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Catalytic systems for the effective fixation of CO₂ into epoxidized vegetable oils and derivatives to obtain bio-based cyclic carbonates as precursors for greener polymers

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Abstract

The chemical fixation of carbon dioxide by cycloaddition to bio-based epoxides e.g., vegetable oils, fatty acids etc. is an efficient, sustainable and clean strategy to obtain bio-based cyclic carbonates. These can be used as feedstocks for the synthesis of environmentally friendly bio-based polymers as an alternative to daily life used polymers such as polyurethanes (PUs) and/or polycarbonates (PCs). Nevertheless, this reaction is not trivial at all due to both the low reactivity of the CO₂ molecule and the nature of the needed substrates (bio-based epoxides) where the epoxide groups are internal and sterically hindered, hampering the CO₂ cycloaddition reaction. Therefore, the design of efficient catalytic systems to overcome these hurdles is mandatory. Most of the catalytic systems developed for this transformation aim to facilitate the rate-determining step in the CO₂ cycloaddition catalytic cycle. They comprise an ionic liquid or an ionic compound with a nucleophilic anion alone or in the presence of a co-catalyst to assist the epoxide ring-opening. The most commonly used catalyst is the tetrabutylammonium bromide [TBA][Br] ionic liquid, but other ammonium-, phosphonium-, sulfonium-based ionic liquids in combination or not with a co-catalyst have also been disclosed in the literature. This review presents a structured overview of the reported catalytic systems, both homogeneous and heterogeneous catalysts, employed in the transformation of any epoxidized vegetable oil or derivatives into bio-based carbonated materials. The different catalytic systems have been discussed and compared in terms of catalytic performance, employed substrates, and reaction conditions.

Introduction

Since the beginning of the industrial revolution, the employment of fossil fuels as both energy and feedstock source has had a collateral and unavoidable generation of large amounts of CO₂.¹ Nowadays, it is well known that CO₂ is one of the gases, among others, that contribute significantly to the greenhouse effect. As a consequence of the overexploitation of fossil fuels current society is facing the global warming and the search for alternatives to achieve its mitigation.² Therefore, there is a clear global tendency, driven by industrial and academic sectors, to look for greener solutions in all production sectors, within the concept of circular economy, to avoid the evident impact of global warming on living beings and the planet.^{3,4} This situation turns CO₂ into a promising C1 building block due to its availability, abundance, renewability, low toxicity, and low cost so far.⁵ As a matter of fact, added value products (molecules, building blocks) are already produced from CO₂ as feedstock, e.g., organic chemicals,⁶ polymers,⁷ fuels,⁸ etc.. Furthermore, some CO₂-derived products such as methanol,⁹⁻¹¹ urea,¹² or salicylic acid¹³ are manufactured at industrial level. Among CO₂-derived molecules, cyclic carbonates are of special interest due to their vast application fields. Cyclic carbonates such as ethylene carbonate or propylene carbonate are employed as polar aprotic solvents representing a greener and more environmentally friendly alternative to traditional organic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) or acetonitrile, due to their lower vapor pressure, higher flash point and lower toxicity.^{14,15} Cyclic carbonates application in Li-ion batteries technology is a hot topic nowadays and are identified as appropriated in electrolytes formulations due to their high polarity and affinity to lithium.^{16,17} Cyclic carbonates can be used as well as intermediates in chemical synthesis as an alternative to toxic compounds such as phosgene, isocyanate etc. e.g., in the synthesis of polyurethanes, polycarbonates, etc.¹⁸⁻²⁰ Their versatility and inherent properties make cyclic carbonates highly attractive from both economic and chemical process perspective. However, most of the currently employed cyclic carbonates are synthesized from fossil-based diols and highly toxic phosgene.^{21,22} In this sense, the CO₂ cycloaddition to epoxides is emerging as a greener and safer alternative synthetic route to avoid the use of phosgene.^{23,24} Nevertheless, most of the employed epoxides nowadays are derived from fossil fuels.²⁵⁻²⁹ Therefore, the scientific community is looking for epoxides from renewable sources to improve the overall process sustainability.³⁰⁻³² Among the renewable available raw materials as epoxides precursors, vegetable oils and their derivatives are a plausible alternative to fossil-based raw materials for the production of epoxides.³³⁻³⁵ In fact, the oxidation of the double bonds present in vegetable oils and their derivatives has gained much attention in the last decades. For instance, their epoxidized molecules have been used mainly in polymer chemistry.³⁶⁻³⁸ Consequently, the synthesis of cyclic carbonates from CO₂ and epoxidized vegetable oils or their derivatives represents a green, safe and sustainable route to produce bio-renewable feedstocks for a plethora of applications

contributing to the circular economy. In this sense, the cycloaddition of CO₂ to an epoxidized vegetable oil was reported for the first time by Tamami et al. two decades ago.³⁹ Due to the significant potential of carbonated oils in different fields, these bio-based materials have gained much attention. In fact, the possibility of producing it from a greenhouse gas substantially increases the interest in these products. However, owing to the low activity of CO₂ molecule and the high steric hindrance of vegetable oils or derivatives structure, effective catalytic systems are necessary in order to obtain the carbonated vegetable oil or carbonated vegetable oil-derivative. Thereby, to solve these issues, much effort and intensive research have been devoted to the development of homogeneous and heterogeneous catalytic systems to circumvent both the low reactivity of the CO₂ molecule and the steric hindrance of the epoxidized vegetable oils and their derivatives. Among the materials employed as catalysts in this reaction, ionic liquids are of special mention because they are the most used ones. Ionic liquids are preferred over other catalysts because they possess several inherent properties that make them special for this particular reaction, are noteworthy good thermal and chemical stability, low toxicity, negligible vapor pressure, good solubility and easy functionalization that make them tuneable for a given application.^{40,41}

In this review, a journey through the employed catalytic systems up today in the CO₂ chemical fixation to epoxidized vegetable oils or derivatives by cycloaddition in terms of conversion and selectivity to the targeted bio-based carbonated products is proposed.

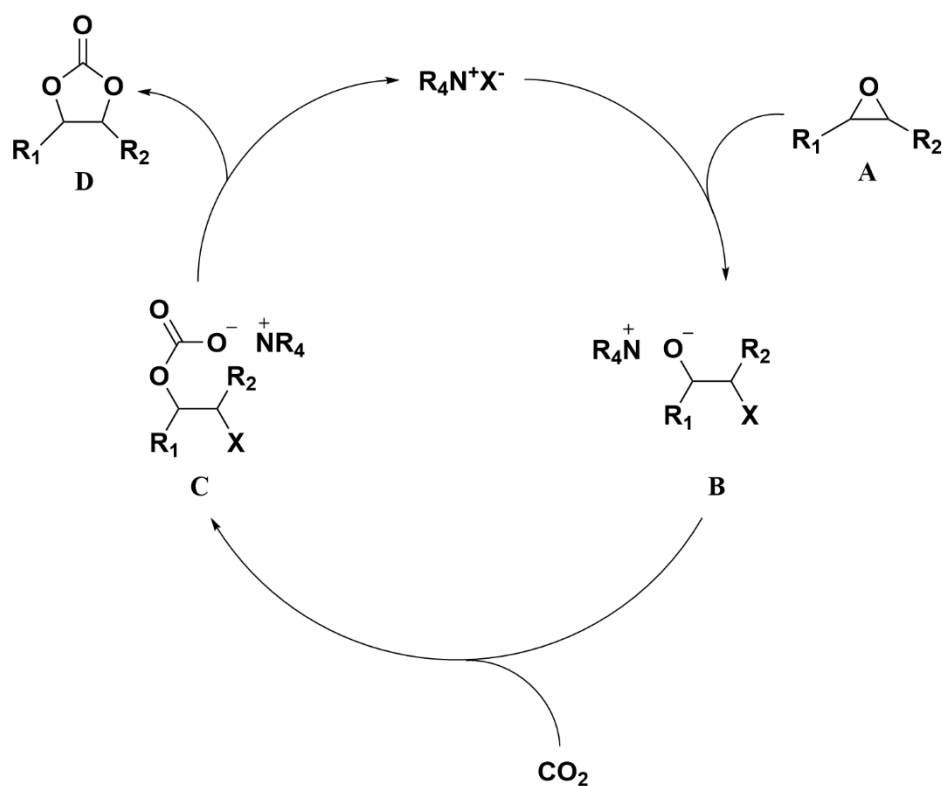
1. Homogeneous catalytic systems

In a homogeneous catalytic system, the catalyst and the reactant are presented in the same phase, generally the liquid phase. These types of systems usually are more efficient compared with heterogeneous catalytic ones, allowing higher conversion and selectivity at milder reaction conditions (lower temperature, lower catalyst concentration and reduced reaction time).⁴² Indeed, a wide variety of homogeneous catalytic systems with different compositions has been developed for the cycloaddition reaction of CO₂ with epoxidized vegetable oils or derivatives.

1.1 Non-functionalized ionic liquids

Organic salts and ionic liquids have gained much attention in catalysis (both as catalysts and as reaction solvents) due to their low toxicity, availability, and affordability. The ones used as homogeneous catalysts in the CO₂ cycloaddition reaction are typically organic halides acting as Lewis bases, e.g., ammonium or phosphonium salts. In **Scheme 1** is depicted the commonly accepted reaction mechanism for the CO₂ cycloaddition to an epoxide. First, an alkoxide intermediate (**B**) is formed by the oxirane (**A**) opening with a nucleophile species (e.g., halide). Then the alkoxide attacks the CO₂ molecule forming the corresponding alkyl carbonate compound (**C**). Finally, the alkyl carbonate undergoes an intramolecular ring-closure

forming the cyclic carbonate (**D**). When these Lewis bases are employed as the only catalyst, the nucleophilic attack of the halide anion to epoxide becomes the rate-determining step.⁴³⁻⁴⁵



Scheme 1. General three-step mechanism for the CO₂ cycloaddition to an epoxide catalyzed by a tetraalkylammonium ionic liquid.

