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Review

Synthesis of Propylene Carbonate by Urea Alcoholysis—Recent Advances

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Abstract: Organic carbonates are considered the chemicals of the future. In particular, propylene carbonate is widely used as a non-reactive solvent, plasticizer, fuel additive, and reagent, especially in the production of environmentally friendly polymers that are not harmful to human health. This paper reviews recent literature findings regarding the development of propylene carbonate synthetic methods starting from propane-1,2-diol and urea. The ammonia formed during the synthesis is recycled to obtain urea from carbon dioxide.

Keywords: propylene carbonate; urea alcoholysis; propylene glycol

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1. Introduction

In recent decades, increasing attention has been paid to environmental protection practices. The progression of industrialization, overexploitation of earth's resources, and continuous interference with the natural environment, which gained momentum during the nineteenth century, led to many detrimental phenomena, including global warming-induced climate change, a gaping hole in the ozone layer, and vast pollution of ecosystems. One of the greatest challenges facing mankind in the 21st century is reducing the concentration of carbon dioxide (CO_2) in the atmosphere. The emission of this greenhouse gas due to human activity in 2019 amounted to 33.4 Gt, and in 2020 it was "only" 31.5 Gt; the main reason for the decline in emissions was the outbreak of the COVID-19 pandemic [1]. It is urgently necessary to reduce CO_2 emissions by replacing conventional power plants with nuclear reactors, solar panels, and/or wind turbines, and at the same time, it is imperative to protect the forests that serve as the lungs of our planet.

One important tool in the fight against global warming is the reuse of CO_2 emitted by humanity as a raw material for the synthesis of chemical compounds. Carbon dioxide as a renewable source of elemental carbon and a safe, cheap, and readily-available compound that can be an alternative to other C1 building blocks, e.g., phosgene [2–9], carbon monoxide (CO) [10–13], methane [14–17], or methanol [18–21]. Unfortunately, the disadvantages of CO_2 lie in its low reactivity and enthalpy of formation ($\Delta H^0 = -394$ kJ/mol), which strongly limit the use of carbon dioxide as a substrate [22,23]. Urea, which can be obtained on an industrial scale from carbon dioxide and ammonia [24], is a more reactive compound, and is also safe and environmentally friendly.

Currently, the scientific community is striving to introduce ecological products and technologies to replace currently used strategies and goods that have a negative impact on the natural environment and humanity. Highly toxic compounds are still used in the chemical industry [25], and one particularly difficult task is the disposal of spent volatile organic compounds (VOCs) [26]; these compounds must be replaced in order to protect the environment.

Organic carbonates represent possible alternative to VOCs [27] because they are ecological compounds with a wide range of potential applications. These compounds can be used to synthesize important products, including polymers [28,29] and surfactants [30,31], whereas organic carbonates themselves can be used as plasticizers [32,33] and fuel additives [34,35]. One of the most widely used organic carbonates is propylene carbonate (PC), which is a biodegradable and non-toxic organic solvent. It has a high boiling and ignition point, and other selected properties of PC are presented in Table 1.

Table 1. Selected properties of propylene carbonate.

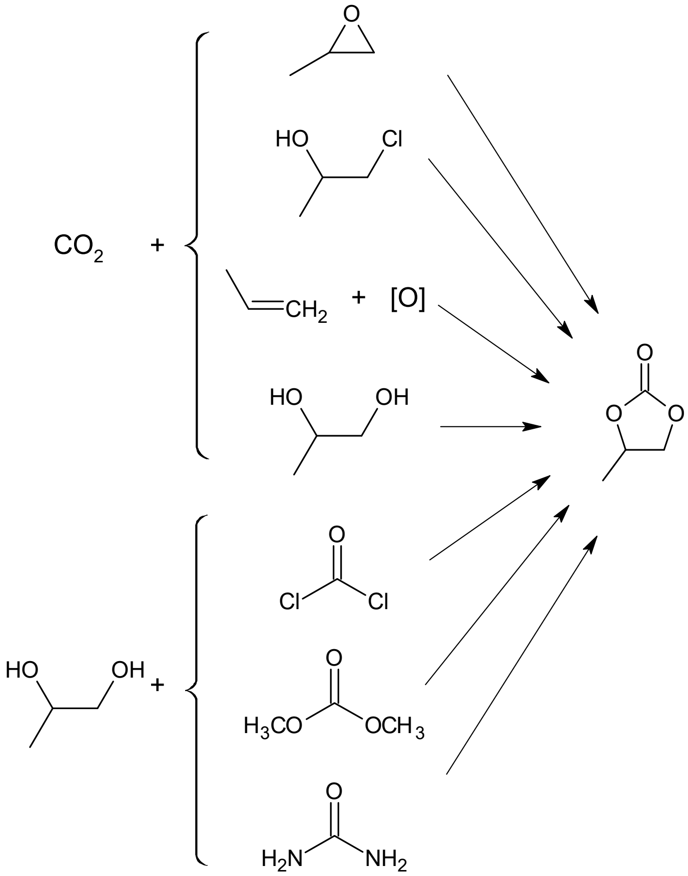
Properties	Value	Reference
Melting point, °C	−49	[36]
Boiling point, °C	242	[36]
Flash point, °C	128	[36]
Relative permittivity	66	[36]
Density (30 °C), g/cm^3	1.195	[37]
Enthalpy of vaporization (150 °C), kcal/mol	13.19	[37]
Specific heat capacity (25 °C), J/(g·K)	1.20	[38]
Standard molar enthalpy of formation, kJ/mol	−614.1	[38]

Propylene carbonate has many applications. For example, it is a component of cosmetics and body care products [39], it can be a solvent for electrolytes in lithium-ion batteries [40,41], and it is a component of fusible polyurethane compositions used as binding agents in the footwear industry [42]. Moreover, PC improves the properties of polyurethanes obtained by the reaction injection molding (RIM) method [43]. It is often used as a hardener in the production of sand silicate forms [44], and it can also be used as a component that extracts metals from acidic solutions [45]. In addition, PC is present in antifreeze agents [46], and it can also be used in brake fluids owing to its low hygroscopicity and low-temperature viscosity [47]. Importantly, PC is also a substrate for the synthesis of other organic carbonates, such as dimethyl carbonate (DMC) [48].

On an industrial scale, propylene carbonate is obtained mainly through the carboxylation of propylene oxide (PO) (Scheme 1) [49]. This method is characterized by 100% atom economy. Moreover, the carboxylation method uses carbon dioxide which is both a renewable source of C1 and an abundant greenhouse gas. On the other hand, the second substrate, propylene oxide, is a highly reactive and unstable chemical compound, which means that the carboxylation method requires the integration of a propylene oxide synthesis unit within the propylene carbonate plant.

