as shown in Eq. (4)), a useful material for fertilizer. Also being insoluble in methanol and DMC, ammonium polyphosphate formed in the reaction can easily be separated from the mixture. Under optimal conditions, 67.4% DMC yield was obtained. The mechanism is shown in Fig. 5b

$$NH_2CONH_2 + 2CH_3OH + 2H_3PO_4$$
$$\leftrightarrow CH_3OCOOCH_3 + 2NH_4H_2PO_4 \tag{4}$$

Wang et al. ([81]) used a solid base catalyst and distinguished between basicity and basic strength allowing to establish that the basic strength is the most important parameter for the synthesis of DMC from methanol. CO_2-TPD confirmed that La_2O_3 had more basic strength than MgO. Hence, basic catalyst activated methanol by abstracting H^+ ion from methanol, leaving CH_3O^- which further reacts with MC to give DMC.

Zhao et al. (82) studied the synthesis of DMC from MC using $ZnCl_2$ where the role of Zn^{+2} ion was evaluated. For direct synthesis of DMC from MC, ZnO was highly inactive. Here, Zn^{+2} ion plays a major role in its activity. This was confirmed by the use of $ZnCl_2$ and $ZnBr_2$ which also showed similar activity. When NaCl and KCl were used as a catalyst, they provided lower yields and selectivities as compared to $ZnCl_2$ and $ZnBr_2$. This observation confirmed the importance of Zn^{2+} ion in catalytic activity.

Hydrotalcites (HTC) derived catalyst are largely used for such reactions due to their basicity and layered structure.(83) Wang et al.(84) synthesized DMC from MC using hydrotalcite derived catalyst and compared the yield of DMC obtained with different mixed oxides (ZnAlO, ZnCrO, and ZnFeO) catalyst prepared by co-precipitation method. ZnFeO was found to possess high basic strength, and hence, performed best giving 31.48% DMC yield.

Wang et al. (85) reported the reasons for ZnO not showing activity for the synthesis of DMC from MC while it works as a good catalyst for DMC synthesis from urea. ZnO was found to form a homogenous compound ($Zn(NCO)_2(NH_3)_2$) which showed less activity toward DMC synthesis from MC. Later, Gao et al. (86) studied the reaction mechanism through density function theory simulations and suggested that the $Zn(NH_3)_2(NCO)(NHCOOCH_3)$ was active component responsible for the high activity.

Trivalent elements La^{+3} was also used as catalyst for the synthesis of DMC from MC. The role of La^{+3} was established when $NaNO_3$ and $Cu(CO_3)_2$ were used, and they did not show any activity. $La(NO_3)_3$ was the best performing catalyst giving 53.7% DMC yield.

Homogenous catalyst like $ZnCl_2$ showed good activity for synthesis of DMC through MC, however, problem of separation of catalyst after the reaction should be met. Hence, Wang et al. (87) synthesized Zn-Fe mixed oxides using the co-precipitation method and compared its performance with ZnO and Fe_2O_3. It was found that the number of catalytic sites didn't matter although the Zn/Fe ratio affected the yield of DMC. A 30.7% DMC yield was obtained under optimal conditions (which were close to that obtained with $ZnCl_2$). The insolubility of the catalyst was confirmed by an element analysis of the products, which showed very low concentration of Zn and Fe in the product solution.

Considering earlier reports that CeO_2 can enhance the acidity and basicity of ZnO, Joe et al. (88) used a ZnO-CeO_2 mixed oxide as catalyst for DMC production. The DMC yield was found to be directly proportional to the basicity of the catalyst while the acidity of the catalyst had no linear relationship with its performance. $ZnO_{0.7}$-$CeO_{20.3}$ was the most basic catalyst among all mixed oxides synthesized, and hence, it performed best giving DMC yield of 28.9%. Transition metal doping on Ce-Zn catalyst is also known to affect the acidity or basicity of the catalyst (89). Doping with La_2O_3 maximized its basicity, and hence, its catalytic activity was optimized. The doped catalyst showed 50.4% DMC yield under optimal conditions.

CaO has also been widely used as catalyst for trans-esterfication and because of its high basicity, it was shown to activate the methanol for the reaction. Accordingly, Wu et al. (90) used ZnO-CaO mixed oxide to synthesize DMC. The acid-base sites on ZnO-CaO mixed oxides provided highest yield (41.2%) using a Zn/Ca ratio of 4.

Yang et al. (91) reported an approach allowing the production of DMC from methanol and urea at ambient temperature. In this study, urea along with the catalyst was solvated using polyethylene glycol dimethyl ether (PGDE). Methanol was used in vapor form which was also preheated to the reaction temperature. Methanol vapors were bubbled through the solution converting to MC and DMC. Finally, DMC and unreacted methanol were cooled in a condenser to room temperature. Different metal oxides were used as the catalyst for this method. A DMC yield of 28.8% was obtained under optimal conditions when ZnO was used.

Reactions under supercritical conditions have recently attracted more attention. Hou et al. (92) synthesized DMC under supercritical condition with 98% DMC yield. Synthesizing DMC under supercritical conditions is more environment friendly as it requires less reaction time and doesn't requires strict requirements of chemicals (93).

2.4. Ionic liquids

Although DMC yield has increased because of continuous research efforts, however the problem of low selectivity needs to be amended. The reaction between DMC and MC producing NMMC is highly favorable at high temperature and pressure which is not a desirable for DMC synthesis (94). Research on the use of ionic liquids as catalyst has grown recently (20,95–97). Wang et al. (97) synthesized DMC from urea and methanol using ionic liquids as catalyst (Fig. 6a). The ionic liquid $Et_3NHCl–ZnCl_2$ helped in achieving 100% selectivity, however, the yield was only 26%. The high activity of ionic liquids is due to the high polarity and electrostatic field which can stabilize charged intermediates, and thus promoting the reaction to the right side thereby increasing its selectivity.