In **Figure 1** are shown selected non-functionalized ionic liquid-based catalysts employed in the cycloaddition of CO₂ to epoxidized oleochemicals collected from the scientific literature.

tetrabutylammonium ionic liquid (**1-4**) or even the employment of a hydroxyl group (**5**) as nucleophile.^{44,47-50} Despite the differences in reaction conditions and vegetable oil derivatives used, it was found that the optimum balance between highest activity and highest selectivity was achieved when bromide was used as anion. The highest reactivity was due to a good balance between nucleophilicity ($F^- > Cl^- > Br^- > I^-$) and leaving group character ($I^- > Br^- > Cl^- > F^-$) of the bromide anion. In this regard, M. Alves et al. attributed the highest catalytic activity shown by ionic liquids bearing a bromide anion compared with those bearing an iodine anion to the smaller bromide size favouring its diffusion towards internal epoxides in the linseed oil triglycerides.⁴⁸ K. Doll et al. also performed the reaction between CO₂ and epoxidized soybean oil or epoxidized methyl oleate with a non-halide catalyst, such as tetrabutylammonium hydroxide ([TBA][OH], **5**). While [TBA][Br] showed the total conversion of the epoxide substrate, the catalyst bearing the hydroxide anion (**5**) exhibited null activity. This fact reveals the key role of halide anion in the synthesis of carbonated oleochemicals.⁴⁶ Moreover, J.L. Zheng et al. tested [TBA][Br] catalytic system in the cycloaddition of CO₂ to epoxidized cottonseed oil methyl esters to the corresponding cyclic carbonated compounds using a microwave irradiated continuous-flow recycle batch reactor. The effect of microwave irradiation compared with conventional heating on the reaction kinetics was studied by the authors in the temperature range of 100-120 °C and the pressure range of 2.5 bar to 6 bar. As could be expected, the authors found that the activation energy of the carbonation reaction was slightly lower when MW irradiation was used as a heating source, achieving slightly higher conversion at 120 °C, 6 bar, [TBA][Br] 4 wt.% and 950 rpm after 7 h.⁵¹ Apart from tetrabutylammonium-based ionic liquids, other ammonium-based ionic liquids were successfully tested as catalysts. V. dos Santos et al. carried out a selection of the most suitable ionic liquids to be employed as catalysts in the synthesis of oleochemical carbonates by quantitative structure-property relationship (QSPR) modelling and exploratory analysis.⁵² This theoretical approach allowed the authors the selection of 122 potential available catalysts for the target reaction. The molecular targets via a virtual screening and the structure-property relationship analysis, led to the selection of cetyltrimethylammonium bromide ([CTMA][Br], **6**) as the most promising one based on its well-balanced properties such as bulkiness, lipophilicity, and nucleophilic character. In addition, experimental results confirmed QSPR analysis, achieving with 5 wt.% [CTMA][Br] high conversions ($\geq 98\%$) using several epoxidized vegetable oils (rice, soybean and canola oil) as starting materials at 120 °C and 50 bar after 48 h of reaction. J. Langanke et al., tested tetraheptylammonium bromide ([THA][Br], **7**) as catalyst (5 mol%) in the synthesis of a series of carbonated methyl esters showing slightly higher yield than the benchmark catalyst [TBA][Br] (**1**) 99% vs. 96% after 24 h reaction at 100 °C and 117 bar.⁴⁴

Imidazolium-based ionic liquids have also been extensively explored as catalysts in the cycloaddition reaction of CO₂ to epoxidized vegetable oils and derivatives. J. Langanke et al. were pioneer in employing 1-*n*-tetradecyl-3-methylimidazolium bromide ([TDMeIm][Br], **8**) as catalyst in the cycloaddition of CO₂ to

several oleo derivatives achieving a yield comparable to the one obtained with [TBA][Br] (**1**) 94% vs. 96% after 24 h reaction at 100 °C and 117 bar.⁴⁴ Afterwards, M. Alves et al. tested 1-*n*-octyl-3-methylimidazolium halides (**9-11**) as catalysts in the cycloaddition reaction of CO₂ to epoxidized linseed oil (ELSO). Not surprisingly, also in this case, bromine stood out as the best-suited anion. Indeed, [OMeIm][Br] (**10**) reached the same conversion (30%) than benchmark catalyst [TBA][Br] (**1**) after 5 h at 100 °C and 100 bar.⁴⁸ B. Schäffer and co-workers used 1-*n*-butyl-3-methyl imidazolium chloride ([BMeIm][Cl], **12**) as a catalyst in the synthesis of carbonated fatty acid esters from epoxidized methyl linoleate.⁴⁷ However, in contrast to the work of J. Langake and M. Alves, the catalytic activity of [BMeIm][Cl] (**12**) was found to be much lower than the benchmark catalysts [TBA][Br] (**1**) (25% vs. 68% yield). Phosphonium-based ionic liquids have also been tested as catalysts in the cycloaddition of CO₂ to epoxidized vegetable oils and their derivatives. N. Tenhumberg et al., studied the influence of the anion in the selected tetrabutylphosphonium-based ionic liquids ([TBP][X], where X is an halide = [Cl] (**13**), [Br] (**14**) or [I] (**15**)), as catalysts instead of the traditional [TBA][Br] (**1**) ionic liquid, in the cycloaddition reaction of CO₂ to an epoxidized methyl oleate.⁵³ Concerning the halide anion influence, the authors found the same trend as previously observed for [TBA][X] (**1-4**), confirming that the ionic liquid formed with bromide as anion shows the best catalytic performance. Indeed, in the presence of the bromide anion, 49% of epoxide was converted with 94% of selectivity towards the desired product. On the other hand, the employment of chloride and iodine anions returned lower conversions 39% and 35%, with a selectivity towards the target products of 99% and 71%, respectively. Moreover, [TBP][Br] (**14**) showed superior activity than the benchmark [TBA][Br] (**1**) ionic liquid in terms of conversion 49% vs. 39% and selectivity 94% vs. 82% towards the desired carbonated methyl ester. On the other hand, [TBP][Br] (**14**) and [TBA][Br] (**1**) were also tested as catalyst by M. Alves et al. for the synthesis of carbonated linseed oil. In contrast to N. Tenhumberg work, phosphonium-based catalyst (**14**) exhibited similar epoxide conversion to those achieved by using [TBA][Br] (**1**) as catalyst 28% vs. 30%, but selectivity was not reported in this work.⁴⁸ Very few articles have reported the use of triphenylphosphonium-based ionic liquids as catalysts for the synthesis of carbonated oleochemicals by cycloaddition of CO₂ to the corresponding epoxidized compound. A. Centeno-Pedraza et al. designed, prepared, characterized, and tested triphenylphosphonium-based ionic liquids. The reached conversion and selectivity were compared with the benchmark catalyst [TBA][Br] (**1**) for the cycloaddition of CO₂ to an epoxidized soybean oil.⁵⁴ Three of the eight (**17-24**) non-functionalized ionic liquid catalysts prepared by the authors (dodecyltriphenylphosphonium bromide [DTPP][Br] (**19**), hexadecyltriphenylphosphonium bromide [HTPP][Br] (**20**), and eicoxyltriphenylphosphonium bromide [ETPP][Br] (**21**)) showed better performance than the benchmark catalyst (**1**) at same reaction conditions (20 bar CO₂ pressure, 120 °C, 5 mol% catalyst; 2 h). Moreover, using [DTPP][Br] (**19**) as catalyst, highly carbonated soybean oil was obtained after 5h at 160 °C and 40

bar. The improvement in catalytic performance was attributed to three balanced factors, the catalyst solubility in the reaction medium, the bromide anion nucleophilicity enhancement, and the ionic liquid high thermal stability compared with the benchmark ionic liquid [TBA][Br] (**1**). Indeed, the authors suggested that the solubility of the catalyst was enhanced due to the presence of a long aliphatic chain in the ionic liquid cation, increasing the affinity between the epoxidized oil and the catalyst. On the other hand, the enhanced bromide anion nucleophilicity was attributed to the steric hindrance and rigidity provided by the substituents and the cyclic aromatic structure of the phosphonium cation. Unlike [TBA][Br] (**1**), [DTPP][Br] (**19**) can be used at temperatures above 120 °C due to its higher thermal stability up to 12 h at 160 °C. This allowed increasing the reaction temperature up to 160 °C without risk of decomposition, obtaining a highly carbonated soybean oil within 5 h. L. Peña Carrodeaguas et al. achieved the synthesis of carbonated methyl ester at relatively mild reaction conditions (70 °C, 10 bar, 24 h, 5 mol%) using bis(triphenylphosphine)iminium chloride ([PPN][Cl] (**25**)) as catalyst.⁴⁹ In this work, both [TBA][Br] (**1**) and [PPN][Cl] (**25**) reached quantitative conversion in the synthesis of carbonated methyl oleate. However, while the use of [PPN][Cl] (**25**) provided high chemo-selectivity and stereo control towards *cis*-isomer (96:4), [TBA][Br] (**1**) significantly reduced this stereoselectivity (51:49). Therefore, the authors proved that the use of [PPN][Cl] (**25**) was beneficial to produce almost exclusively the *cis*-configured carbonated methyl oleate. Other ionic liquids composed by different cations (**26-31**) were scarcely investigated. M. Alves et al. tested triethylsulfonium iodide ([TES][I] (**26**)), 1-butyl-1-methylpyrrolidinium iodide ([BMPyr][I] (**27**)), 1-butylpyridinium ([BPy][I] (**28**)), 1-butyl-2,3,4,5,7,8,9,10-octahydropyrido[1,2-*a*][1,3]diazepin-1-ium bromide ([BDBU][Br] (**29**)) and 1-butyl-3,4,6,7,8,9-hexahydro-2H-pyrimido [1,2-*a*]pyrimidin-1-ium bromide ([BTBD][Br] (**30**)) as catalysts (1 mol%) in the cycloaddition reaction of CO₂ to ELSO oil at 100 °C and 100 bar for 5 h.⁴⁸ [TES][I] (**26**), [BMPyr][I] (**27**) and [BPy][I] (**28**) ionic liquids were less efficient evidenced by the poor performance in terms of conversion to the carbonated linseed oil (CLSO), 0%, 19% and 12%, respectively. The authors attributed their poor performance to the poor solubility of these ionic liquids in the reaction media. However, [BDBU][Br] (**29**) and [BTBD][Br] (**30**) exhibited much higher activity achieving conversions of 28% and 36% respectively to the CLSO, improving the results achieved by the benchmark catalyst [TBA][Br] (**1**) that was found to be 30% to the CLSO. B. Schäffner et al. employed 1-butyl-4-methyl pyridinium iodide ([BMePh][I], (**31**)) in the cycloaddition of CO₂ to epoxidized methyl linoleate at 100 °C, 100 bar for 17 h. The catalytic activity resulted similar as the one of [TBA][Br] (**1**) in terms of conversion (65% vs. 69%, respectively), and selectivity towards target product > 99% with both ionic liquids.⁴⁷ In **table 1** are shown selected non-functionalized ionic liquids employed as catalysts, the reaction conditions, the conversion, and the selectivity to target products (when given) in the CO₂ cycloaddition to different vegetable oils or similar molecules.