The phosgenation of propylene glycol (PG) was widely used for the synthesis of organic carbonates [4]. However, because of the toxicity of phosgene and the hydrogen chloride formed during the process, which corrodes the equipment, this method has lost its importance in favor of the carboxylation of propylene oxide.

A variety of new non-phosgene-based methods have been developed for the synthesis of organic carbonates, including propylene carbonate. One of them is the method based on the reaction of diols and carbon dioxide [50,51]. Although the raw materials are cheap and readily available, the thermodynamics of this process is unfavorable, and the water formed as a by-product deactivates the catalyst. An interesting method for the preparation of propylene carbonate is the oxidative carboxylation of olefins in which propylene, carbon dioxide and an oxidant, e.g., oxygen, are used as substrates [52,53]. During the process, propylene oxide is formed as an intermediate that does not need to be isolated. However, the problem is the difficulty in achieving high selectivity and yield of propylene carbonate.



Scheme 1. Selected methods for synthesis of propylene carbonate.

Other routes to obtain propylene carbonate include the reaction between a halohydrin and carbon dioxide [54,55] or propan-1,2-diol and dimethyl carbonate [56,57].

Researchers have devoted significant efforts to the preparation of PC via urea alcoholysis owing to the inexpensive, stable, and readily-available nature of the required raw materials (e.g., urea and PG) and the favorable thermodynamics of the reaction. Moreover, ammonia, which is a co-product in the synthesis of propylene carbonate, can be returned to the urea plant by reacting it with CO_2. Cyclic alkylene carbonates were obtained through the urea alcoholysis method for the first time in 1991 by Su and Speranza [58] who used a tin salt (i.e., dibutyltin dilaurate ($Bu_2Sn(C_{11}H_{23}COO)_2$) as a catalyst.

To our knowledge, there is no review covering the recent advancements in the synthesis of propylene carbonate by urea alcoholysis in the scientific literature; a review on this topic can be found in the Chinese scientific literature, but it is more than ten years old [59]. Shukla and Srivastava [60] carried out an extensive literature review highlighting the synthesis of selected organic carbonates (e.g., dimethyl, diethyl, glycerin, ethylene, and propylene) by urea alcoholysis.

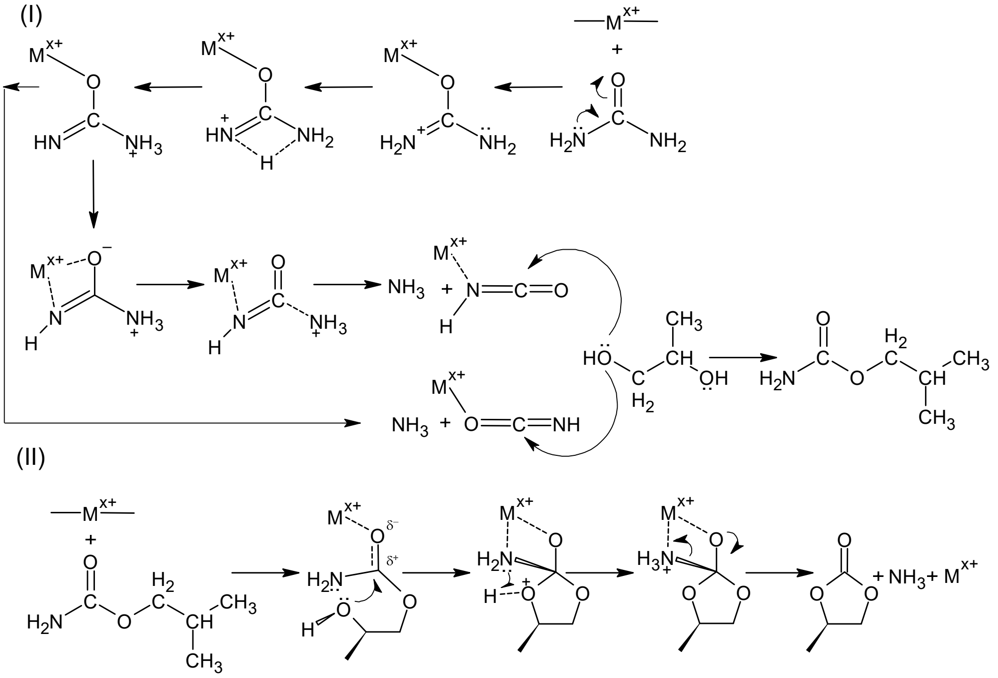
This article focuses on research findings related to the synthesis of propylene carbonate from urea and propylene glycol. Herein, we analyze the last three decades of progress regarding catalytic systems and the prospects for applying urea alcoholysis for the large-scale synthesis of propylene carbonate.

2. Types of Catalysts Used for Propylene Carbonate Synthesis by Urea Alcoholysis

2.1. Metal Oxides

Most scientific reports focusing on the production of propylene carbonate from urea and PG refer synthetic methods involving metal oxide catalysts, which are often used as catalysts owing to their simple synthesis, availability, and various properties [61].

Zinc-based oxides are the most common catalysts used for PC synthesis from propylene glycol and urea [62–89]. ZnO has favorable acid-base properties, which make it an active and selective catalyst in the synthesis of PC. The proposed mechanism of the ZnO-catalyzed reaction is shown in Scheme 2 [85].



Scheme 2. Mechanism of propylene carbonate synthesis via urea alcoholysis catalyzed by zinc oxide. Reprinted from [85] with permission from Elsevier.

The urea molecule is stable because of its resonance structures [90]. The zinc atom activates the urea by coordinating with the oxygen atom of its carbonyl group. Electron transfer leads to the formation of zinc isocyanate complexes, which are soluble in the reaction mixture and react further with the propylene glycol molecule. This results in the generation of an intermediate product (i.e., 2-hydroxypropyl carbamate (HPC)), which cyclizes to form propylene carbonate. The cyclization of HPC is also catalyzed by ZnO through the formation of a coordination bond with the carbonyl oxygen of HPC.

Li et al. [85] synthesized propylene carbonate from urea and PG using various metal oxides and zinc sulfide (Table 2). The best results were obtained with ZnO (yield = 98.9%). Furthermore, researchers determined the acidity and basicity of the catalysts based on temperature-programmed desorption (TPD) tests (Table 3). These measurements indicated that the excellent results of the zinc oxide-catalyzed synthesis were due to low acidity and basicity. According to the authors, the acidic nature of certain catalysts (e.g., Al_2O_3, ZrO_2, ZnS) led to low catalytic activity, which resulted in large amounts of the intermediate product, HPC, in the post-reaction mixture. In contrast, catalysts with low acidity (e.g., ZnO, MgO, CaO, La_2O_3) were active, and as a result, the HPC and urea contents in the product were low. This work also revealed that catalysts dominated by basic character (i.e., $A/B < 1$) were less selective. After using CaO, MgO, or La_2O_3 as the catalyst, 4-methyl-2-oxazolidone (MOD) was present in the post-reaction mixture. The authors explained that the strongly basic catalyst active sites tended to interact with the hydrogen of the HPC hydroxyl group, which increased the electrophilicity of the carbon atom bound to the hydroxyl group. Subsequently, HPC cyclization, followed by the elimination of water when the nitrogen atom's electron pair attacked the carbon bound to the hydroxyl group, resulted in the formation of the MOD molecule (Scheme 3).