2.5. Kinetics of dimethyl carbonate from methanol

Lin et al. (73) studied the kinetics of DMC synthesis from methanol and urea using dibutyl oxide as catalyst. The kinetic parameters of the main as well as side reactions were estimated using genetic algorithm. Rate constants at different temperatures were estimated, and they well represented the experimental data. Results showed that the activation energy of the secondary reactions was more than that of the main reactions. Hence, the
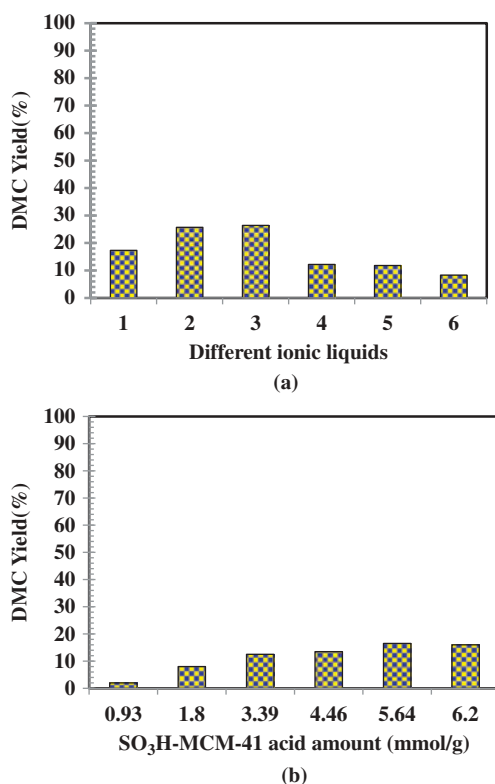
Figure 6. (a) Performance of different ionic liquids (1: Et$_3$NHCl–FeCl$_3$, 2: emimBr–ZnCl$_2$; 3: Et$_3$NHCl–ZnCl$_2$; 4: emimBr–ZnCl$_2$; 5: Et$_3$NHCl–ZnCl$_2$; 6: Et$_3$NHCl–ZnCl$_2$), source of data: (94); and (b) effect of acidic amount of MCM-41, source of data: (101); on DMC yield during DMC synthesis from urea and methanol.

higher temperature supports secondary reactions (formation of by-products).

Zhao et al. (98) studied the effect of catalyst on the activation energy and pre exponential factor. The value of exponential factor for the reactions (1) and (2) was 1.26×10^6 and 8.12×10^2 Lmol^{-1}s^{-1}, respectively. Respective activation energies of Equations (1) and (2) were 84.7 and 75.3 kJmol^{-1}, respectively. The activation energy of the reactions with catalyst was found to be high as compared to that without catalyst. However, the pre exponential factor of the reaction with catalyst was very high. Hence, Zn-based catalyst only increased the collision frequency without reducing the energy of bond breaking.

Zhang et al. (99) studied the kinetics of DMC synthesis from urea using ZnO as catalyst in an isothermal fixed bed reactor. The models were validated accordingly with experimental data. MC conversion to DMC was found to be the rate determining step. The activation energies of Equations (1) and (2) were found to be 43.54 and 90.87 kJmol^{-1}, respectively.

2.6. *Other processes apart from autoclave-based synthesis*

Wang et al. (100) introduced reactive rectifying system using PPA as catalyst and optimized the reaction parameters yielding 92.2% DMC from urea. ΔG_r^0 for the reaction is negative (-30.2 kJmol^{-1}) and, hence, is spontaneous. Although PPA, a Bronsted acid, gave very high yield, it showed problem of separation. This problem was reduced to a large extent by grafting sulfonic acid to MCM-41. Sulfonic acid, a bronsted acid, can absorb ammonia and shift the equilibrium towards the product side. The effect of sulphonic acid amount on DMC yield is shown in Fig. 6b. To enhance the DMC yield and suppress the yield of N-methyl urea and N-methyl methyl carbonate, reactive rectification method was used (100,101). The process was compared with the conventionally used batch reactor and the yield of N-methyl urea and N-methyl methyl carbonate was found to be less for the reactive rectification rather than for batch reactor. Also, the pressure was comparatively less than that used in normal batch reactors. A high DMC yield of 92% was obtained as an efficient removal of DMC from the reactors didn't allow the formation of N-methyl urea and N-methyl methyl carbonate.

Wang et al. (102) synthesized DMC using methanol and urea using a catalytic distillation process and compared the performance with a batch reactor. Different metal oxides were used as catalyst both for the batch reactor and catalytic distillation process. Batch reaction gave a mere DMC yield of 35% as compared to 50-60% that obtained in the catalytic distillation process.

Zhang et al. (103) used a fixed bed reactor to synthesize DMC from urea and methanol using Zn based mixed oxides. The fixed bed reactor maximized the DMC yield by minimizing the side reactions due to the separation of DMC as it was formed. The ZnO-Al$_2$O$_3$ catalyst performed best giving 34.6% DMC yield.

Various metal oxides have been used as catalysts for the synthesis of DMC, among them zinc-based catalysts have shown better activity. However, due to its homogenous nature, its separation is difficult. Other metal oxides like La-based have also shown good activity.
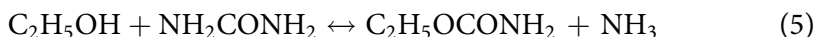
A number of methods can be used to increase the DMC yield. These methods involve removal of one of the products so that the reaction equilibrium shifts toward product side. Absorption of NH$_3$ may lead the reaction towards the product side, and hence, PPA has been tried as the catalyst which enhanced the DMC yield. Removal of DMC during the reaction also increases the overall DMC yield. A catalytic distillation method has been used for this purpose, and it increased the DMC yield by several folds (102). Reactive distillation, in which reaction along with distillation is carried out at the same time, can also be used to ease separation along with reaction, as it has not been reported for DMC synthesis from urea (104).

3. Synthesis of diethyl carbonate from urea or ethyl carbamate with ethanol

3.1. *General overview of reactions and applications of diethyl carbonate*

DEC is an organic compound which on degradation gives ethanol and carbon dioxide (105,106). It contains more oxygen as compared to MTBE. Its high blending octane (104–106) and low vapor pressure allow it to be contender as a fuel additive (107). It was reported that addition of DEC reduces particulate emission from diesel by almost 50%. Also, its gasoline/water distribution coefficient is more favorable than DMC which makes it more miscible with fuel, which eases its separation from water. Presence of ethyl and carbonyl group makes it very effective for ethylization and carbonylation of other organic compounds. Being an excellent solvent, it is also used in lithium ion batteries (108,109).

DEC synthesis from urea (similar to DMC) occurs in two steps. First, urea reacts with ethanol to produce ethyl carbamate, ECE ($C_2H_5OCONH_2$) which then reacts with ethanol in the second step to give DEC.

$$C_2H_5OH + NH_2CONH_2 \leftrightarrow C_2H_5OCONH_2 + NH_3 \qquad (5)$$

$$C_2H_5OCONH_2 + C_2H_5OH \leftrightarrow C_2H_5COOC_2H_5 + NH_3 \qquad (6)$$

The NH_3 involved in the process can be recycled back and could be used for urea synthesis. The first step can occur even without catalyst, however, the second step essentially requires catalyst. Therefore, the second step is the rate controlling step. Considering this, many researchers have investigated synthesis of DEC from ECE rather than from urea.

Studies on the synthesis of DEC from the ethanolysis of urea and ECE are summarized in Table 3. Performances of various catalysts used are shown in Figs. 7a and 7b. Mg-Zn-Al derived from HTCs performed best giving the best DEC yield from urea while MgO nano oxides performed best for the synthesis of DEC from ECE.