Table 1. Non-functionalized ionic liquid catalysts used in carbonated oleochemicals synthesis

Catalyst	Epoxidized oleochemical	Reaction conditions				Conv. (%)	Select. (%) ^b	Ref.
		<i>T</i> (°C)	<i>P</i> (bar)	<i>Time</i> (h)	<i>Cat</i> (mol%)			
1	Soybean oil	110	1	70	5	100	-	39
	Methyl oleate	100	>103	20	5	100	-	46
	Soybean oil	100	>103	40	5	100	-	46
	Methyl linoleate	100	100	17	5 ^a	69	99	47
	Fatty acid methyl ester	100	117	24	5	97	>99	44
	Linseed oil	100	100	5	1	30	-	48
	Methyl oleate	100	50	16	2	39	82	53
	Fatty acid methyl ester	70	10	24	5	>99	>99	49
	Methyl oleate	100	5	24	5	83	87	50
Cottonseed oil methyl ester	120	6	7	4 ^a	52	-	51	
2	Fatty acid methyl ester	100	117	24	5	21	95	44
	Linseed oil	100	100	5	1	17	-	48
	Fatty acid methyl ester	70	10	24	5	6	99	49
	Methyl oleate	100	5	24	5	44	99	50
3	Fatty acid methyl ester	100	117	24	5	62	0	44
4	Fatty acid methyl ester	100	117	24	5	80	92	44
	Methyl linoleate	100	100	17	5 ^a	75	98	47

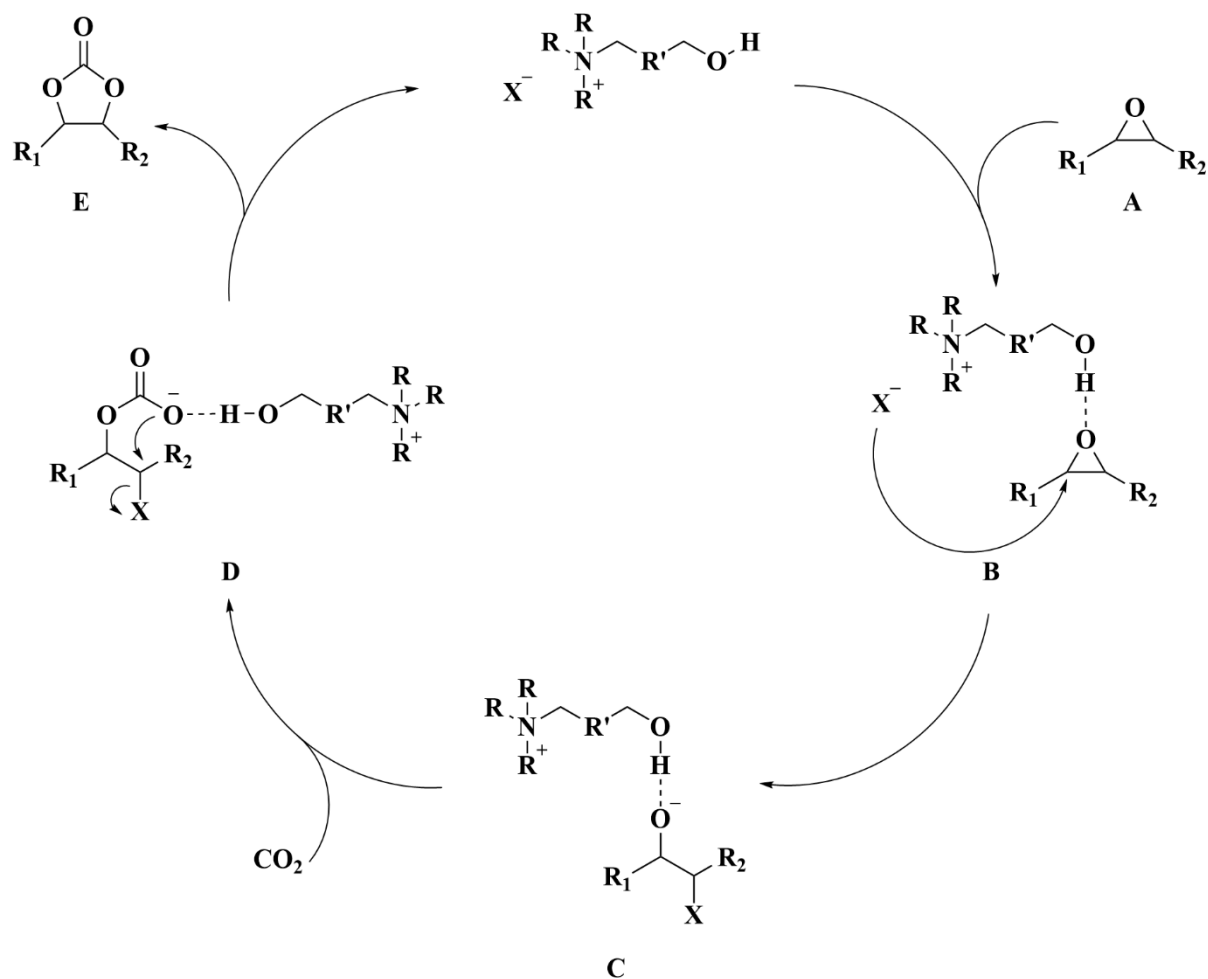
	Methyl oleate	100	5	24	5	70	59	50
	Linseed oil	100	100	5	1	26	-	48
5	Methyl oleate	100	>103	20	5	6	-	46
	Rice bran oil					98	-	
6	Canola oil	120	50	48	5 ^a	>99	-	52
	Soybean oil					>99	-	
7	Fatty acid methyl ester	100	117	24	5	99	99	44
8	Fatty acid methyl ester	100	117	24	5	97	97	44
9	Linseed oil	100	100	5	1	20	-	48
10	Linseed oil	100	100	5	1	30	-	48
11	Linseed oil	100	100	5	1	25	-	48
12	Methyl linoleate	100	100	17	5 ^a	26	99	47
	Linseed oil	100	100	5	1	19	-	48
13	Methyl oleate	100	50	16	2	38	99	55
	Methyl oleate	100	50	16	2	39	99	53
	Linseed oil	100	100	5	1	28	-	48
14	Methyl oleate	100	50	16	2	38	99	55
	Methyl oleate	100	50	16	2	49	94	53
	Linseed oil	100	100	5	1	21	-	48
15	Methyl oleate	100	50	16	2	35	72	55
	Methyl oleate	100	50	16	2	35	71	53

19	Soybean oil	160	40	5	2	>99	84	⁵⁴
25	Fatty acid methyl ester	70	10	24	5	53	99	⁴⁹
26	Linseed oil	100	100	5	1	-	-	⁴⁸
27	Linseed oil	100	100	5	1	19	-	⁴⁸
28	Linseed oil	100	100	5	1	12	-	⁴⁸
29	Linseed oil	100	100	5	1	28	-	⁴⁸
30	Linseed oil	100	100	5	1	36	-	⁴⁸
31	Methyl linoleate	100	100	17	5 ^a	65	>99	⁴⁷

^acatalyst in wt.%; ^bselectivity to the cyclic carbonate product.

1.2 Functionalized (task-specific) ionic liquids

Functionalized ionic liquid refers to an ionic liquid that possesses a functional group or extra functionality, generally on the cation. These ionic liquids are known as task-specific ionic liquids and their functionalization helps to enhance the performance of the ionic liquid in a specific application e.g., in catalysis.^{56,57} In the cycloaddition reaction of CO₂ to low molecular weight epoxides, such as propylene oxide, butylene oxide, etc., it is found that the use of task-specific ionic liquids bearing an -OH, -COOH or -NH₂ functionalities (hydrogen donors) able to form hydrogen bonds enhance the catalytic performance of the ionic liquid.^{25,58-60} Indeed, reported works suggest that these functionalities able to donate hydrogen increased the rate of the epoxide ring opening (rate-determining step on the catalytic cycle) due to a synergetic effect between anion and hydrogen bond donor. As depicted in **scheme 2**, the hydrogen donor moiety is able to polarize the C-O bond in the epoxide ring (**A**), making the carbon atom more electrophilic, thus facilitating the attack of the anion. It results in an easier epoxide ring-opening (**B**), yielding the corresponding alkoxide (**C**). Then the alkoxide attacks the CO₂ molecule forming the corresponding alkyl carbonate compound (**D**). Finally, the alkyl carbonate undergoes an intramolecular ring-closure forming the cyclic carbonate (**E**). In view of the promising results obtained by using task-specific ionic liquids in the CO₂ cycloaddition to low molecular weight epoxides, they were tested in the more challenging internal epoxides present in epoxidized vegetable oils and derivatives.



Scheme 2. General mechanism of CO₂ cycloaddition to an epoxide catalyzed by a tetraalkylammonium halide salt with hydroxyl terminal group.

In **Figure 2** are shown selected task-specific ionic liquid-based catalysts described in the literature for this process.