Table 2. Catalytic performance of metal oxides for the synthesis of propylene carbonate [1]. Reprinted from [85] with permission from Elsevier.

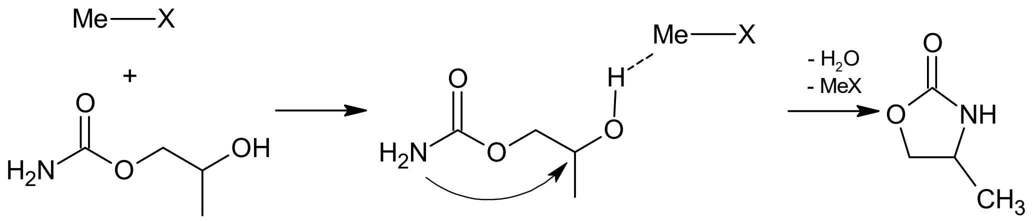
Catalysts	Conversion, %, Urea	Yield, %		
		2-Hydroxypropyl Carbamate	Propylene Carbonate	4-Methyl-2-Oxazolidone
Blank	89.3	48.6	40.7	0
Al_2O_3	90.4	51.5	38.9	0
ZrO_2	92.8	52.7	40.1	0
ZnS	89.8	50.3	39.5	0
ZnO	100.0	1.1	98.9	0
MgO	97.7	2.8	92.9	1.4
La_2O_3	94.3	5.6	86.8	2.2
CaO	85.6	7.2	74.6	3.8

[1] Reaction conditions: temperature: 170 °C, pressure: 280 mmHg, time: 2 h, PG: 0.75 mol, urea: 0.5 mol, amount of catalyst: 0.6 g.

Table 3. BET surface area and acid-base properties of metal oxides. Reprinted from [85] with permission from Elsevier.

Entry	Catalyst	S_{BET}, m^2/g	Acidity, μmol/g	Basicity, μmol/g	A/B [a]
1	CaO	9.5	2.30	63.66	0.04
2	La_2O_3	21.0	0.54	1.69	0.32
3	MgO	7.4	3.93	17.82	0.22
4	ZnO	6.7	1.02	0.98	1.04
5	ZnS	35.2	31.31	0.54	57.64
6	ZrO_2	33.4	29.10	3.22	9.04
7	Al_2O_3	136.5	20.90	6.93	3.02

[a] Acidity/basicity ratio.



Scheme 3. Scheme of a side reaction of MOD formation.

Table 4 presents the results of the ZnO-catalyzed synthesis of propylene carbonate, where the reactions were carried out with an excess of PG relative to urea. This was due to the minimization of the formation of nitrogen-containing byproducts, e.g., the biuret reagent and its homologues, and MOD. These reactions were carried out for 2–5 h. Zhao et al. [88] found that extending the reaction time reduced the yield of PC synthesis resulting from its polymerization. The syntheses of propylene carbonate were carried out at temperatures between 138–170 °C; higher reaction temperatures favored both PC polymerization [89] and MOD formation [78].

The problem with dissolving the zinc (ZnO) catalyst in the reaction mixture was noticed by Hao et al. [77], who reported that during the urea alcoholysis process, a $Zn(NCO)_2(NH_3)_2$ complex soluble in the reaction mixture was formed. Losses resulting from catalyst dissolution prompted scientists to conduct research on the effective immobilization of active ingredients on appropriate carriers.

Table 4. Catalytic activity of ZnO in the synthesis of propylene carbonate.

Urea:PG Molar Ratio	Time, h	Temperature, °C	Urea Conversion, %	Selectivity, %	Yield, %	Ref.
1:1.04	3	138	100	99.1	-	[72]
1:2	Continuous process in a flow tank reactor (residence time—3 h)	170	100	99.4	-	[75]
1:2.5	2	145	100	56.2	-	[76]
2:3	2	170	100	98.9	-	[85]
1:1.5	4	170	99.8	99.8	-	[86]
1:6	5	170	-	-	67	[88]
1:1.35	3	150	77	91	-	[89]

Yu et al. [84] synthesized PC using ZnO immobilized on NaY zeolite (ZnO/NaY). The process was carried out in a tubular reactor with a fixed catalyst bed. The catalyst was obtained by impregnating the support in an aqueous solution of $Zn(NO_3)_2$. The precatalyst obtained after the impregnation process was then dried and calcined in air for 3 h at 500 °C. The obtained catalyst was highly active and selective at 150 °C, achieving a PC yield of 82.3%, corresponding to a urea conversion of 86.2%. A four-fold molar excess of PG relative to urea was used for this reaction, and the catalyst was stable under the applied conditions; there was no significant decrease in the yield of PC after 35 h of running the synthetic process (the yield remained >80%). The authors determined that the properties and activity of the catalyst depended strongly on the amount of immobilized ZnO. The best results were obtained when ZnO accounted for 5 wt.% of the catalyst, whereas higher or lower ZnO contents resulted in lower catalytic activity and lower selectivity. This study also showed that ZnO/NaY containing 5 wt.% ZnO exhibited the most balanced strength of the acidic and basic sites, which was crucial for high PC production performance.

Researchers have investigated numerous catalytic systems comprising ZnO and other oxides (Table 5). Zhang et al. [81] used a catalyst composed of zinc and magnesium oxides (ZnO-MgO), which was prepared by co-precipitation from an aqueous solution of zinc and magnesium nitrates using urea as a precipitating agent [91]. The obtained precipitate was then washed and calcined at 600 °C for 6 h. Experimental results showed that the increased basicity and specific surface area positively impacted the final reaction yield. The authors evaluated the catalytic properties of systems containing various ZnO:MgO molar ratios. For catalysts with a molar ratio in the range from 4:1 to 1:4, an increase in specific surface areas (from 3.49 m^2/g to 15.06 m^2/g, respectively) was observed along with an increase in MgO content. Higher content of magnesium caused a reduction in ZnO coalescence. The highest yield of PC (94.8%) was obtained when the ratio was 1:4. However, a further increase in the MgO content (Zn/Mg 0.1) led to a lower area (3.83 m^2/g) and lower PC yield (80.4%) as an aggregation of the crystals was observed. According to the authors, the higher catalytic activity exhibited by the two-component oxide system could be attributed to the modification of the catalysts' electronic properties and porosities. Experimental results showed that the increased basicity and specific surface area positively impacted the final reaction yield.