3.2. *Synthesis of diethyl carbonate from urea*

Organo tin showed the best results as catalyst, however, because of its homogenous nature, it is difficult to recover. The estimated equilibrium constant from Benson group contribution and Constantinious group contribution model were plotted with reaction temperature and a brisk increase in equilibrium constant was noticed after reaction temperature was increased above 450 K. The estimated ΔG_r^o of reactions was 0.66 kJmol^{-1} and 20.09 kJmol^{-1} for Equations (5) and (6), respectively.

Wang et al. (110) reported ethanolysis of urea to ECE and DEC using various metal oxides. ZnO and ZrO_2 gave better yield as compared to

Table 3. Studies reported on the synthesis of diethyl carbonate from ethanolysis of urea and ethyl carbamate.

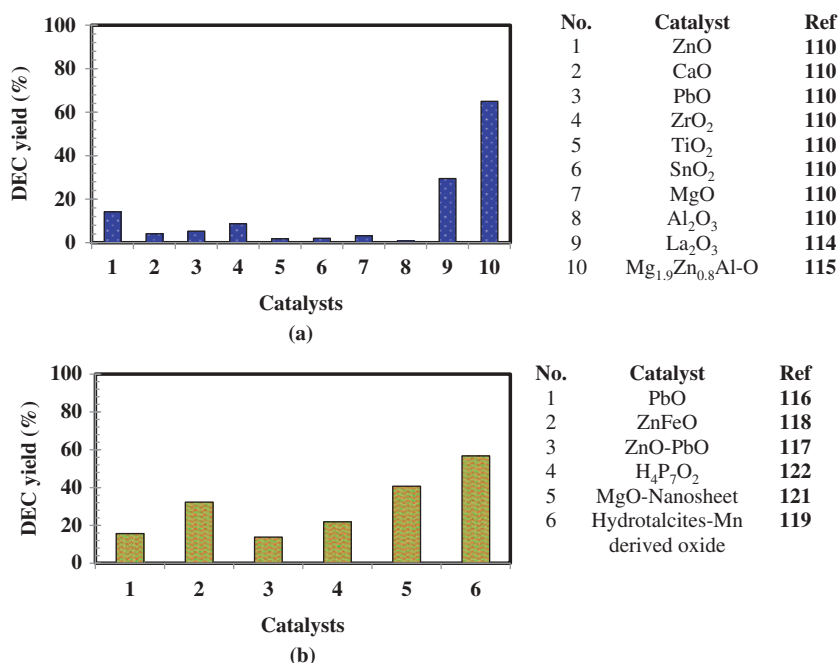| Catalyst	Catalyst preparation method	Reactants	Reaction time (h)	Reaction temperature (K)	Reactor type	Molar yield DEC (%)	Reference
Metal oxides, ZnO*	Commercially obtained	Ethanol and urea	5	463	Autoclave	14.2	110
ZnO	Commercially obtained	Ethanol and urea	10	453	Autoclave	34	113
Zn/Fe Hydrotalcite-like Compounds, ZnFeO-500*	Thermal decomposition	EC and ethanol	10	453	Autoclave	32.3	118
PbO based binary oxides, ZnO-PbO*	Thermal decomposition	EC and ethanol	7	453	Autoclave	20.6	117
Lewis and Bronsted acid, Pyrophosphoric acid*	Commercially obtained	EC and ethanol	6	453	Autoclave	21.9	122
–	–	EC and ethanol	0.5	573	Autoclave	22.9	126
Slag-based catalysts, SN-450*	Precipitation method	EC and ethanol	3	473	Autoclave	33.1	128
Metal oxides, lanthanum oxide*	Precipitation method	Ethanol and urea	3	483	Autoclave	38.6	114
		EC and ethanol	0.5	573	Autoclave	22.9	126
Mg–Zn–Al hydrotalcites, MgZn$_{1.7}$Al-450*	Co-precipitation method	Ethanol and urea	4	473	Autoclave	65	115
Magnesium oxide nanosheets, MgO-SC-450 *	Thermal decomposition and precipitation methods	EC and ethanol	3	473	Autoclave	40.7	121
Transition metal-modified mesoporous Mg-Al mixed oxides, HTC-Mn*	Co-precipitation method	EC and ethanol	8	463	Autoclave	56.7	120

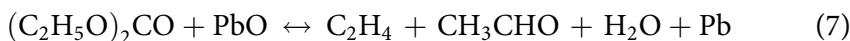Figure 7. Performances of various catalysts during synthesis of DEC from urea or ECE with ethanol.

other catalyst due to the presence of weak acidic and basic sites (111,112). ZnO was found to get transformed into $Zn(NH_3)_2(HCO)_2$ which was found to be main species for accelerating DMC synthesis (113). The problem of recovery of the catalyst remained although yield obtained was best with ZnO.

Rare earth metals are known to catalyze a number of reactions, and hence, find many applications as catalyst. The large size of La^{3+} combined to its low charge permits its basic property as well La^{3+} can act as an acidic site. Xin et al. (114) used La_2O_3 as catalysts for the two-step synthesis of DEC from urea and ethanol. Basic sites with medium strength were responsible for the good yield of DEC as well no leaching was observed. The role of carbonate species removal which could ease the regeneration of the catalyst was also highlighted in the study.

Wang et al. (115) synthesized Mg-Zn-Al oxides derived from HTCs for the synthesis of DEC from urea and ethanol. These catalyst were found to possess high specific area combined with nanoplate morphology. Weak and medium basic sites on $MgZn_{1.7}Al$ calcined at 450°C were attributed for its better performance with 67.5% DEC yield. Its reusability was also examined and very little deactivation of catalyst was obtained when the catalyst was reused five times.

3.3. *Diethyl carbonate synthesis from ethyl carbamate and ethanol*

PbO was also reported to perform well for similar type of reactions, and hence it was tried as catalyst for second step of DEC synthesis from ECE (116). DEC yield of 16.2% was obtained. PbO was found to get converted to metal Pb and PbO_2 as per the following equation:

$$(C_2H_5O)_2CO + PbO \leftrightarrow C_2H_4 + CH_3CHO + H_2O + Pb \qquad (7)$$

The synergistic effect of the Pb cubic metal and orthorhombic PbO_2 was found to be responsible for its high activity. Hence, An et al. (117) synthesized DEC from ECE using PbO-based binary metal oxides whereas the other metal oxides studied included MgO, CaO, SrO, BaO, ZnO, Al_2O_3, Fe_2O_3, CuO, NiO, TiO_2, and La_2O_3. These binary oxides were prepared by calcinating their corresponding metal salts precursor. Overall, ZnO-PbO performed best giving a 13.8% yield. The effect of precursors was also examined which showed $Zn_2(OH)_2CO_3$ and $PbCO_3$ to be the best. $Zn(NCO)_2(NH_3)_2$ was found to be real specie which increased the activity.