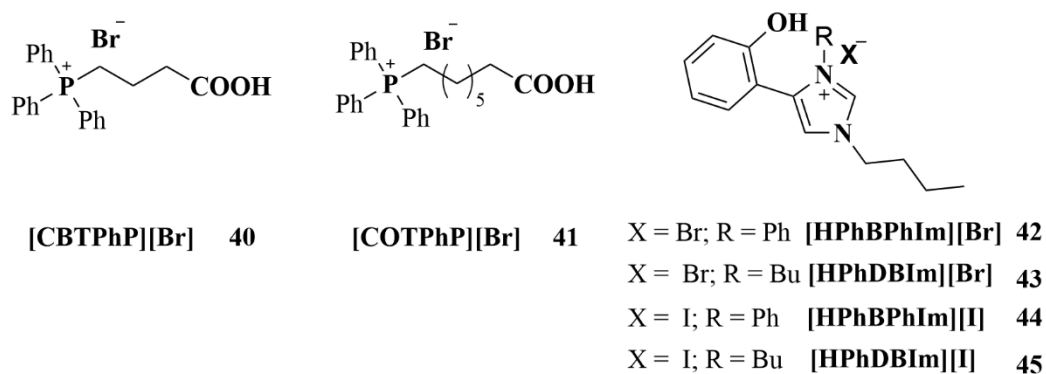
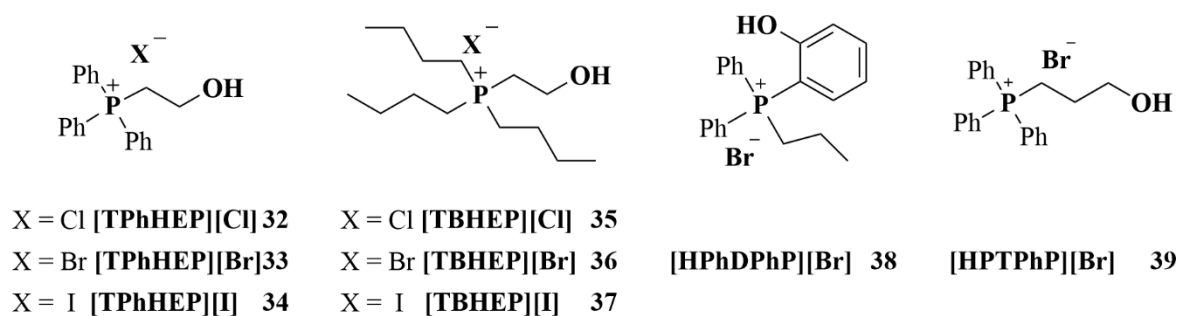


Figure 2. Task-specific ionic liquid catalysts used in the CO₂ cycloaddition to epoxidized oleochemicals.

H. Büttner et al. tested several functionalized phosphonium-based ionic liquids (**32-38**) in the cycloaddition of CO₂ to epoxidized oleochemicals.⁶¹ In this work, triphenylphosphonium- (**32-34**) and tributylphosphonium-based (**35-37**) ionic liquids lead to low conversion (5-24%) of methyl oleate epoxide in its cycloaddition with CO₂ to form in the corresponding carbonated methyl oleate at 100 °C, 50 bar for 16 h. Despite the low activity observed, the same authors prepared a series of phosphonium ionic liquids derived from phenol. Among them, 2-hydroxyphenyldiphenylpropyl phosphonium bromide ([HPhDPhP][Br] (**38**)) exhibited high potential in the synthesis of carbonated methyl oleate from the corresponding epoxide yielding good results in terms of conversion (99%) and selectivity (98%) at 100 °C and 25 bar after 16 h. The authors attributed the catalytic activity enhancement to different factors, the bromide anion, the presence of an -OH group and its position (*ortho*) in the aromatic ring. In addition, due to its potential, the same ionic liquid (**38**) was tested as well in the synthesis of other three carbonated oils (high oleic sunflower oil, soybean oil, and linseed oil) with excellent reaction yields (isolated) up to 88% after 24 h reaction at 80 °C and 25 bar. Centeno-Pedraza et al. reported the synthesis of triphenylphosphonium-based task-specific ionic liquids (**39-41**).⁵⁴ These task-specific ionic liquids were employed as catalysts in the synthesis of CSBO at 120 °C and 20 bar. Nevertheless, the conversion achieved with these catalysts was found to be poor, between 1% and 10% after 2 h of reaction, compared with the employed benchmark catalyst [TBA][Br] (**1**) that showed conversions of 40% at the same reaction

conditions. The authors attributed the poor performance of the synthesized phosphonium-based catalyst to the poor/low solubility of these ionic liquids in the reaction media. J. Martinez et al. synthesized waste oil-derived cyclic carbonates using as catalyst imidazolium-based task-specific ionic liquid bearing a phenolic ring in 5 position and [Br] and [I] as anions (**42-45**), achieving excellent conversion ($\geq 97\%$) and selectivity ($\geq 93\%$) to the target products after 16 h at 100 °C and 20 bar with catalyst **45**.⁶² The excellent catalytic performance of catalysts **45** was attributed to the high solubility of the catalyst boosted with the presence of butyl chains on nitrogen 1 atom instead of a phenyl ring compared with catalyst **44**. Furthermore, unlike previous works, the catalyst containing the iodine anion (**45**) showed higher activity than a similar one containing the bromide anion (**43**), achieving at 100 °C and 20 bar 97% and 75% conversion, respectively, after 16 h of reaction with 1 mol% of catalyst. These authors performed a recyclability test with task-specific ionic liquids, being one of the scarce examples of recyclability of the catalysts in the cycloaddition of CO₂ to vegetable oils epoxides. The ionic liquid **45** was reused for at least 5 times at different reaction times (2h, 5 h and 16 h) at 100 °C and 20 bar with 1 mol% of catalyst without significant loss of its activity. In addition, the catalyst could be recovered (up to 100%) from the reaction media by simple precipitation with diethyl ether. In **table 2** are shown some task-specific (functionalized) ionic liquids employed as catalysts, the reaction conditions, the conversion, and the selectivity to target products (when given) in the CO₂ cycloaddition to different vegetable oils or similar molecules.

Table 2. Task-specific (functionalized) ionic liquid catalysts used in carbonated oleochemicals synthesis.

Catalyst	Epoxidized oleochemical	Reaction conditions				Conv. (%)	Select. (%) ^a	Ref.
		<i>T</i> (°C)	<i>P</i> (bar)	<i>t</i> (h)	<i>Cat</i> (mol%)			
32	Methyl oleate	100	50	16	2	5	0	61
33	Methyl oleate	100	50	16	2	9	99	61
34	Methyl oleate	100	50	16	2	14	80	61
35	Methyl oleate	100	50	16	2	10	>99	61
36	Methyl oleate	100	50	16	2	22	97	61
37	Methyl oleate	100	50	16	2	24	98	61

	Methyl oleate	100	25	16	5	99	98	
38	Sunflower oil					99	80	61
	Soybean oil	80	25	24	5	97	77	
	Linseed oil					99	88	
39	Soybean oil	120	20	2	5	>1	99	54
40	Soybean oil	120	20	2	5	10	99	54
41	Soybean oil	120	20	2	5	1	65	54
	Sunflower oil					97	98	
	Halzenut oil					98	93	
	Olive oil					98	98	
45	Pistachio oil	100	20	16	1	99	94	62
	Almond oil					98	97	
	Rapeseed oil					99	95	
	Pumpkin oil					97	95	

^aSelectivity to the cyclic carbonate product.

1.3 Ionic liquid/Lewis acidic compound binary catalytic systems

As previously mentioned, ionic liquids with a nucleophilic anion such as [TBA][Br] (**1**) are often used as catalysts in the synthesis of cyclic carbonated oils and derivatives from the cycloaddition of CO₂ to the corresponding epoxidized compounds. However, the steric hindrance of the internal epoxide rings in the vegetable oil structure makes difficult the epoxide ring-opening (generally the rate-determining step), hampering the overall reaction rate as well as the selectivity to the target products. Therefore, high temperatures (70-120 °C) and pressures (5-117 bar), as well as long reaction times (> 20 h) are generally required to achieve reasonable conversions. These harsh conditions can affect both the selectivity to the desired products and their industrial implementation. In this regard, several research groups tried to improve