Liu et al. [79] investigated a three-component catalytic system comprising zinc, calcium, and aluminum oxides (i.e., $ZnO\text{-}CaO\text{-}Al_2O_3$). The $CaO\text{-}Al_2O_3$ system was obtained by mixing powdered CaO and $\gamma\text{-}Al_2O_3$ in a 10% HNO_3 solution. The resulting paste was then extruded and dried, and the extrudates were calcined at 540 °C for 4 h. The obtained $CaO\text{-}Al_2O_3$ was then impregnated in an ethanolic $Zn(NO_3)_2$ solution. After the impregnation process, the precatalyst was dried and calcined at 540 °C for 4 h. The authors evaluated the influence of the catalyst composition on the efficiency of the process. Their results confirmed that the catalyst should embody balanced acid-base properties. Based on catalyst composition screening tests, they determined that the mass percentage of CaO should be 30% (in relation to $\gamma\text{-}Al_2O_3$), and the mass percentage of ZnO should be 20% (in relation to the $CaO\text{-}Al_2O_3$ system). The highest reaction yield (90.8%) was obtained in the synthesis of PC over 3 h at 184 °C using a three-fold molar excess of PG relative to urea. The authors reported that it was not possible to obtain a higher yield for propylene carbonate synthesis owing to the presence of CaO, the basic nature of which caused HPC dehydration to form MOD, as well as PC decomposition.

Table 5. Catalytic action of ZnO-containing metal oxide catalytic systems.

Catalyst	Urea:PG Molar Ratio	Time, h	Temperature, °C	Urea Conversion, %	Selectivity, %	Yield, %	Leaching of the Catalyst	Ref.
NiO/ZnO	1:4	Continuous process in a flow tank reactor with a stirrer	160	100	95	-	n/a [1]	[64]
Fe_2O_3/ZnO	1:4	3.5	170–180	-	-	93.5	n/a	[66]
MgO/ZnO	1:4	3.5	170–180	-	-	93	n/a	[66]
ZnO-Al_2O_3	1:1.9	Continuous process in 2 horizontal reactors	1. reactor: 130 2. reactor: 180	-	-	97	n/a	[67]
La_2O_3-CeO_2/MgO-ZnO	1:3.5–1:4.5	1.5–2.5	150–170	98	-	85	n/a	[68]
ZnO-CaO	1:10	0.5	170	-	-	99.1	n/a	[69]
ZnO-MgO	1:1	2	140	-	-	99.6	n/a	[69]
ZnO-Al_2O_3-Fe_2O_3	1:5	2	170	-	-	96.8	n/a	[69]
ZnO-Al_2O_3	1:3	20	250	-	-	95.7	n/a	[69]
ZnO-MgO-Fe_2O_3	1:2	6	180	-	-	99.4	n/a	[69]
ZnO-ZrO_2-Fe_2O_3	1:2	0.5	250	-	-	98.0	n/a	[69]
ZnO-Al_2O_3	1:1.9	Continuous process in a cascade of 3 flow-through tank reactors	1. reactor: 130 2. reactor: 150 3. reactor: 180	100	-	97	n/a	[70]
ZnO-MgO	1:1	2	140	-	-	90	n/a	[71]
ZnO-Al_2O_3-Fe_2O_3	1:5	2	170	-	-	98	n/a	[71]
ZnO-CaO	1:4	6	200	-	-	85	n/a	[71]
ZnO-Al_2O_3	1:3	20	250	-	-	86	n/a	[71]
ZnO-MgO-Fe_2O_3	1:2	6	180	-	-	87	n/a	[71]
ZnO-ZrO_2-Fe_2O_3	1:2	0.5	250	-	-	83	n/a	[71]
MgO-ZnO	1:4	2	170	-	-	92	n/a	[73]
CoO-ZnO	1:4	3	170	-	-	90	n/a	[73]
ZnO-Al_2O_3	2:3	3.3	170	100	-	96.6	Zn—2.3% Al—6.1%	[77]
ZnO-CaO-Al_2O_3	1:3	3	184	-	-	90.8	ZnO content dropped from 20.2% to 12.6% after 5th reuse	[79]
ZnO-Al_2O_3	1:6	Continuous process in a fixed bed reactor (LHSV = 1.0 h^{-1})	140	-	97.7	85.1	n/a	[80]
ZnO-MgO	1:1.5	0.5	170	-	-	94.8	n/a	[81]
ZnO-Cr_2O_3	1:1.5	6	180	-	-	97.8	n/a	[83]
ZnO-$ZnFe_2O_4$	1:4	2	170	-	-	78.4	n/a	[87]

[1] not available information.

Zinc-free oxide catalysts have also been described in the literature (Table 6) [66,73–76,85,88]. Many studies in this group describe catalytic systems containing magnesium oxide (MgO), which has specific properties that make it an active catalyst for PC synthesis via urea alcoholysis; however, this compound can promote the formation of MOD [85]. Lead-based catalysts also have favorable catalytic properties. For example, high selectivity for PC synthesis (93.9%) was observed when using lead dioxide (PbO_2) as a catalyst [76]. Unfortunately, the significant disadvantage of such catalysts lies in their toxicity. Other oxides, such as Al_2O_3, ZrO_2 [85], or dubityl tin oxide (Bu_2SnO) [88] were not active catalysts for this synthesis.

Table 6. Catalytic performance of zinc-free oxide catalysts.

Catalyst	Urea:PG Molar Ratio	Time, h	Temperature, °C	Urea Conversion, %	Selectivity, %	Yield, %	Ref.
MgO/Al_2O_3	1:4	3.5	170–180	-	-	92.5	[66]
CaO/MgO	1:4	3.5	170–180	-	-	93.5	[66]
Fe_2O_3-MgO	1:4	3	180	-	-	93	[73]
MgO	1:2	1	190	100	98.9	-	[75]
MgO	1:4	1	165	100	96.5	-	[76]
PbO_2	1:2	2	165	100	93.9		[76]
CaO	1:2	2	165	100	95.4	-	[76]
Al_2O_3	2:3	2	170	90.4	-	38.9	[85]
ZrO_2	2:3	2	170	92.8	-	40.1	[85]
MgO	2:3	2	170	97.7	-	92.9	[85]
La_2O_3	2:3	2	170	94.3	-	86.4	[85]
CaO	2:3	2	170	85.6	-	74.6	[85]
MgO	1:6	5	170	-	-	75	[88]
MgO-ZrO_2	1:6	5	170	-	-	45	[88]
PbO	1:6	5	170	-	-	57	[88]
Bu_2SnO	1:6	5	170	-	-	61	[88]
$Pb/Fe_3O_4/SiO_2$	1:4	2	180	-	-	87.7	[92]