Wang et al. (118) derived spinel shaped mixed oxide $ZnFe_2O_4$ from a Zn/Fe HTC. ZnO and $ZnFe_2O_4$ present in the catalysts promoted the activity and a DEC yield of 32.3% from ECE and ethanol was obtained. Owing to advantages like high surface area, stability, and mild basicity of Mg-Al mixed oxides (119), Wang et al. (120) synthesized DEC from ECE and ethanol using transition metal (modified Mg-Al) mixed oxides as catalyst. HTC-based catalyst exhibited maximum activity giving DEC yield of 56.7%.

Li et al. (121) synthesized MgO nanosheets using a combination of precipitation and thermal decomposition methods. MgO nanosheets were prepared from the precipitation method using different precipitants such as sodium carbonate, sodium hydroxide, and ammonia. MgO nanosheet prepared from sodium carbonate possessed high surface area, was found to be the best for DEC synthesis because of its larger amount of mild basic sites. Co-adsorption of ECE and ethanol on MgO surface with nucleophilic ethoxy group was found during FTIR study. Yield of 58% with selectivity of 92% was obtained.

In order to increase the yield of DEC or push the reaction equilibrium towards product side, the ammonia produced in large amount should be absorbed. To achieve this, various Lewis and Bronsted acids were tried as catalyst (122). The best yield of 21.9% was obtained when PPA was used as a catalyst.

Supercritical ethanol can also be used for the synthesis of DEC. Zhao et al. (126) synthesized DEC under catalyst free supercritical conditions using only ethanol in a stainless steel reactor (123–126). Compared to other methods, this method gave DEC yield of 22.9% after only 30 min of operation.

Slag which contains Mg, Ca, Al, and other metals, is a major by-product of the manufacturing sector and its recycling is a major challenge (127). Wang et al. (128) synthesized DEC using waste slag as catalyst. The slag was first dissolved in a HCl solution and then the hydroxides were precipitated using NaOH in the pH range of 2–10.5. The hydroxides were further calcined at different temperatures to get compositions of various metal oxides. As different metal hydroxides have different tendency to get precipitated at same pH, the catalyst composition of different proportions of hydroxides were obtained. The slag was then calcined at different temperatures leading to give various metal oxides compositions. 33% DEC yield was obtained with the slag calcined at 450°C.

Synthesis of DEC from urea or ECE is not thoroughly reported as compared to DMC due to poor acidity or poor reactivity of ethanol. La_2O_3 and HTCs derived oxides are best reported catalysts.

4. Synthesis of glycerol carbonate from urea

4.1. *General overview of reaction and applications of glycerol carbonate*

The use of biodiesel as renewable energy source is being thoroughly researched, and trans-esterification of vegetable oils is the main process for producing biodiesel. In order to make this process economical, large amount of glycerol (which is produced as by-product) needs to be converted into valuable products like glycerol carbonate (GC) (129–145). GC is a cyclic carbonate which is widely used as aprotic solvent in plastic and resin industry, and as wetting agent for cosmetics and solvents in pharmaceutical synthesis. The presence of cyclic and hydroxyl groups in GC makes it reactive and other valuable chemicals like glycidol can be produced form GC. GC is also used as a component in gas separation membranes such as poly urethane foams which is used in paints (146–148).

Synthesis of GC from urea has been studied thermodynamically by Li and Wang (149). The GC reactions, shown below, occur in two steps. First glycerol urethane ($C_4H_9O_4N$) is formed which breaks to form GC:

$$C_3H_8O_3 + NH_2CONH_2 \leftrightarrow C_4H_9O_4N + NH_3 \tag{8}$$

$$C_4H_9O_4N \leftrightarrow C_4O_4H_6 + NH_3 \tag{9}$$

Values of $\Delta H_r°$, $\Delta S_r°$, $\Delta G_r°$ and equilibrium constant are reported to be 126.2 kJmol^{-1}, 314.52 JK^{-1}mol^{-1}, 32.43 kJmol^{-1}, and 2×10^{-6}, respectively (149). Value of equilibrium constant increases with temperature, while it decreases with an increase in pressure. Research work reported on the synthesis of GC from glycerol and urea is summarized in Table 4 and performances of various catalysts are summarized in Fig. 8.

Table 4. Studies reported on the synthesis of glycerol carbonate from glycerol and urea.

Catalyst	Catalyst preparation method	Reactants	Reaction time (h)	Reaction temperature (K)	Reactor type	Molar yield GC(%)	Reference
Co_3O_4/ZnO	Dry dispersion process	Glycerol and urea	4	418	Round bottom flask	69	156
Hydrotalcites catalyst, HTc-Mg 0.25*	Co-precipitation method	Glycerol and urea	5	323	Glass batch reactor	82	163
Sm_2O_3, La_2O_3*, CeO_2, Nd_2O_3, Y_2O_3, Pr_2O_3	Precipitation method	Glycerol and urea	10	413	Round bottom flask	90.8	151
Au based catalysts, Au/MgO*	Impregnation and deposition precipitation method	Glycerol and urea	4	423	Round bottom flask	56	157
Zn based catalysts, $ZnCl_2$*	–	Glycerol and urea	2	423	Round bottom flask	80.2	142
Gold–palladium supported, 1 wt% AuPd/MgO* nanoparticles	Impregnation and sol-immobilisation	Glycerol and urea	4	423	Round bottom flask	93	161
Co_3O_4/ZnO	Dry nanodispersion method	Glycerol and urea			Reactive distillation	90.0	172
Lanthanum-based mixed oxides, $LaCoO_3$*	Sol-gel	Glycerol and urea	4	423	Round bottom flask	33.6	152
Gypsum based catalyst		Glycerol and urea	4	423	Round bottom flask	83.6	167
Heteropoly tungstate catalysts, $Ta_{0.4}TPA$*		Glycerol and urea	4	413	Round bottom flask	71	165

No.	Catalyst	Ref
1	La_2O_3	152
2	$LaCrO_3$	152
3	$LaMnO_3$	152
4	$LaFeO_3$	152
5	$LaCoO_3$	152
6	$LaNiO_3$	152
7	La_2CuO_4	152
8	$LaAlO_3$	152

(a)

No.	Catalyst	Ref
1	Sm_2O_3	151
2	Eu_2O_3	151
3	CeO_2	151
4	Nd_2O_3	151
5	Y_2O_3	151
6	Pr_2O_3	151
7	La_2O_3	151

(b)

No.	Catalyst	Ref
1	Au/TiO_2	157
2	Au/Fe_2O_3	157
3	2.5% Au/C	157
4	2.5%Au/SiO_2	157
5	2.5% Au/Nb_2O_5	157
6	2.5% Au/TiO_2	157
7	2.5% Au/ZnO	157
8	2.5%Au/MgO	157
9	AuPd/MgO	157

(c)

No.	Catalyst	Ref
1	Htc-Mg(0.25) derived oxide	142
2	ZnF_2	142
3	$ZnCl_2$	142
4	$ZnBr_2$	142
5	ZnI_2	142
6	$Zn(NO_3)_2.6H_2O$	142
7	$Zn(OAC)_2.2H_2O$	142
8	ZnO	142
9	$Zn(NH_3)_2Cl_2$	142
10	$Zn(C_3H_6O_3)$	142
11	$Zn(C_3H_6O_3)/NH_4Cl$	142

(d)

Figure 8. Performance of various catalysts during synthesis of glycerol carbonate (GC) from glycerol and urea.