the catalytic performance in terms of conversion and selectivity towards desired products by adding a Lewis acid metal complex. The CO₂ cycloaddition reaction mechanism of the catalytic systems formed by these catalytic systems is similar to that proposed for the task-specific ionic liquids (**scheme 2**). In this case, the role of the functional group (epoxide ring-opening facilitation) is played by the metal complex that, due to its Lewis acid character, interacts with the oxygen atom making the adjacent carbon more electron deficient and prompt for a nucleophilic attack by the anion of the employed ionic liquid.⁶³ These catalytic systems formed by an ionic liquid, mainly [TBA][Br] (**1**), and a Lewis acidic metal complex have been employed by several authors. Z. Li et al. used a catalytic system formed by 1 equivalent (3 mol%) of [TBA][Br] (**1**) and 0.3 equivalents (1 mol%) of a Lewis acid compound with the objective of improving the catalytic performance in the synthesis of carbonated soybean oil by cycloaddition of CO₂ to the corresponding epoxidized soybean oil at 120 °C and 10 bar in 20 h.⁶⁴ The addition of SnCl₄.5H₂O (0.3 equiv.) as Lewis acidic compound improved the catalytic performance of the employed ionic liquid (**1**) (1 equiv.) by around 25%, increasing the conversion from 71% to 89%. Under the optimized reaction conditions (140 °C and 15 bar), the catalytic system afforded the full conversion of epoxidized soybean oil after 30 h. The same catalytic system but at different ratio of [TBA][Br] (**1**) 7.8 mol% (3.5 wt.%) and SnCl₄.5H₂O 9 mol% (5 wt.%) was tested by B. Schäffner et al. in the obtention of carbonated methyl linoleate via the CO₂ cycloaddition to the corresponding epoxide at 100 °C and 100 bar, achieving a conversion and selectivity of 64 % and 82 %, respectively after 17 h.⁴⁷ Nevertheless, in this case, the [TBA][Br] (**1**) ionic liquid without the presence of the co-catalyst exhibited higher conversion (69% vs. 64%) and better selectivity (> 99% vs. 82%) towards the desired carbonated product than the binary catalytic system. The authors justified the lower selectivity found to the strong Lewis acid character of SnCl₄.5H₂O co-catalyst, which could promote the hydrolysis of the epoxide methyl ester to the corresponding diol, thus decreasing the selectivity. J. Langanke et al. promoted the reaction between CO₂ and epoxidized methyl oleate using a catalytic system formed by 1 equivalent of [TBA][Br] (**1**) ionic liquid (2 mol%) and 1 equivalent of THA-Cr-Si-POM (tetraheptylammonium silicotungstates containing Cr (III), ((*n*-C₇H₁₅)₄- N)₅[CrSiW₁₁O₃₉]) (2 mol%).⁴⁴ After 6 h at 100 °C and 125 bar the desired carbonate product was formed with high epoxide conversion (95%) and selectivity (98%). This binary catalytic system substantially improved the performance of [TBA][Br] (**1**) 11% vs. 95% and 81% vs. 98% in terms of conversion and selectivity, respectively. However, using epoxidized soybean oil as starting material, the catalytic activity was reduced in terms of conversion (41 % vs. 47%) and selectivity (60% vs. 73%) with respect to [TBA][Br] (**1**), even when increasing the reaction time to 24 h. The worst catalytic performance achieved by the binary system compared with the [TBA][Br] (**1**) when using an epoxidized soybean oil as starting material, was attributed to the higher viscosity of the obtained carbonated products compared with the carbonated methyl oleate and the strong Lewis acidity character of the co-catalyst, thus hampering the reaction rate and favouring the hydrolysis of

the epoxide rings, decreasing both the conversion and the selectivity of the studied reaction. B. Schäffner et al. tested a binary catalytic system formed by [TBA][Br] (**1**) ionic liquid (3.5 wt.%) and Al-Salen complex (5 wt.%) in the synthesis of carbonated methyl linoleate from CO₂ and the corresponding epoxide at 100 °C and 100 bar.⁴⁷ The catalytic performance of the binary catalytic system was found to be better than the [TBA][Br] (**1**) ionic liquid catalyst in terms of yield (75% vs. 65%) after 17 h reaction. A. Farhadian et al. employed a catalytic system formed by 1 equivalent [TBA][Br] (**1**) ionic liquid (4 mol %) and 1 equivalent of Mn-based porphyrins as Lewis acid co-catalyst (4 mol%) to achieve the synthesis of fully carbonated (yield >99 %) sunflower oil (CSFO) from the cycloaddition of CO₂ to epoxidized sunflower oil (ESFO) after 30 h at mild reaction conditions, 100 °C and atmospheric pressure.⁶⁵ A binary system formed with [TBA][Br] (**1**) ionic liquid (17 wt.%) and several Metal-Organic-Frameworks (MOFs) (10 wt.%) was tested by T. Cai et al. in the preparation of carbonated *o*-acetyl methyl ricinoleate from the cycloaddition of CO₂ to the corresponding epoxidized precursor.⁶⁶ Among the different binary catalytic systems tested by the authors, the one formed by [TBA][Br] (**1**) ionic liquid and UiO-66-NH₂ MOF showed the best catalytic performance achieving 94% conversion of the epoxidized compound after 12 h at 120 °C and 30 bar. N. Tenhumberg et al., tested several binary catalytic systems formed by a combination of 1 equivalent of [TBP][Br] (**14**) ionic liquid (2 mol%) with 1 equivalent of different metals as Al, Ca, Mo and W (2 mol%) in the synthesis of carbonated methyl oleate from CO₂ and the corresponding epoxide at 100 °C and 50 bar for 16 h.⁵³ In all cases, the yield to the desired cyclic carbonates was considerably increased with conversions up to 99% by adding 2 mol% of a metal transition complex as co-catalyst compared to the conversion (49%) obtained using only [TBP][Br] (**14**) ionic liquid as catalyst, while the selectivity towards the desired carbonated product was comparable (93% vs. 94%). The best catalytic performance was achieved with the binary system containing MoO₃ as Lewis acidic co-catalyst, doubling the yield of the carbonated product compared with the use of the [TBP][Br] (**14**) ionic liquid as the only catalyst (84% vs. 46%). Under the optimized reaction conditions (100 °C and 50 bar), the catalytic system composed of 1 equivalent of [TBP][Br] (**14**) ionic liquid and 0.125 equivalents of MoO₃ afforded the conversion of four epoxidized vegetable oils into the corresponding carbonates with both conversion and selectivity towards the carbonated compounds higher than 99% after 20 h reaction. The same authors tested binary catalytic systems formed by [TBP][Br] (**14**) or [TOP][Br] (**16**) as the ionic liquids and different iron salts FeF₃, FeCl₃, FeCl₃·6H₂O, FeBr₃, FeBr₂, Fe(acac)₃, Fe(OTf)₃, Fe(OAc)₂, Fe(stearate)₃, FeSO₄·7H₂O and Fe(citrate)₃·(aq) as the Lewis acidic co-catalyst in the synthesis of carbonated methyl oleate from cycloaddition of CO₂ to epoxidized methyl oleate at 100 °C and 50 bar lasting for 16 h.⁵⁵ Among the studied binary catalytic systems, the most efficient at the studied conditions was the one composed by 1 equivalent of [TOP][Br] (**16**) ionic liquid (2 mol%) and 0.125 equivalents of FeCl₃ (0.25 mol%) as Lewis acid achieving yields of the target product as high as 95%. The presence of an iron-based Lewis acid as co-

catalysts enhanced 100 % the conversion compared to the employment of only [TOP][Br] (**16**) (> 99% vs. 49%). The same catalytic system was tested in the optimized reaction conditions (100 °C and 50 bar), in the synthesis of four carbonated oil by CO₂ cycloaddition to the corresponding epoxidized oils exhibiting excellent yields ranging from 88% to 94% after 24 h reaction. L. Peña Carrodeaguas et al. developed a catalytic system formed by 1 equivalent [PPN][Cl] (**25**) ionic liquid (5 mol%) and 0.1 equivalents of Aluminium(III)aminotriphenolate complex (0.5 mol%) as Lewis acidic co-catalyst in the synthesis of carbonated fatty acids methyl esters from CO₂ cycloaddition to their corresponding epoxidized compounds.⁴⁹ The binary system, [PPN][Cl] (**25**) and Al-complex, afforded the production of carbonated methyl esters with excellent yields (up to > 99%) at relatively mild reaction conditions, 70 °C and 10 bar, after 24 h. The presence of Lewis acid as co-catalyst enhanced the conversion in a range of ca. 18% to 150% compared with the catalytic system without a Lewis acidic metal complex, depending on the epoxidized fatty acid employed as starting material. In **table 3** are shown selected ionic liquid/Lewis acidic compound binary catalytic systems employed in the literature, the reaction conditions, the conversion, and the selectivity to target products (when given) in the CO₂ cycloaddition to different vegetable oils or similar molecules.

Table 3. Ionic liquid/Lewis acidic compound binary catalytic systems used in carbonated oleochemicals synthesis.

Catalyst (equiv.)	Lewis acidic compound (equiv.)	Epoxidized oleochemical	Reaction conditions				Conv. (%)	Select. (%) ^b	Ref.
			<i>T</i> (°C)	<i>P</i> (bar)	<i>t</i> (h)	<i>Cat</i> (mol%)			
1 (1)	SnCl ₄ ·5H ₂ O (0.3)	Soybean oil	140	15	30	3	98.6	-	64
1 (1)	SnCl ₄ ·5H ₂ O (1.4)	Methyl linoleate	100	100	17	3.5 ^a	64	82	47
1 (1)	<i>(n</i> -C ₇ H ₁₅) ₄ -N) ₅ [CrSiW ₁₁ O ₃₉] (1)	Methyl oleate	100	125	6	2	95	98	44
		Soybean oil	100	130	24	2	41	60	44
1 (1)	Al-salen (1.4)	Methyl linoleate	100	100	17	3.5 ^a	80	94	47
1 (1)	Mn-Porphyrin (1)	Sunflower oil	100	1	30	4	100	99	65
1 (1)	UiO-66-NH ₂ (0.6)	Methyl recinoleate	120	30	12	17 ^a	94	-	66
		Methyl oleate	100	50	16	2	95	91	
14 (1)	MoO ₃ (0.125)	High oleic sunflower oil					>99	95	53
		Sunflower oil	100	50	20	2	99	98	
		Soybean oil					99	90	

		Linseed oil					97	79	
		Methyl oleate	100	50	16	2	≥99	96	
		Linseed oil					99	90	
16 (1)	FeCl ₃ (0.125 eq)	High oleic sunflower oil	100	50	24	2	99	88	⁵⁵
		Soybean oil					99	94	
25 (1)	Al-complex (0.1)	Fatty acid methyl ester	70	10	24	5	99	99	⁴⁹

^acatalyst in wt.%; ^bselectivity to the cyclic carbonate product.