Synthetic compounds with perovskite structures represent a special type of oxides that have been tested for their activity as catalysts for the synthesis of propylene carbonate by urea alcoholysis (Table 7) [93,94]. These oxides have the general formula, ABO_3, where A is a large-diameter metal cation, and B is a small-diameter metal cation [95]. Du et al. [94] investigated how the $MgTiO_3$ preparation method influenced its catalytic properties in terms of PC synthesis. The catalyst was prepared using a sol-gel method; specifically, a solution of magnesium nitrate ($Mg(NO_3)_2$) was added dropwise to a solution of tetrabutoxy titanium (IV) ($Ti(OBu)_4$) in acetic acid. Anhydrous ethanol was added to this mixture, which was then concentrated in a vacuum evaporator, and the resulting gel was calcined at various temperatures (600, 700, 800, or 900 °C). The $MgTiO_3$ catalyst with the highest activity was obtained when the Mg:Ti molar ratio was 1:1 and the gel calcination was carried out at 700 °C for 3 h. Under these conditions, $MgTiO_3$ was obtained with the highest quantity of basic centers, which resulted in an increase in catalytic activity and selectivity. However, it was also shown that MgO aggregated on the catalyst surface when $Ti(OBu)_4$ and $Mg(NO_3)_2$ were used in a 1:1 molar ratio during catalyst preparation. As a result, after the fourth catalytic cycle, the yield of propylene carbonate decreased from 93.5% to approx. 60% because of the leaching of MgO from the catalyst surface. XRD tests showed that the intensity of the MgO diffraction peak ($2\Phi = 42.9°$) decreased with a decrease in the molar ratio of Mg:Ti, whereas for the MTO-0.8 catalyst (with a molar ratio of Mg:Ti = 0.8:1) no peaks corresponding to MgO were detected. Researchers also showed that in the case of the MTO-1.5 catalyst (Mg:Ti = 1.5:1), the peaks corresponding to $MgTiO_3$ were shifted to the right, which may be due to distortion of the structure.

Table 7. Catalytic activities of catalysts comprising oxides with perovskite structures.

Catalyst	Urea:PG Molar Ratio	Time, h	Temperature, °C	Selectivity, %	Yield, %	Ref.
$LaMnO_3$	1:4	2	170	88.3	75.2	[93]
$La_{0.5}Pb_{0.5}MnO_3$	1:4	2	170	90.3	74.7	[93]
$La_{0.8}Pb_{0.2}MnO_3$	1:4	2	170	91.5	70.2	[93]
$La_{0.9}Ag_{0.1}MnO_3$	1:4	2	170	85.1	72.9	[93]
$LaMn_{0.5}Fe_{0.5}O_3$	1:4	2	170	84.3	64.8	[93]
$La_{0.5}Pb_{0.5}Mn_{0.5}Co_{0.5}O_3$	1:4	2	170	88.2	60.2	[93]
$Ce_{0.5}Pb_{0.5}MnO_3$	1:4	2	170	66.7	55.8	[93]
$CaTiO_3$	1:40	2	170	90.5	84.7	[93]
$BaTiO_3$	1:20	2	170	87.2	71.1	[93]
$Ba_{0.5}Na_{0.5}TiO_3$	1:4	2	170	90.1	80.5	[93]
$PbZrO_3$	1:4	2	170	91.3	82.4	[93]
$CaSnO_3$	1:4	2	170	90.8	85.4	[93]
$KNbO_3$	1:4	2	170	92.3	88.4	[93]
$Na_{0.5}K_{0.5}NbO_3$	1:4	2	170	92.3	88.4	[93]
$MgTiO_3$	1:4	2	170	99.0	93.5	[94]

To date, there are few publications in the scientific literature describing the kinetics of PC synthesis from urea and PG. To implement this method into industrial practice, it is necessary to determine the kinetic equation corresponding to the reaction where propylene carbonate is obtained through urea alcoholysis.

Shi et al. [96] designed a two-step process for the preparation of DMC. The first stage of the process involved the synthesis of propylene carbonate via urea alcoholysis, and the second stage involved PC transesterification with methanol. The authors considered Wang's previous findings [97], and on that basis, they proposed the kinetic Equation (1) for the synthesis of PC from urea and PG catalyzed by 2 wt.% MgO:

$$r_{PC} = 1.5888 \times \exp\left(-\frac{562.602}{T}\right) \times C_{urea} \times C_{PG} \tag{1}$$

r_{PC}—reaction rate of propylene carbonate synthesis, mol/(L·min)

T—reaction temperature, K

C_{urea}—urea concentration, mol/L

C_{PG}—concentration of propylene glycol in the reaction mixture, mol/L.

The authors also determined the total annual operating cost of the designed installation for several synthetic variants. On the basis of calculations, they showed that obtaining propylene carbonate by reactive distillation was more profitable than using a cascade of three continuous stirred-tank reactors (CSTRs). Analogous simulations were carried out by Patraşcu et al. [98] using the same kinetic equation for the PC synthesis reaction. Overall, studies have shown that the synthesis of DMC from propylene carbonate and methanol can proceed with excess PC, which facilitates the preparation of high-purity DMC.

In the patent literature, there are several examples of PC synthesis catalyzed by metal oxides in the CSTR cascade [64,70,99]. One innovative solution involves the use of a horizontal reactor with partitions increasing the turbulence of the flow and helping the reaction system imitate a cascade of reactors [67]. Another method of PC synthesis in a reactive column with a metal oxide catalyst was also patented [100]. The reports discussed herein suggest that the preparation of PC through urea alcoholysis catalyzed by metal oxides is relatively advanced.

2.2. Metal Salts

Metal salts have also been tested for their potential applications as catalysts for PC synthesis from urea and PG. As in the case of metal oxides, most of the salts used as catalysts are advantageous because they are inexpensive and readily available.

Among the salts used for this reaction, compounds of zinc [76,88,101,102], magnesium [76,102], lead [101], and tin [103] exhibited the best catalytic properties. Doya et al. [76] used various zinc salts (e.g., $ZnCO_3$, $ZnCl_2$, $Zn(NO_3)_2$, and $Zn(OAc)_2$) and magnesium acetate ($Mg(OAc)_2$) and compared their catalytic properties with those of $Bu_2Sn(C_{11}H_{23}COO)_2$, which was employed by Su and Speranza in the first published studies on cyclic alkylene carbonate synthesis [58]. The results showed that the zinc and magnesium salts had similar catalytic properties (PC selectivities ranged from 88.1% to 89.5%) and were more selective than $Bu_2Sn(C_{11}H_{23}COO)_2$, which only achieves up to 64.6% selectivity for PC synthesis. In the patent, Sun et al. [103] presented examples of PC synthesis using various salts, among which the highest yield (93.47%) was obtained for tin(II) chloride; however, it should be noted that the reactions with other catalysts were carried out under conditions that may not be optimal for the desired process.