4.2. Heterogeneous catalysts being studied for the reaction

Aresta et al. (150) synthesized γ-zirconium phosphate and obtained good yields at ambient conditions. Moreover, as the catalyst was insoluble in glycerol, it was fully recovered after the experimental runs. Good conversion of glycerol (80%), high selectivity (100%), and easy recoverability of catalyst along with recycling of NH_3 makes this process suitable for commercialization. As GC was obtained at low pressure, the process is favorable also.

GC was also synthesized with 80% yield using $ZnSO_4$ as catalyst (65). However, the salt was soluble in glycerol and recovery of the catalyst was difficult. ZnO was used as heterogeneous catalyst in presence of $MgSO_4$. The reactions were performed at reduced pressure in order to shift the reaction toward product side.

Various La-based oxides have been reported for the production of GC whose performances have been summarized in Fig. 8a. Lanthanum-cobalt and lanthanum-copper based oxides performed best. Wang et al. (151) reported the effect of calcination temperature on the crystalline phases of La_2O_3. Other oxides have also been studied and their performances were compared to La_2O_3 (Fig. 8b). $La_2O_2CO_3$ phase was found on the catalyst (in addition to La_2O_3 phase) in varying compositions depending on the calcination temperature. The presence of $La_2O_2CO_3$ phase during preparation of La_2O_3 altered the basicity of the catalysts. The yield obtained by La_2O_3 calcined at 600°C (90.8%) was much higher than other catalysts calcined at different temperatures due to higher presence of the $La_2O_2CO_3$ phase (151). Pursuing this work, Zhang et al. (152) synthesized lanthanum-based mixed oxides using sol gel method and studied their performance. Among different catalyst, La_2CuO_4 favored the effective selective carbonylation of glycerol. This activity was further enhanced by doping Fe into La_2CuO_4. $La_2Cu_{0.5}Fe_{0.5}O_4$ showed combined effect of enhancing glycerol conversion and GC selectivity (152). Overall the mixture was shown to be the best for GC synthesis.

Co-ZnO was used as a catalyst for glycerol-based reactions and performed better (153,154). Marcos et al. (155) synthesized Co_3O_4/ZnO using solvent-free dry nano-dispersion method, and compared the performances with ZnO and Cr_3O_4. They showed the necessity to control the phase mixed during formation of Co_3O_4/ZnO. The activity of this oxide was better than individual oxides (due to the formation of $ZnCo_3O_4$) and the calcinations had adverse effects on its activity (156).

Since Au-based catalysts were studied thoroughly in glycerol oxidation (157–160), gold, zinc, and gallium impregnated ZSM-5 was studied for GC synthesis from urea. The promotion of the intermolecular cyclisation of the carbamate intermediate was considered as the reason for good yield and selectivity. The use of gold and other noble metals in place of other metal oxides improved the recoverability. Later, Rahim et al. (161) used gold, palladium, and gold-palladium supported nanoparticles for the synthesis of GC from urea. Au and Pd nanoparticles supported on MgO were the active ingredients promoting GC formation from urea and glycerol, however, their synergestic effect was not as good. The transformation of magnesium oxide (as support) to magnesium carbonate was observed. Performances of these catalysts are summarized in Fig. 8c.

Park et al. (142) studied the effect of the acidity and solubility of Zn-based compounds. ZnF_2 was found to be less efficient as compared to $ZnCl_2$ and

$ZnBr_2$ due to its low solubility. $Zn(C_3H_6O_3)$ and NH_4Cl played major role in the glycerolysis of the urea. The performances are summarized in Fig. 8d. Fujita et al. (162) studied the GC synthesis in presence of Zn-based catalysts such as HTCs-based catalyst, ZnO, and smectite. Reaction proceeded homogenously not heterogeneously as active Zn species got dissolved. Zinc halides performed better as compared to others (162).

Climent et al. (163) used mixed oxides Al-Ca derived from HTCs as the catalysts and studied the role of acid-base pairs on the glycerol conversion and selectivity of GC in the reaction. For good conversion and highly selective synthesis of GC from urea and glycerol, it is necessary to maintain a good balance between acidity and basicity of the solid catalyst (83). Calcined HTCs with $pK_a \geq 14$ performed better. They are able to neutralize proton or activate glycerol. Lewis basicity was enhanced by substituting Li to Mg which allowed working at much lower temperature and catalytic loading. A high conversion and selectivity of 98% was obtained when Li was substituted by Mg.

Metal-oxygen clusters of transition metals, known as polyoxometalates, are a class of inorganic compounds that are known to possess high Bronsted acidity combined with high thermal stability. Their most important aspect, however, is its ions exchange capacity. Kumar et al. (164) reported high GC yield using samarium-exchanged heteropoly tungstate (Sm_xTPA) owing to its high Lewis acidic sites which depends directly on the Sm content of the catalyst. $Sm_{0.66}$TPA catalyst was more efficient than other catalysts. It was found to be reusable as well. Following this work, Babu et al. (165) synthesized tantalum in tungstophosphoric acid (TPA) for the synthesis of GC. The effect of the protons exchange of TPA with tantalum ions for generation of Lewis acidic sites was also explored.

Jagadeeswaraiah et al. (133) prepared tin-tungsten mixed oxide catalyst by co-precipitation method and studied the synthesis of GC from glycerolysis of urea. The activity was found to depends upon Sn/W ratio and calcination temperature. The catalyst was reusable many a times.

Similarly, Zn-W-based binary oxides were prepared by co-precipitation method and studied for the synthesis of GC from urea carbonylation of glycerol. Bimetallic oxides (combination of their metal cations in mixed phase) possess hybrid acid-base properties, which plays important role in their activities (143,166).

Gypsum is the most abundant sulphur bearing mineral. It is also produced as waste in various industries. Its use as a catalyst for glycerol conversion can make the process greener, if its activity is good. Zuhaimi et al. (167) synthesized gypsum based catalyst. δ-$CaSO_4$ was the most active phase of gypsum whereas γ-$CaSO_4$ was found to be the real heterogeneous part. The presence of Ca^{+2} served the purpose of Lewis acid which is responsible for catalytic activity. High glycerol conversion of 92.8% and GC selectivity of 90.1% was observed.