1.4 Ionic liquid/hydrogen bond donor binary catalytic systems

These binary catalytic systems are similar to previous ones formed by an ionic liquid and Lewis acidic compound, with the Hydrogen Bond Donor (HBD) playing the role of the Lewis acidic compound, increasing the rate of epoxide ring-opening, that is the rate-determining step in the catalytic cycle. In fact, the HBD has two roles in the catalytic cycle (similar to the one depicted in **scheme 2**): 1) the interaction with the oxygen atom of the epoxide ring, making more electrophilic the adjacent carbon facilitating the ring-opening by the nucleophilic attack of the ionic liquid anion; and 2) the stabilization of the alkoxide formed after the ring-opening through hydrogen bonds formation.⁶¹ The HBD compounds are a more sustainable and cheaper alternative to Lewis acidic ones because most of the Lewis acidic compounds contain a transition metal complex that could be considered as Critical Raw Material (CRM) due the current global situation and geopolitical issues. In addition, the extraction processes of these CRMs are far from being environmentally friendly.⁶⁷ Despite that, still very few research groups work in the design of binary catalytic systems formed by an ionic liquid as the main catalyst and a HBD compound as co-catalyst in the cycloaddition of CO₂ to epoxidized vegetable oils or derivatives to obtain cycle carbonated compounds. In this context, P. Mazo et al. evaluated the performance of a binary catalytic system formed by 1 equivalent of [TBA][Br] (**1**) ionic liquid and 3 equivalents of water as HBD co-catalyst in the synthesis of carbonated soybean oil (CSBO) from CO₂ and epoxidized soybean oil (ESBO) at 120 °C and atmospheric pressure.⁶⁸ They achieved good conversion of the ESBO (87%) but moderate selectivity (89%) towards the CBSO after 70 h. The designed binary catalytic system improved the catalytic performance of [TBA][Br] (**1**) as the sole catalyst in terms of reaction time that was reduced ca. 30% to achieve similar conversion of the epoxide group, proving the promoting effect of H₂O as co-catalyst. Alves et al. tested several binary catalytic systems formed by 1 equivalent of [TBA][Br] (**1**) ionic liquid (1 mol%) and 1 equivalent of a HBD co-catalysts (1 mol%). In total they tested 17 different HBDs compounds (multiphenolic or fluoralcohols), in the production of carbonated linseed oil (CLSO) from CO₂ and corresponding epoxidized linseed oil

(ELSO) at 100 °C, 100 bar and 5 h reaction time.⁴⁸ 14 out of the 17 HBDs tested improved the conversion by at least ca. 33 % compared with the use of [TBA][Br] (**1**) ionic liquid as the sole catalyst ($\geq 42\%$ vs. 32%). Quantitative conversion of ELSO into CLSO was achieved after 10 h by employing a binary catalytic system formed by 1 equivalent of [TBA][Br] (**1**) ionic liquid (2.2 mol%) and 1 equivalent of 2,2,2-trifluoro-tert-butanol (2.2 mol%) as HBD co-catalyst at the optimized reaction conditions (120 °C and 50 bar). A binary catalytic system formed by [TBA][Cl] (**2**) ionic liquid and ascorbic as HBO co-catalyst was designed and its catalytic performance evaluated by W. Natongchai et al. in the synthesis of carbonated vegetable oils and fatty acids esters from CO₂ and the corresponding epoxidized compounds.⁵⁰ This binary catalytic system produced excellent results in the synthesis of targeted oleochemicals reaching conversion and selectivity up to 99% after 48 h at mild reaction conditions, 80-100 °C and 5-10 bar. In **table 4** are shown selected ionic liquid/hydrogen bond donor (HBD) binary catalytic systems, the reaction conditions, the conversion and the selectivity to target products (when given) in the CO₂ cycloaddition to different vegetable oils or similar substrates.

Table 4. Ionic liquid/HBD binary catalytic systems used in carbonated oleochemicals synthesis.

Catalyst (equiv.)	HBD (equiv.)	Epoxidized oleochemical	Reaction conditions				Con. (%)	Select. (%) ^a	Ref.
			<i>T</i> (°C)	<i>P</i> (bar)	<i>t</i> (h)	<i>Cat</i> mol%			
1 (1)	H ₂ O (3)	Soybean oil	120	1	70	5	87	88	⁶⁸
1 (1)	trifluoro-tert-butanol (1)	Soybean oil	120	50	10	2.2	99	-	⁴⁸
		Methyl oleate					99	99	
2 (1)	Ascorbic Acid (1)	Olive oil Soybean oil Canola oil	100	5	48	5	99 99 99	99 89 94	⁵⁰

^aselectivity to the cyclic carbonate product.

1.5 Other homogeneous catalytic systems based on ionic compounds

Abundant, inexpensive, and nontoxic catalysts based on Na, Li or K metal salts are able to catalyze as well the cycloaddition reaction of CO₂ to low molecular weight epoxides with excellent results. Indeed, the synthesis of ethylene carbonate at an industrial scale is patented using alkali metal salts as a catalyst.⁶⁹ Nevertheless, the catalytic performance of this kind of metal salts in the preparation of carbonated oleochemicals and derivatives is generally negligible or poor. K. Doll et al. tested KBr and LiBr (3 mol%) metal salts as catalysts under supercritical conditions in the cycloaddition of CO₂ to epoxidized soybean oil

achieving low conversion ($\leq 6\%$) after 40 h of reaction.⁴⁶ B. Schäffner et al., also observed poor conversions (2%) employing KI (5 wt.%) as a catalyst in the synthesis of carbonate fatty acids methyl esters from CO₂ and epoxidized fatty acid methyl esters at 100 °C and 100 bar for 17 h.⁴⁷ As mentioned in previous catalytic systems, the addition of a co-catalyst (Lewis acid or HBD) often promotes the overall catalytic performance in terms of conversion and selectivity in the cycloaddition of CO₂ to epoxidized oleochemical reaction. Consequently, some authors designed catalytic systems containing a metal salt and an additive (co-catalysts) such as crown ethers or glycols (**figure 3**) to try to improve the catalytic performance of the alkali metal salts in the synthesis of carbonated oleochemicals. The role of the crown ether is to enable the *in-situ* formation of a complex containing the metal (cation) and the halide (anion) of the alkali salt as depicted in **scheme 3**. The “in situ” formed complex allows the epoxide activation due to the Lewis acidic character of the metal facilitating the nucleophilic ring opening by the halide anion in the cycloaddition of CO₂ to epoxides.^{70,71} For the first time, Parzuchowski et al. tested a catalytic system composed by an alkali metal salt and crown ether in the cycloaddition of CO₂ to epoxidized oleochemicals.⁷² This catalytic system was formed by KI (0.3 wt.%) and 18-crown-6 ether (0.2 wt.%) and tested in the synthesis of carbonated soybean oil from CO₂ and epoxidized soybean oil, achieving a conversion of 98.3% at 130 °C and 60 bar after 120 h reaction. B. Schäffner et al. tested several catalytic systems formed by 5 wt.% of an alkali metal salt (KBr, KI, NaI, LiI and CsI) and 3.5 wt.% of a crown ether (18-crown-6, 15-crown-5 and 12-crown-4) in the reaction of CO₂ with epoxidized methyl linoleate at 100 °C, 100 bar and 17 h reaction time.⁴⁷ The best results in terms of conversion (94%) were achieved with the catalytic system formed by NaI and 15-crown-5 while in terms of selectivity (89% vs. 97%) were obtained with the catalytic system formed by KI and 18-crown-6. In general, the second catalytic system produced slightly better results in terms of yield of the targeted carbonated product (84% vs. 87%). All the other catalytic systems formed by other alkali metal salts tested by the authors exhibited insufficient conversions from 10% to 55%. The same authors, tested as well catalytic systems formed by alkali metal salts (5 wt.%) and glycols (HBDs) (3.5 wt.%) as co-catalysts at 100 °C, 100 bar and 17 h reaction time in the reaction of CO₂ with epoxidized methyl linoleate. The authors justified the use of glycols as co-catalyst based on both their tuneable properties and low cost. Among the catalytic systems employed containing a glycol, the one formed by KI and polyethylenglycol 400 (PEG400) showed the best catalytic performance in terms of conversion (84%) and selectivity (99%) although the catalytic system formed by KI and polyethylene glycol 600 (PEG600) showed similar conversion (83%) and selectivity (99%). In this work, the authors observed that the epoxidized oleochemical conversion was reduced considerably when high molecular weight glycols (≥ 1000 Mw) were employed in the catalytic systems due to the limited solubility of the heavy glycols. L. Longwitz et al. developed catalytic systems formed by 1 equivalent of CaI₂ (5 mol%) 1 equivalent of a crown ether (5 mol%) to be tested in the synthesis of carbonated methyl oleate from the epoxidized methyl oleate and CO₂

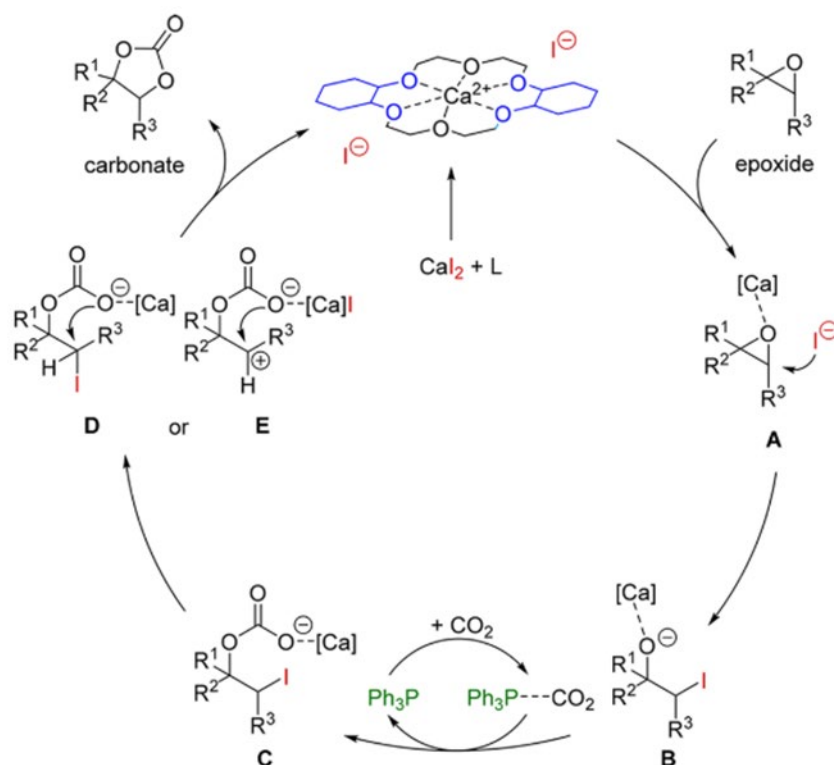
at relatively mild reaction conditions, 60 °C and 20 bar.⁷³ Among the designed catalytic systems, the one containing 18-crown-6-ether showed the highest activity in terms of conversion (> 99%) and selectivity (> 99%) to the targeted carbonated compound after 24 h. The authors attributed the excellent catalytic performance of the catalytic system containing the 18-crown-6-ether to its higher solubility in the reaction media. The authors tested the same catalytic system at milder reaction conditions, 45 °C and 10 bar achieving a yield to the carbonated product of 24% after 24 h of reaction time. To keep the milder reaction conditions (45 °C and 10 bar) and increase the overall reaction yield, the authors added 5 mol% of other additives (co-catalysts) to the catalytic system such as DABCO, TBD, DBU, DMAP or triphenylphosphine (TPP). Indeed, the presence of these co-catalysts improved the overall yield at least in ca. 330% from 24% to 81%. Even in the case of TPP, the yield increased by more than 400%, from 24% to 98%. The authors claimed the improvement was due to the additives (co-catalysts) acting as activators of the CO₂ molecule. Taking into account these results, the authors proposed a mechanism in four steps for a catalytic system formed by CaI₂, 18-crown-6-ether and TPP as shown in **scheme 3**. Before the catalytic cycle starts must take place the “*in situ*” formation of a calcium complex with the crown ether. After, upon addition of the epoxide the Lewis acid character of the calcium makes easier the activation of the epoxide ring by interacting with the oxygen atom (**A**). Then the epoxide undergoes nucleophilic attack by the iodine anion yielding the corresponding alkoxide (**B**). After, the alkoxide attacks the CO₂ molecule previously activated by the TPP yielding the carbonate compound (**C**). Finally, the intramolecular ring closing takes place (**D** or **E**) liberating the catalyst and yielding the desired cyclic carbonate. In **table 5** are shown selected alkali metal salts-based employed catalytic systems, the reaction conditions, the conversion, and the selectivity to target products (when given) in the CO₂ cycloaddition to different vegetable oils or similar substrates.