The highest yield of PC (96.5%) was achieved by Gao et al. [102] using magnesium chloride ($MgCl_2$) as a catalyst. Zhou et al. [101] obtained a 93.5% yield using a mixture of basic zinc carbonate and lead carbonate prepared using a co-precipitation method. According to the authors, the most active catalytic system contained a 1:2 molar ratio of $PbCO_3$:$Zn_5(CO_3)_2(OH)_6$.

Zhao et al. [88] conducted research on the selection of an active catalyst for the synthesis of propylene carbonate. Among the investigated compounds, anhydrous zinc acetate

($Zn(OAc)_2$) exhibited the best activity; therefore, further studies were carried out to evaluate the influence of certain parameters on the efficiency of the process. Under the optimized conditions (mole ratio of urea:PG = 1:4; reaction time = 3 h; temperature = 170 °C), a 94% yield of PC was obtained. The authors also studied the effect of $Zn(OAc)_2$ immobilization on various supports, e.g., activated carbon (AC), zeolite (zeo), and γ-alumina (γ-Al_2O_3). The $Zn(OAc)_2$ was immobilized on these supports by an incipient impregnation process. The catalytic activity of the catalyst was particularly influenced by the physical properties of the support. The best results were achieved for catalysts immobilized on AC, which showed the highest specific surface among the tested carriers, and on γ-Al_2O_3 with the highest average pore size. Using AC and γ-Al_2O_3 as the carrier, the yields of PC synthesis were 77.5 and 77.9%, respectively. Unfortunately, the applied immobilization method was not effective because $Zn(OAc)_2$ easily leached from the support. According to the authors, the fresh $Zn(OAc)_2/AC$ catalyst contained 3 wt.% zinc, and after PC synthesis, the Zn content dropped to 2.3 wt.%. After the zinc acetate was washed off of the catalyst, the yield of PC was only 66% once the catalyst was recycled.

Additional studies on the synthesis of propylene carbonate have used potassium silicate [104] and zinc sulfide as catalysts [85], but these compounds were characterized by low catalytic activity. The relevant patent [105] describes a method for obtaining organic carbonates by urea alcoholysis using silicates as catalysts. Table 8 shows the results of studies probing the catalytic activity of these salts in the synthesis of propylene carbonate.

Polyoxometalates represent a special type of metal salts. Their catalytic activity for the synthesis of propylene carbonate was patented by Liu et al. [106]. The catalysts were obtained by mixing a heteropolyacid with a suitable metal carbonate in water, and then evaporating the water and calcining the precipitated precatalyst at 200–400 °C. The authors emphasized that the separation of the precatalyst from the aqueous mixture was also possible via partial evaporation of the water, cooling to 0–5 °C, and centrifuging to isolate the precipitate. Phosphomolybdic acid ($H_3PMo_{12}O_{40}$), phosphotungstic acid ($H_3PW_{12}O_{40}$), or silicon tungsten acid ($H_4SiW_{12}O_{40}$) could be applied with an appropriate carbonate or hydroxycarbonate (e.g., $ZnCO_3$, $MgCO_3$, $4MgCO_3 \times Mg(OH)_2$, $CaCO_3$, K_2CO_3) to synthesize these catalysts. The catalytic activities of heteropolyoxometalates are presented in Table 9. In general, these heteropolyoxometalates do not have high catalytic activity; the highest PC yield (78.71%) was obtained using $Zn_3(PMo_{12}O_{40})_2$.

Table 8. The catalytic effect of metal salts.

Catalyst	Urea:PG Molar Ratio	Time, h	Temperature, °C	Urea Conversion, %	Selectivity, %	Yield, %	Ref.
$Bu_2Sn(C_{11}H_{23}COO)_2$	1:1.5	3	175	100	64.6	-	[76]
$ZnCO_3$	1:1.5	3	175	100	89.5	-	[76]
$ZnCl_2$	1:1.5	3	175	100	87.8	-	[76]
$Zn(OAc)_2$	1:1.5	3	175	100	88.3	-	[76]
$Zn(NO_3)_2$	1:1.5	3	175	100	88.8	-	[76]
$Mg(OAc)_2$	1:1.5	3	175	100	88.1	-	[76]
ZnS	2:3	2	170	89.8	-	39.5	[85]
$Zn(OAc)_2 \times 2H_2O$	1:6	5	170	-	-	54	[88]
$MgCO_3$	1:6	5	170	-	-	56	[88]
$Mg(OAc)_2$	1:6	5	170	-	-	38	[88]
$Pb(OAc)_2 \times 3H2O$	1:6	5	170	-	-	38	[88]
$Pb(OAc)_2$	1:6	5	170	-	-	58	[88]
$Zn(OAc)_2$	1:4	3	170	-	-	94	[88]
$Zn(OAc)_2/AC$	1:4	3	170	-	-	77.9	[88]
$Zn(OAc)_2/zeo$	1:4	3	170	-	-	66.6	[88]
$Zn(OAc)_2/\gamma\text{-}Al_2O_3$	1:4	3	170	-	-	77.5	[88]
$PbCO_3\text{-}Zn_5(CO_3)_2(OH)_6$	2:3	5	180	-	-	93.5	[101]
$MgCl_2$	1:4	3	160	-	-	96.5	[102]
$ZnCl_2$	1:4	3	160	-	-	92.4	[102]
$SnCl_2$	1:6.3	5	180	-	-	93.47	[103]
$Zn(NO_3)_2$	1:1.6	3	200	-	-	57.36	[103]
$CaCl_2$	1:3.9	20	150	-	-	43.16	[103]
$FeCl_3$	1:3.2	5	170	-	-	83.29	[104]
$PbCl_2$	1:7.9	2	200	-	-	62.89	[103]
K_2SiO_3	1:4	10	150	-	-	72.8	[104]

Table 9. Catalytic activity of heteropolyoxometalates [106].

Catalyst	Carbonate Used in the Synthesis of the Catalyst	Time, h	Selectivity, %	Yield, %
$Mg_3(PMo_{12}O_{40})_2$	$4MgCO_3 \times Mg(OH)_2$	3	140	71.82
$Mg_3(PW_{12}O_{40})_2$	$4MgCO_3 \times Mg(OH)_2$	5	140	43.83
$K_3PMo_{12}O_{40}$	K_2CO_3	3	150	54.48
$Mg_2SiW_{12}O_{40}$	$4MgCO_3 \times Mg(OH)_2$	3	150	62.78
$Zn_3(PMo_{12}O_{40})_2$	$ZnCO_3$	4.5	150	78.71

2.3. Modified Hydroxyapatites

Modified hydroxyapatites are another group of chemical compounds that can be used as catalysts for the preparation of propylene carbonate via urea alcoholysis. Owing to their basic nature, these compounds can also be used as catalysts in the transesterification process [107] or in the Michael addition reaction [108].