Manjunathan et al. (168) synthesized Zn-Sn composite oxides using co-precipitation and evaporation methods. The composite consisted of three components namely Zn_2SnO_4, ZnO, and SnO_2. The catalyst prepared from co-precipitaion gave best selectivity due to presence of more acidic and basic sites. 96% glycerol conversion and 99.6% GC selectivity was obtained.

Boiler ash is widely produced in a number of industries. Since its disposal is alarming, its utilization as a catalyst can be more efficient to make the process more environmental friendly. Indran et al. (169) synthesized GC from glycerol using boiler ash as catalyst. CaO along with MgO and KOH contributed most in boiler ash activity. GC yield of 84.3% and glycerol conversion of 93.6% was achieved when the catalyst was calcined at 900°C.

4.3. *Ionic liquids*

Ionic liquids give better activity because of their polarity. Hence, Lee et al(170) synthesized various quaternary ammonium salts immobilized on montmorillonite clay by ion exchange method (170). Ionic liquids such as polystyrene-supported, metal-containing imidazolium salt (PS-$(Im)_2ZnBr_2$) catalysts proved to be very active for glycerol synthesis and its reusability was also good. Kim et al. (171) synthesized ionic liquids with acid-base properties which were active for the synthesis of GC, and were reusable as well.

4.4. *Reactive distillation method*

Lertlukkanasuk et al.(172) used reactive distillation which combines reaction of raw materials and separation of products by distillation in one process. The results were simulated and were compared to conventionally used batch reactor using Co_3O_4/ZnO as the catalyst. High 90.3% GC yield was obtained with 100% purity. The kinetics was also studied and the activation energy was estimated to be 31.89 kJmol^{-1}.

Overall, lot of surplus glycerol is widely available and needs to be utilized by its transformation. Zn-based and Au-based oxides performed better during glycerolysis of urea. However, no kinetic study has been performed. Separation of GC from other products as soon as it gets formed will increase activity of catalyst but no such study has been reported.
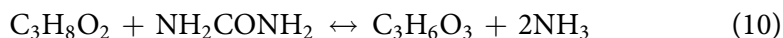
5. Synthesis of propylene carbonate from urea

5.1. *General overview of the reaction and applications of propylene carbonate*

Propylene carbonate (PC) is an excellent organic solvent. It is biodegradable, has high boiling and flash points, less toxic and has low odor levels. It is

widely used as polar, aprotic solvent in gas synthesis, synthetic fiber battery electrolytes, and metal extraction (173). PC also contributes in the synthesis of various other important carbonates such as DMC (174,175). The studies on synthesis of PC and the performances of different catalysts are summarized in Table 5 and Fig. 8. PC is used for synthesizing DMC, DEC, and some polymers as shown in Fig. 9.

PC synthesis from propylene glycol (PG, $C_3H_8O_2$) is as follows (176):

$$C_3H_8O_2 + NH_2CONH_2 \leftrightarrow C_3H_6O_3 + 2NH_3 \qquad (10)$$

Values of $\Delta H_r°$, $\Delta S_r°$, and $\Delta G_r°$ are reported to be 48.59 kJmol^{-1}, 134.56 JK^{-1}mol^{-1}, and 6.46 kJmol^{-1}. The value of equilibrium constant is 836.1. Increase in temperature was found to decrease $\Delta H_r°$, $\Delta S_r°$, and $\Delta G_r°$ (176).

5.2. Heterogenous catalysts studied for synthesis of propylene carbonate from urea

5.2.1. Zinc-based catalysts

Alkylene carbonate has been produced from urea and alkylene glycol using organic tin, calcium, magnesium, zinc and lead as the catalyst (64). Figure 10a summarizes the performances of Zn based catalysts. Pb-Zn based catalyst performed best. Li et al. (177) confirmed the presence of both acidic and basic sites in ZnO which activated urea to give high EC yields. The problem of loss of zinc atom was encountered which caused decrease in activity and PC yield when the synthesis was done using homogenous and supported zinc acetate. Zhao et al. (178) prepared Zn-Fe double oxides and studied the synthesis of PC. The specific surface area didn't correlate with the yield of PC. Strong alkali sites on the catalyst directly affected the yield of PC. However, the surface area and alkaline density mattered more in case of mixed oxides. ZnO-MgO was studied for synthesis of PC. A number of basic sites along with surface area were responsible for better performance of ZnO-MgO (179). Later, ZnO supported on NaY was used for the synthesis of PC from urea. It was observed that as the loading of ZnO increased, the mild basic sites of the catalyst decreased which promoted the reaction (180). Gao et al. (181) used $MgCl_2$ and $ZnCl_2$ as catalyst, and 96.5% PC yield was obtained using $MgCl_2$.

5.2.2. Other heterogeneous catalysts

Zhiping et al. (182) used metal oxides and metal loaded on hydroxyapatites and studied their performance. Hydroxyapetites itself being basic in nature gave 50% yield of PC without any loading. The loading of various metals promoted their activities. The presence of strong basic sites on the surface of La and K supported on hydroxyapatites enhanced the PC yield. Perovksite structures (ABO_3) are well known for their control of basic properties, hence

Table 5. Studies reported on the synthesis of propylene carbonate from propylene glycol and urea.

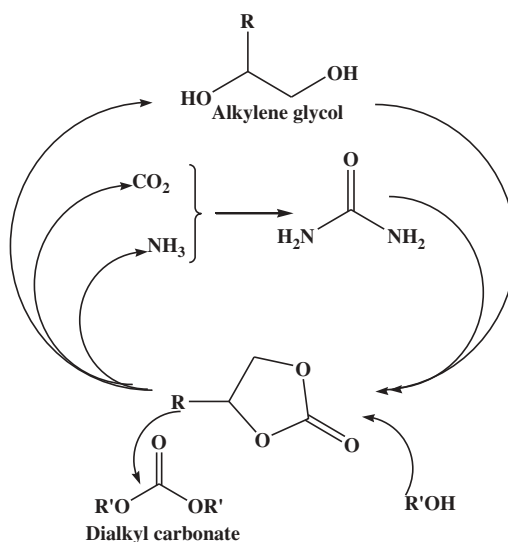| Catalyst	Catalyst preparation method	Reactants	Reaction time (h)	Reaction temperature (K)	Reactor type	Molar yield PC (%)	Reference
Zinc acetate	–	Urea and 1,2-Propylene Glycol	3	443	Four-necked flask	78	177
Zinc–iron double oxide	Precipitation method	Urea and 1,2-Propylene Glycol	2	443	Four-necked flask	78.6	178
$Pb/Fe_3O_4/SiO_2$	Precipitation method	Urea and 1,2-Propylene Glycol	2	473	Four-necked flask	79.4	183
$MgCl_2$ and $ZnCl_2$	–	Urea and 1,2-Propylene Glycol	3	423	Three-necked-flask	96.5	181
ZnO/NaY	Impregnation method	Urea and 1,2-Propylene Glycol	13	423	Fixed bed reactor	82.3	180
Modified hydroxyapatites	Impregnation method	Urea and 1,2-Propylene Glycol	2	443	Three-necked-flask	91.5	182
Zinc–chromium mixed oxide catalyst	Commercially obtained	Urea and 1,2-Propylene Glycol	6	453	Monolithic stirrer reactor	97.8	184
Perovskite $MgTiO_3$	Sol-gel	Urea and 1,2-Propylene Glycol	2	443	Three-necked-flask	93.5	182
Zn–Mg mixed oxide	Urea precipitation	Urea and 1,2-Propylene Glycol	0.5	443	Four-necked flask	94.8	179