Table 5. Alkali metal salts-based catalytic systems used in carbonated oleochemicals synthesis.

Catalyst (equiv.)	co-catalyst (equiv.)	Epoxidized oleochemical	Reaction conditions				Conv. (%)	Select. (%) ^b	Ref.
			<i>T</i> (°C)	<i>P</i> (bar)	<i>t</i> (h)	<i>Cat</i> mol%			
KBr	-	Soybean oil	100	>103	40	3	6	-	46
LiBr	-	Soybean oil	100	>103	40	3	0	-	46
KI	-	Fatty acid methyl ester	100	100	17	5 ^a	2	99	47

KI (1)	18-crown-6 (0.7)	Soybean oil	130	60	120	0.3 ^a	98	-	72
KBr (1)	18-crown-6 (0.7)	Methyl linoleate	100	100	17	5 ^a	55	97	47
KI (1)	18-crown-6 (0.7)	Methyl linoleate	100	100	17	5 ^a	90	97	47
NaI (1)	15-crown-6 (0.7)	Methyl linoleate	100	100	17	5 ^a	94	89	47
LiI (1)	12-crown-6 (0.7)	Methyl linoleate	100	100	17	5 ^a	18	98	47
CsI (1)	18-crown-6 (0.7)	Methyl linoleate	100	100	17	5 ^a	10	99	47
KI (1)	PEG400 (0.7)	Methyl linoleate	100	100	17	5 ^a	84	99	47
		Fatty acid methyl ester					>99	>99	
CaI ₂ (1)	18-crown-6/TPP	Sunflower oil	45	5	24	5	99	99	73
		Soybean oil					99	82	
		Linseed oil					80	65	

^acatalyst in wt.%; ^bselectivity to the cyclic carbonate product.



Scheme 3. Mechanism proposed by L. Lars et al for the CO₂ cycloaddition to an epoxide catalyzed by CaI₂, 18-crown-6-ether and TPP catalytic system.⁷³ Reprinted with permission from *ACS Catal.* **2018**, *8*, 1, 665-672. Copyright 2017 American Chemical Society.

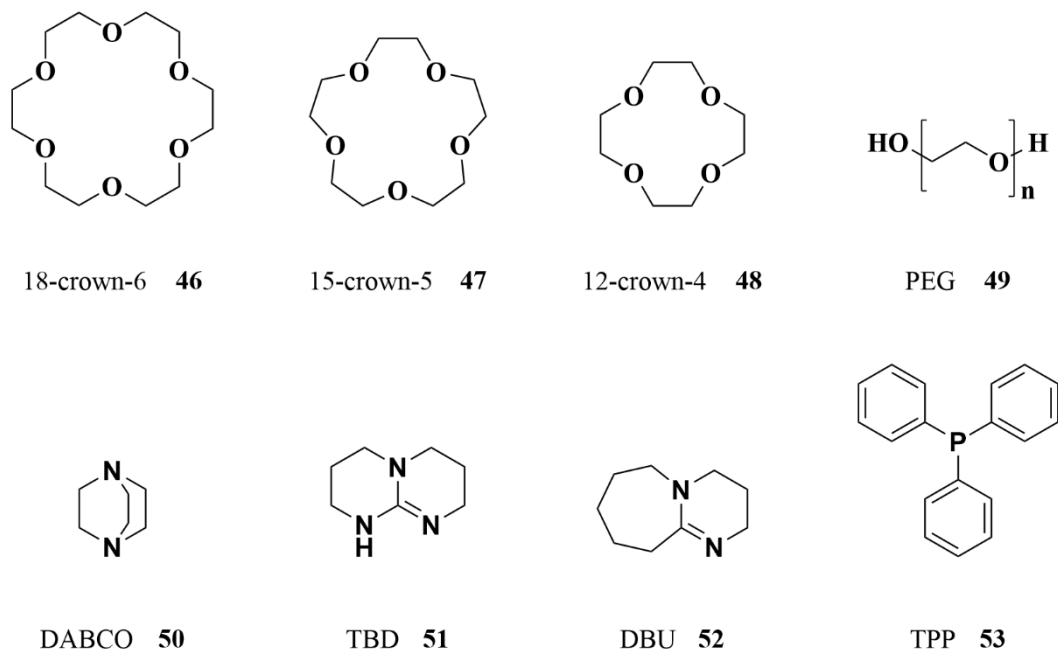


Figure 3. Additives employed as co-catalyst to improve the catalytic performance of alkali metal salts.

2. Heterogeneous catalytic systems

Homogenous catalytic systems are the most extensively studied in the cycloaddition of CO₂ to epoxidized oils and/or derivatives to yield the corresponding cyclic carbonates. However, the relevance of an efficient and easy separation and reutilisation of the catalyst, as well as the development of more sustainable processes strongly push researchers to design easily recoverable and reusable heterogeneous catalytic systems.⁷⁴ Despite this strong interest in the use of heterogeneous catalytic systems due to their remarkable advantages, very few works (only 5 to the best of our knowledge) reported the use of them in the synthesis of carbonated oleochemicals from CO₂. In this regard, M. Bähr et al. compared the catalytic performance of the benchmark [TBA][Br] (**1**) ionic liquid catalyst with a heterogeneous catalyst in the CO₂ cycloaddition to epoxidized linseed oil to yield the corresponding carbonated compound to be employed in the non-isocyanate polyurethanes synthesis⁷⁵. The catalyst was a silica-supported 4-pyrrolidinopyridinium iodide (SiO₂-I). At 140 °C and 30 bar, full conversion of the epoxidized linseed oil was achieved with [TBA][Br] (**1**) ionic liquid as catalyst after 20 h reaction time, while to achieve same conversion with the heterogeneous catalysts (SiO₂-I) 45 h were needed. The authors attributed the longer reaction time needed with the heterogeneous catalyst to the size of the silica pores, which limited the approach of the bulky epoxidized linseed oil. In fact, the authors suggest that as solution to improve the catalytic performance of SiO₂-I catalysts, would be to increase the silica pore size, tailoring the pore compartments as well as to increase the spacer length (linker) between the silica support and the alkyl ammonium groups. B. Schäffner et al. tested a heterogeneous catalytic system prepared by impregnation of the benchmark [TBA][Br] (**1**) ionic liquid homogeneous catalyst on silica as support in the synthesis of carbonated methyl linoleate from CO₂ and epoxidized methyl linoleate at 100 °C and 100 bar.⁴⁷ After 17 h of reaction, the conversion of the homogeneous system was found to be 4.6 times higher compared with the heterogenized system (15% vs. 69%) but the selectivity with both systems was similar > 99% towards the carbonated product. The authors attributed the drop in conversion of the heterogeneous systems to well-known mass transfer limitations in this kind of catalysts. With the objective of developing a kinetic model for the synthesis at industrial scale of carbonated oleo compounds, X. Cai et al. tested a heterogeneous catalyst obtained by supporting via a noncovalent linkage a task-specific ionic liquid [HBIIm][Cl] (1-hydroxypropyl-3-*n*-butylimidazolium chloride) and NbCl₅ on protonated carboxymethyl cellulose (HCMC) as support. The heterogeneous catalytic system ([HBIIm][Cl]-NbCl₅/HCMC) was tested in the synthesis of carbonated fatty acid methyl esters obtained from cottonseed oil, and parameters such as temperature, pressure, stirring rate, particle size, and catalyst loading were investigated.⁷⁶ The optimal parameters to afford high carbonation of the epoxidized compounds were found to be 170 °C, 30 bar, 500 r.p.m., 652 μm particle size and 0.71 mol/L catalyst amount. A. Akhdar et al. prepared several heterogeneous catalytic systems by covalent support of