Du et al. [109] developed a method for obtaining propylene carbonate and ethylene carbonate through urea alcoholysis using metal-modified hydroxyapatites as catalysts, and the catalytic activities of these systems were compared with those of the corresponding metal oxides [110]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; HAP) was obtained by co-precipitation from a solution containing ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and calcium nitrate ($Ca(NO_3)_2$). The resulting precipitate was then filtered, dried, and calcined at 900 °C. The obtained HAP was impregnated in an aqueous solution of the metal nitrate, then dried and calcined at 400 °C. The authors explained that during HAP impregnation, ion exchange occurred, which involved the replacement of Ca^{2+} cations in the crystal structure of the hydroxyapatite with ions of a given metal. Lanthanum-modified HAP (La-HAP) demonstrated the best catalytic properties among the evaluated catalysts. The yield of PC catalyzed by La-HAP was 91.5%; for comparison, the yield was lower (79.6%) when using the corresponding metal oxide, La_2O_3. The BET surface analysis showed that the HAP surface area after the impregnation process in the $La_3(NO_3)_3$ solution decreased from 9.0 m^2/g to 7.3 m^2/g. The researchers explained that this was due to the amorphous lanthanum blocking the pores The authors reported that the high activity of the La-HAP catalyst was due to the presence of strongly basic adsorption centers. XRD analysis showed that the diffraction peaks of HAP and La/HAP were similar, indicating that the major phase of La/HAP was HAP. As the authors explain, some La^{3+} ions were introduced into the HAP crystal lattice by ion exchange with Ca^{2+} ions, but the HAP structure was preserved. In the case of La^{3+}, which were not exchanged in the HAP crystal lattice, they were strongly dispersed on the HAP surface.

2.4. Ionic Liquids

Ionic liquids (ILs) are chemical compounds composed of ions with a melting point lower than 100 °C [111]. Gabriel and Weiner (1888) were the first to document the synthesis of an ionic liquid, specifically, ethanol-ammonium nitrate (mp = 52–55 °C) [112], although Walden is often considered the father of ILs, following the reported synthesis of nitrate ethylammonium liquid at room temperature (mp = 12 °C) in 1914 [113]. However, scientific interest in ionic liquids increased significantly around the beginning of the 21st century and has continued to this day [114].

Table 10 summarizes the catalytic activities of selected modified hydroxyapatites. These catalysts are characterized by high selectivity (over 90%), which is undoubtedly their great advantage.

Because ionic liquids can be designed by selecting the appropriate cations and anions, it is possible to obtain a chemical compound with the desired properties. This advantage means that ionic liquids can be used in many fields of science; however, only some of them are currently produced on an industrial scale [115]. In general, the low availability of starting materials limits their production possibilities. The low cost of key reagents and abundance of their manufacturers are essential for a given ionic liquid to be produced on a commercial scale.

Table 10. Catalytic activity of modified hydroxyapatites.

Catalyst	Urea:PG Molar Ratio	Time, h	Temperature, °C	Selectivity, %	Yield, %	Ref.
Na-HAP	1:4	2	170	99.0	88.6	[109]
Li-HAP	1:4	2	170	95.5	72.5	[109]
K-HAP	1:4	2	170	99.1	70.4	[109]
Sr-HAP	1:4	2	170	99.0	72.1	[109]
Ba-HAP	1:4	2	170	99.0	74.3	[109]
Mn-HAP	1:4	2	170	99.5	77.9	[109]
Co-HAP	1:4	2	170	93.8	32.7	[109]
Pb-HAP	1:4	2	170	98.2	69.1	[109]
Zn-HAP	1:4	2	170	99.6	73.8	[109]
Ce-HAP	1:4	2	170	96.3	50.5	[109]
Zn-Pb-HAP	1:4	2	170	98.4	85.5	[101]
Pb-Mn-HAP	1:4	2	170	97.6	80.8	[101]
HAP	1:4	2	170	-	50.6	[110]
La-HAP	1:4	2	170	-	91.5	[110]

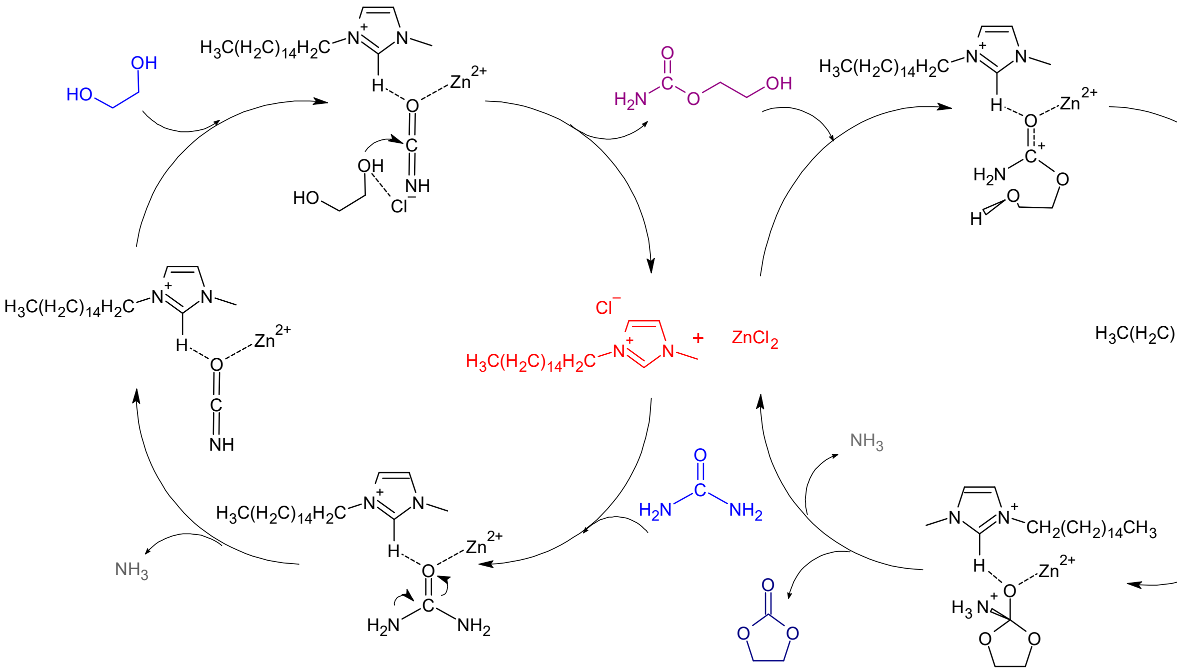
The scientific literature contains thousands of publications discussing the use of ionic liquids as catalysts in chemical synthesis. However, to date, few scientific reports have detailed the synthesis of propylene carbonate by ionic liquid-catalyzed urea alcoholysis. Kuznetsov et al. [116] synthesized cyclic alkylene carbonates using a two-phase reaction system comprising a deep eutectic solvent (DES) [117,118] and a chlorinated organic solvent. The DES was an equimolar mixture of zinc chloride, urea, and glycol, which formed a transparent colorless solution when heated to above 50 °C. The synthesis of propylene carbonate was carried out at low temperature (84 °C) and required a long reaction time (24 h) to ultimately reach a maximum yield of 70%.