Figure 9. Scheme showing synthesis of alkylene carbonates from urea and dialkyl carbonate from alkylene carbonates.
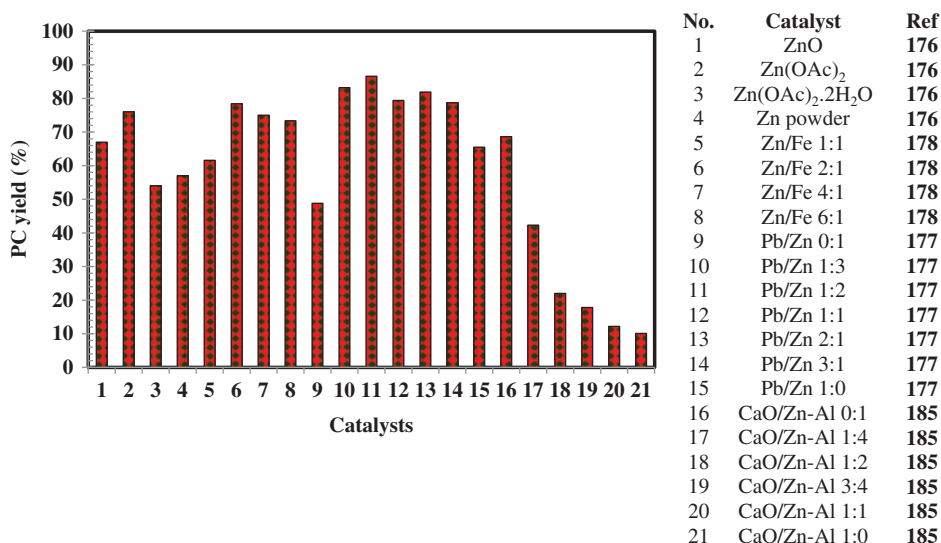

No.	Catalyst	Ref
1	ZnO	176
2	$Zn(OAc)_2$	176
3	$Zn(OAc)_2.2H_2O$	176
4	Zn powder	176
5	Zn/Fe 1:1	178
6	Zn/Fe 2:1	178
7	Zn/Fe 4:1	178
8	Zn/Fe 6:1	178
9	Pb/Zn 0:1	177
10	Pb/Zn 1:3	177
11	Pb/Zn 1:2	177
12	Pb/Zn 1:1	177
13	Pb/Zn 2:1	177
14	Pb/Zn 3:1	177
15	Pb/Zn 1:0	177
16	CaO/Zn-Al 0:1	185
17	CaO/Zn-Al 1:4	185
18	CaO/Zn-Al 1:2	185
19	CaO/Zn-Al 3:4	185
20	CaO/Zn-Al 1:1	185
21	CaO/Zn-Al 1:0	185

Figure 10. Performances of Zn-based catalysts on PC yield.

they have been examined as the catalyst. The basic properties of $MgTiO_3$ were controlled by controlling the MgO content of the catalyst by calcinating the catalyst at different temperatures (39). Mg/Ti ratio of one gave 90% PC yield.

Reaction of PG with urea was carried out under vacuum which requires high operating cost and high PG to urea ratio, thus enhancing the separation problem. Lead carbonate and zinc carbonate were the most effective catalyst giving highest yield because of the synergistic effects of crystalline phases of hydrozincite and lead carbonate. 96.3% PC yield was obtained at 180°C and 5 h.

The problem of recovery of catalyst is usually encountered with homogenous catalyst. Fe_3O_4 with good dispersion stability and ease of separation is widely used as the catalyst. An et al. (183) prepared $Pb/Fe_3O_4/SiO_2$ by sol-gel and impregnation method, and used it for the synthesis of PC. The PC yield obtained was 79.4%.

A newly developed monolithic stirred reactor was also used for the synthesis of PC and process optimization was done when various metal oxides were used as the catalysts. Mixed metal oxides performed better than individual metal oxides irrespective of the type of reactor (184). The problem of scrapping out was addressed. The performance o,f mixed slurry reactor increased with an increase in temperature. The best PC yield was 97.8%.

Since PC itself is the reactant for the formation of DMC, it can be termed as first step for the synthesis of DMC. Therefore to synthesize DMC directly from one pot method from PG would serve the purpose of energy savings and formation of most green chemical at the same time. Hence, one pot method was tried using Ca-Zn-Al oxides which contained both strong and weak basic sites (185). Maximum DMC yield of 82.9% was obtained.

PC being a high boiling point solvent has application in lithium ion batteries. Basic mixed metals oxides performed well.

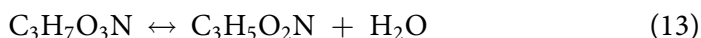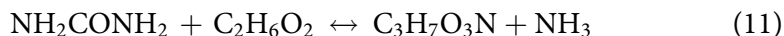## 6. Synthesis of ethylene carbonate from urea with ethylene glycol

6.1. General overview of reaction and ethylene carbonate applications

EC is an important five member cyclic carbonate with low toxicity, biodegradability and has high boiling point. Its applications include use in production of polyacrylonitrile fibers as an accelerant in dying and printing, additive in fuel, lube, and hydraulic fluids. They can be used as monomer for the synthesis of polycarbonates and can also work for sequestration of CO_2 (186–190). It can be used for the synthesis of important compounds like DMC and DEC. The studies on synthesis of EC are summarized in Table 6 and performances of different catalysts are given in Fig. 10. $\Delta H_r°$ for the

Table 6. Studies reported in synthesis of ethylene carbonate from ethylene glycol and urea.