imidazolium-based ionic liquids with thermomorphic polyethylene (TMPE).⁷⁷ The catalytic performance of these prepared catalytic systems was evaluated for the ring opening of epoxidized methyl oleate with CO₂. Among the heterogeneous catalytic systems tested, the one composed by bromide anion and N-methylimidazole cation ([MeIm][Br]-TMPE) produced the highest epoxide conversion (> 99%) with a selectivity of 93% towards carbonated methyl oleate after 20 h at 100 °C, 20 bar and using 4 mol% catalyst. Comparable catalytic activity to homogeneous [TBA][Br] (**1**) ionic liquid catalyst was achieved with this catalyst in terms of conversion (> 99% vs. 96%) and selectivity (93% vs. 97%) at the same reaction conditions. However, while [TBA][Br] could not be recovered and reused, the prepared heterogeneous catalyst could be easily recovered and reused up to 10 times without any significant loss of catalytic activity. W. Y. Perez-Sena et al. evaluated the performance of various organic salts supported on silica gel and SBA-15 in the synthesis carbonated methyl oleate.⁷⁸ Among the tested catalytic systems, the 4-pyrrolidino pyridine supported on SBA-15 and doped with a molar ratio of 0.12 Zn/Si (Zn-SBA-15(0.12)-4PPI) (7.4 wt.%) was found to be the most active, reaching a suitable epoxide conversion (75%) and carbonate selectivity (91%) at 140 °C and 30 bar after 32 h of reaction. The same catalytic system was used for the synthesis of carbonated methyl esters from cottonseed oil and tall oil under similar reaction conditions (140 °C, 30 bar, 7.4 wt.% and 23 h). Nevertheless, the catalytic activity was considerably lower in terms of conversion (47% and 57%) and selectivity (85% and 60%) comparing with using methyl oleate as precursor. In **table 6** are shown selected employed heterogeneous catalytic systems, the reaction conditions, the conversion, and the selectivity to target products (when given) in the CO₂ cycloaddition to different vegetable oils or similar substrates.

Table 6. Heterogeneous catalytic systems used in carbonated oleochemicals synthesis.

Catalyst	Epoxidized oleochemical	Reaction conditions				Conv (%)	Select (%) ^c	Ref.
		<i>T</i> (°C)	<i>P</i> (bar)	<i>t</i> (h)	<i>Cat</i> (mol%)			
SiO ₂ -I	Linseed oil	140	30	45	3	100	-	⁷⁵
1 on SiO ₂	Methyl linoleate	100	100	17	2	15	99	⁴⁷
HBimCl-NbCl ₅ /HCMC	Cottonseed oil methyl ester	170	30	8	0.71 ^a	> 90	-	⁷⁶
[MeIm][Br]-TMPE	Methyl oleate	100	20	20	4	> 99	93	⁷⁷
Zn-SBA-15(0.12)-4PPI	Methyl oleate	140	30	32	7.4 ^b	75	91	⁷⁸
	Cottonseed oil methyl ester	140	30	23	7.4 ^b	47	85	
	Tall oil methyl ester	140	30	23	7.4 ^b	57	60	

^acatalyst in mol/L; ^bcatalyst in wt.%; ^cselectivity to the cyclic carbonate product.

Conclusion and outlook

Unquestionably, polymers are present elsewhere (homes, car, clothes etc.). Therefore, they were, they are and they will be essential in our civilization development and daily life. Among the used polymers, polyurethanes (PUs) and polycarbonates (PCs) are of particular interest due to their vast field of applications. Unfortunately, these synthetic polymers are mainly manufactured employing petroleum-based feedstocks. The depletion of petroleum resources, the market instability, the rising environmental awareness, and health concerns are strongly pushing the scientific community to look bio-based feedstocks for the synthesis of more environmentally friendly polymers. Bio-based cyclic carbonates that can be obtained from CO₂ chemical fixation into epoxidized vegetable oils and/or their derivatives are of special importance because they can be used in the synthesis of more sustainable non-isocyanate PUs (NIPUs) and PCs. For this reason, the chemical fixation of CO₂ into bio-based epoxidized compounds to bio-based cyclic carbonates has aroused enormous interest in both the scientific community and industry. In the chemical fixation of CO₂, the catalytic systems are essential to produce the desired bio-based cyclic carbonates efficiently. Therefore, the development of efficient catalytic systems for the CO₂ chemical fixation via cycloaddition is probably the most determining step towards both conversion and selectivity of the targeted bio-based cyclic carbonates. The catalyzed CO₂ cycloaddition with bio-based epoxidized compound generally follows a three-step mechanism 1) ring-opening, 2) CO₂ insertion, and 3) ring closure, being the ring-opening the rate-determining step. Different ionic liquid-based or ionic compound-based have revealed promising catalytic systems in the cycloaddition of CO₂ to epoxidized vegetable oils or derivatives. Nevertheless, their catalytic performance depends largely on the nature of the bio-based epoxidized compound e.g., vegetable oil, fatty acid etc., having internal epoxides difficult to reach due the increased steric hindrance. The diversity of ILs and their easy functionalization make them materials with great potential to develop catalytic systems able to perform the targeted reaction for example by employing a more nucleophilic anion or by adding a functionalization on the cation. The majority of the catalytic systems reported so far have the objective of facilitating the rate-determining step in the catalytic cycle. One of the most widely employed catalyst is the tetrabutylammonium bromide ionic liquid [TBA][Br], occasionally used as a benchmark catalyst to compare new catalytic systems. In order to find alternatives to the benchmark ionic liquid catalyst few authors have developed different homogenous catalytic systems e.g., non-functionalized ionic liquids using different ammonium, phosphonium, pyridinium, etc., as cations, functionalized ionic liquids with different moieties such as hydroxyl, carboxyl; catalytic binary systems by combination of an ionic liquid with a Lewis acidic compound or a HBD molecule; and other ionic compounds such as alkali metal salts. In spite of their many practical advantages, heterogeneous catalytic

systems are less developed in the synthesis of bio-based cyclic carbonates, and only few examples have been reported so far with limited success. In all the ionic catalytic systems developed the most common anions employed are halogens, being the bromide and the iodide the preferred ones. This is usually attributed to their high nucleophilicity and leaving group ability that is key for the ring-opening step. Regarding the cations, those bulkier are preferred because their higher steric hindrance allows a lower interaction with the anion improving its nucleophilicity. Nevertheless, it is difficult to extract conclusions about what is the best catalytic system, if any, reported so far due to the vast and diverse conditions employed in the different scientific literature dealing with this topic. Nevertheless, it seems clear that the selection of the catalytic system strongly depends on the nature of the selected bio-based substrate.

During the last decade, great advances that have been made on the development of catalytic systems for the CO₂ cycloaddition to bio-epoxides to yield the corresponding cyclic carbonates. Nevertheless, it is difficult to compare their efficiency due to the lack of common conditions and/or the vast number of different bio-based vegetable oil-derived epoxides. Therefore, in our opinion, to develop more robust, efficient and versatile catalytic systems that can make more attractive to the polymer industry the CO₂ cycloaddition reaction the following points should be taken into account.

- The catalytic performance of the different catalytic systems requires in some way more standardization. The catalyzed CO₂ cycloaddition to bio-based epoxidized compounds was carried out under a vast range of reaction conditions in terms of temperature and pressure, reaction times, using different substrates (from the relatively easily to carbonate methyl oleate to less reactive vegetable oils. High yields to desired bio-based products were often achieved at high temperatures and pressures within short reaction times while under mild conditions the bio-based targeted compounds were achieved increasing the reaction time. Consequently, the different reaction conditions and systems hamper the direct comparison of the catalytic performance. The calculation of TON and TOF values could help in the catalytic performance comparison between the catalytic systems. Additionally, there is a lack of kinetic studies in most of the literature on this topic. Kinetic information could provide useful information for better catalytic systems design.
- The nature of the bio-based epoxidized compound will strongly determine the final application of the obtained bio-based carbonated compound. The use of epoxidized methyl oleate (where only one epoxide group is present) is more or less established as a benchmark substrate for testing new catalytic systems, even if the reaction conditions change substantially from work to work. However, it should be taken into account that in bio-based NIPUs and PCs synthesis at least two epoxide groups would be required in the bio-based substrates to allow the polymerization reaction. Therefore, the employment of other bio-based substrates such as epoxidized linoleic or lionoleic acid (containing 2 epoxide groups) should be implemented before moving to use more complex substrates such as epoxidized vegetable oils.

- It looks clear from the reported scientific literature that the addition of a co-catalysts such as HBD molecules, Lewis acidic metal sites or crown-ethers has a positive effect promoting the chemical CO₂ fixation to bio-based epoxidized compounds and rarely inhibits the performance of the catalytic system. The promoting effect is mainly attributed to the synergy of the co-catalysts with the ionic moieties of the employed catalysts. Nevertheless, there is not a deep understanding of the mentioned synergistic effect. Experimental and theoretical research would be needed to understand better the catalytic system. All the collected information would provide a better understanding for a more accurate and efficient catalytic systems design.
- Most of the published works dealing with the obtention of bio-based cyclic carbonates from CO₂ cycloaddition to be used in bio-based polymer synthesis use pure epoxidized bio-based materials as substrates e.g., epoxidized vegetable oil. Nevertheless, most of the available vegetable oils are edible and compete with the food chain. Therefore, the employment of non-edible (e.g., used cooking vegetable oil) should be encouraged. To the best of our knowledge, there are no examples in the scientific literature dealing with the carbonatation of epoxidized used cooking vegetable oil by CO₂ chemical fixation, which remain a huge and exciting challenge, just like the efficient recovery and reuse of the catalytic system by developing biphasic or heterogenization methods. In addition, the employment used vegetable oils as feedstock and CO₂ will contribute undoubtedly to the circular economy. An evaluation from the industrial viewpoint would be required to “catalyze” in a realistic frame of time, the transfer of the catalytic systems designed at the laboratory level towards industrial implementation.

In summary, taking into account the scarce scientific literature on the topic of this review, there is a need of further improvement and a better understanding of the CO₂ chemical fixation by cycloaddition to complex bio-based epoxidized compounds such as vegetable oils to yield bio-based cyclic carbonates as intermediates in the synthesis of more sustainable polymers. Indeed, a deeper and more conscientious understanding will lead in the next future to a more efficient design of versatile and recoverable catalytic systems able to conduct this challenging transformation at mild reaction conditions representing a huge step towards its sustainability and industrial implementation.

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