A patent from 2016 [119] describes a method for obtaining PC through a reactive distillation method, in which the catalytic system consisted of zinc oxide, a zinc salt, and a quaternary ammonium salt. Another patent [120] details the synthesis of cyclic alkylene carbonates using a catalytic system containing a metal salt and an ionic liquid with an imidazolium cation. The preparation of PC by urea alcoholysis at 160 °C for 3 h under reduced pressure (150 kPa) using a catalytic system containing 1-hexadecyl-3-methylimidazolium chloride and zinc chloride ($[C_{16}mim]Cl-ZnCl_2$) led to a 94.1% yield of PC. The catalytic system did not lose significant activity in this case; after its 5th cycle, the PC yield was 90.1%. The proposed mechanism of the reaction catalyzed by this system (Scheme 4) [121] assumes an increase in urea reactivity due to (i) the interaction between the oxygen of the urea carbonyl group and Zn^{2+} and (ii) the formation of a hydrogen bond between this oxygen and the hydrogen of the imidazole ring at the C(2) position.

Owing to the relative novelty of PC synthesis via urea alcoholysis using ionic liquid catalysts, it can be expected that there will be more publications on this subject in the coming years.

2.5. Others

Apart from metal oxides, metal salts, modified hydroxyapatites, and ionic liquids, the catalytic properties of other substances have also been tested in the context of PC synthesis by urea alcoholysis (Table 11). In particular, several reports have described the synthesis of PC catalyzed by pure metals, such as zinc and lead. These studies verified that metallic zinc had inferior catalytic properties relative to ZnO [77,89], whereas metallic lead and PbO achieved comparable PC yields [88].



Scheme 4. Mechanism of propylene carbonate synthesis via urea alcoholysis catalysed by the system [C_{16}mim]Cl, $ZnCl_2$. Reprinted from [121] with permission from Elsevier.

Table 11. Catalytic activity of other catalysts.

Catalyst	Urea:PG Molar Ratio	Time, h	Temperature, °C	Urea Conversion, %	Selectivity, %	Yield, %	Ref.
Zn	1:1.5	3	175	100	73	-	[76]
Zn	1:6	5	170	-	-	57	[88]
Pb	1:6	5	170	-	-	59	[88]
Zinc monoglycerolate	1.5:1	24	140	PG conversion 99	-	80	[122]
BA 900	1:4	10	150	-	-	73.2	[104]
PT-800-4	1:4	2	170	-	95.6	81.8	[123]

Kulasegaram et al. [122] used zinc monoglycerolate as a catalyst in the reactions of urea with various glycols. When using vicinal diols (e.g., propylene glycol, ethylene glycol), the corresponding cyclic alkylene carbonate was the main product of the reaction. In contrast, when using terminal diols as the substrate (e.g., 1,3-propanediol, 1,4-butanediol), the corresponding dicarbamates were obtained. These syntheses were carried out with an excess of urea at 140 °C. Propylene carbonate was obtained from urea and PG with 80% selectivity and almost complete conversion (99%) of PG.

Indran et al. [104] used boiler ash as a catalyst for the synthesis of cyclic alkylene carbonates. The ash was obtained from the combustion of palm fruits, kernels, shells, and fibers. Raw ash was prepared via calcination at 900 °C to obtain the "BA 900" catalyst, which contained mainly K_2SiO_3 (43.53 wt.%) and SiO_2 (33.14 wt.%), as well as small amounts of potassium, calcium, magnesium, aluminum, iron, phosphorus, and zirconium oxides. Upon using BA 900 as a catalyst for the synthesis of PC, the yield of the reaction was 73.2%.

Xiao et al. [123] used phosphate tailings as the raw materials to prepare a catalyst for the synthesis of propylene carbonate from urea and propylene glycol. The phosphate tailings were ground and washed with deionized water, and then, the precipitate was dried and calcined at 800 °C for 4 h to obtain the PT-800-4 catalyst. This compound achieved a yield and selectivity for PC synthesis via urea alcoholysis of 81.8% and 95.6%, respectively.

3. Conclusions

This review presents recent advances regarding the synthesis of propylene carbonate by urea alcoholysis, highlighting key findings. Numerous catalysts applied in this reaction are discussed in terms of the important aspects of their preparation and potential reaction mechanisms. This review confirms that a good catalyst for the preparation of PC from urea and PG should have balanced acid-base properties. Catalysts with numerous acidic sites are less catalytically active, whereas overly basic catalysts are less selective. The catalyst of greatest interest is zinc oxide, including catalytic systems composed of ZnO and other metal oxides.

Owing to its physicochemical properties, non-toxicity, and biodegradability, propylene carbonate is an extremely desirable chemical compound, whose demand on the global market is growing. The search for new, more ecological PC production methods is therefore extremely important for increasing its global production. The main method currently used to obtain propylene carbonate, i.e., carboxylation of propylene oxide, requires permanent access to epoxide; hence, its implementation is limited to petrochemical plants that have this raw material on site.

The preparation of PC by urea alcoholysis is a sustainable, economical and convenient alternative to the currently used method on the industrial scale. Compared with the synthesis of propylene carbonate by propylene oxide carboxylation, urea alcoholysis offers the use of inexpensive, stable and readily available raw materials (urea and propylene glycol) and favorable thermodynamics of the reaction. In addition, ammonia, which is a co-product in the synthesis of propylene carbonate, can be recycled to the urea synthesis plant.

Obtaining propylene carbonate by urea alcoholysis represents an alternative approach for companies that do not produce propylene oxide. This method requires stable raw materials that can be safely imported. However, because ammonia is released during the synthesis, it is reasonable to develop chemical installations for urea alcoholysis-based PC synthesis in companies already containing a urea plant; this would allow for the recycling of NH_3, thereby closing its circulation. The main beneficiaries of this solution may be chemical plants producing nitrogen fertilizers, which offer urea. However, for the urea alcoholysis method to be commonly used in the chemical industry, it is necessary to further understand the kinetics of this process, and unfortunately, there is currently not enough data on this subject.

Therefore, it seems that the urea alcoholysis method discussed herein will not replace the method of obtaining propylene carbonate by carboxylation of PO in the near future. As long as the petrochemical industry continues to develop and fossil resources, such as crude oil, natural gas, and coal are still used, the current method of producing PC will continue to dominate. Nevertheless, the method for obtaining propylene carbonate via urea alcoholysis may be an alternative for enterprises with a different raw material base.

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