Catalyst	Catalyst preparation method	Reactants	Reaction time (h)	Reaction temperature (K)	Reactor type	Molar yield EC (%)	Reference
Metal oxides	Commercially obtained/thermal decomposition	Ethylene glycol and urea	3	423	Three-necked-flask	93.1	177
La(NO$_3$)$_3$	–	Ethylene glycol and urea	3	413	Round bottom flask	93	192
Zinc-yttrium oxides	Co-precipitation method	Ethylene glycol and urea	4	423	Round bottom flask	–	193

synthesis of EC from urea is 116 kJmol^{-1}. Synthesis occurs in two steps. First, hydroxy ethyl carbamate ($C_3H_7O_3N$) is formed from ethylene glycol ($C_2H_6O_2$) which in the second step gets converted to EC. The main side reaction causes formation of 2-oxazolidone ($C_3H_5O_2N$) which is formed when hydroxy ethyl carbamate dehydrates. The reactions can be summarized as follows:

$$NH_2CONH_2 + C_2H_6O_2 \leftrightarrow C_3H_7O_3N + NH_3 \tag{11}$$

$$C_3H_7O_3N \leftrightarrow C_3H_4O_3 + NH_3 \tag{12}$$

$$C_3H_7O_3N \leftrightarrow C_3H_5O_2N + H_2O \tag{13}$$

6.2. Catalysts studied

Bhanage et al. (112) used metal oxides to synthesize EC and DMC in single pot. Figure 11a shows the performances of all metal oxides among which ZnO performed best. First ethylene glycol gets converted to EC and it further converts to DMC. ZnO gave 97% ethylene glycol conversion and 98% EC
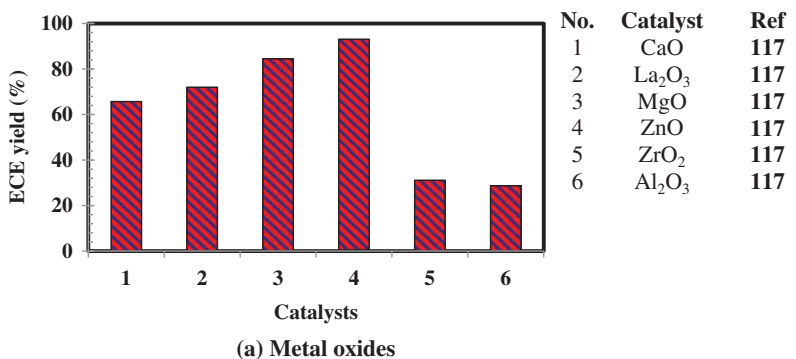
Figure 11. Performance of various catalysts for the synthesis of EC.

selectivity. The process is termed as a green one as it synthesizes DMC and EC, both important carbonates from urea and ethylene glycol.

Various studies have been reported for synthesis of cyclic carbonates (187, 191). Li et al. (177) examined the synthesis of EC from ethylene glycol using different metal oxides and established that more acidic sites on the catalysts promote the formation of isocyanic acid (HNCO) which is necessary for the EC synthesis while the more basic sites cause more formation of by-products, hence the medium acidic and basic sites bearing ZnO performed best among all catalysts. Zhao et al. (164) synthesized Zn-Fe mixed oxide and established that the synergistic effect of ZnO and $ZnFe_2O_4$ promote the activity of catalyst. $La(NO_3)_3$ was further used by Qiu et al. (192) and the effects of various parameters on the EC yield was studied. The EC yield was increased to 91% by removal of NH_3, at low pressure.

Wang et al. (193) synthesized DMC from EG by converting it to EC in one pot synthesis using Zn-based oxides. The performances are compared in Fig. 11b. Due to combined acid-base properties of mixed oxide, the performance of Zn-Y oxides was best among all catalysts which were also stable when it was reused after regeneration.

7. Summary and future perspectives

Organic carbonates are capturing wide attention recently due to their peculiar properties like high reactivity, high oxygen to carbon ratio, and good biodegradability. These can be used as fuel additive to improve fuel combustion characteristics. Being a good solvent, they will always capture precious place in the market. As polycarbonates are finding their way in daily life, their demand is increasing the production of organic carbonates which act as a monomer for polycabonate synthesis.

Synthesis of organic carbonates from phosgene is no longer continued due to toxicity of phosgene and production of HCl as the side product. Many processes have been developed to replace the phosgenation of alcohols for the synthesis of organic carbonates. Among the methods, urea alcoholysis route for synthesizing organic carbonates has generated a lot of interest due to abundant availability of raw materials and no azeotrope formation. Since NH_3 is evolved in these reactions, it can be recycled back to urea, and hence this process can be easily scaled-up.

Among various carbonates, important compounds like DMC, DEC, GC, PC, and EC have been mostly researched because of their wide applications. In the present article, synthesis of various carbonates from urea has been reviewed with main emphasis on type of catalysts used.

DMC and DEC are the simplest carbonates which are termed as the green compounds of the 21st century. DMC has been thoroughly synthesized and many studies have been reported. On the other hand, reports on

DEC have been fewer in number because of weak acidity and weak reactivity of ethanol. However, ethanol is more abundant as compared to methanol. Therefore, research on DEC synthesis should be more focused. Although articles have been growing exponentially for the synthesis of DMC from methanolysis of urea but still some shortcomings need to be overcome. The reaction proceeds in two steps with the formation of MC or EC. The formation of MC or EC doesn't requires any catalyst while formation of DMC and DEC requires catalyst and is the slow step. Synthesis of DMC or DEC requires presence of both acidic and basic sites. Zn-based catalysts have performed well due to the presence of weak acidic and basic sites. Constant evolution of NH_3 restricts the process which needs to be removed from the reactor in order to forward the reaction. The yields can be improved during DMC or DEC synthesis if the product is removed as soon as it is formed in the reactor. Catalytic distillation process well served this objective and increased the selectivity and the yield. Although the yield and selectivity increased several folds, however, the cost of synthesis also increased. Up until now, the studies are too focused on the catalysis and yield of products.

Production of surplus glycerol in the biodiesel industry is pressing the process industry for its utilization and transformation into valuable products such as GC. Glycerolysis of urea proceeds under reduced pressure in order to make it favorable for GC. Zn-based and Au-based catalysts have been used widely for enhancing selectivity of GC. The reactions have been mostly conducted in autoclave, however, no study is reported on GC synthesis using reactive distillation, which can ease its separation. No kinetics has been reported in the process which restricts its scale-up.

PC and EC find their applications in lithium ion batteries as solvents due to their high boiling points. The presence of cyclic group raises its boiling point. Therefore, the usage of lithium ion batteries will pressurize synthesis of PC and EC. Among various routes of synthesizing PC and EC, urea alcoholysis of glycols is one of the best routes for their synthesis. Various catalysts have been reported in this route but still yield and selectivity needs to be improved many folds. Ionic liquids, which are capturing attention as the catalyst, must be tried as for other carbonates as well. No kinetics has been reported which can provide insight activity of the catalyst and its effect on Arrhenius constant and frequency factor. Reaction as well as separation of products must be assembled at a same place in order to have a commercial scale production of PC and EC.

This article is an attempt to critically evaluate the studies in synthesis of important organic carbonates, catalysts used, and their performances. Mechanisms and process improvements have been highlighted in order to develop an understanding towards these synthesis routes. Research gaps and further improvements have also been discussed.

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