

Recent advances in the use of catalysts based on natural products for the conversion of CO₂ into cyclic carbonates

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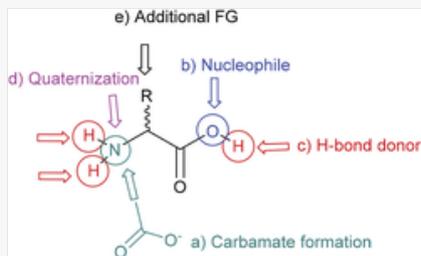
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Abstract

The cycloaddition of carbon dioxide to epoxides is an efficient and clean method to obtain cyclic carbonates, which are used as green solvents, as electrolytes for lithium batteries and as intermediates for the synthesis of polymers and chemicals. This reaction requires a catalyst to overcome the low reactivity of carbon dioxide. The best catalysts for this transformation include a Lewis acid or hydrogen-bond donor to activate the epoxide and a Lewis base as a nucleophile to open the ring of the oxirane cycle. The most commonly used catalysts are alkali halides, ammonium and phosphonium salts, which are organocatalysts containing hydrogen-bond donor groups and metal-based systems. To increase the sustainability and decrease the toxicity of the catalytic systems, many bio-based products derived from natural sources have been used as catalysts or in combination with catalytic materials. The high functionality of natural products that contain amino and/or hydroxyl groups is used to activate an epoxide or reversibly capture carbon dioxide when used directly. But these products can also behave as auxiliaries, for instance, as ligands in metal-based complexes, as biopolymer active supports for catalysts, as components for the skeleton of metal organic frameworks or to form ionic liquids or as deep eutectic solvents serving as an active medium for catalytic reactions. In this literature review, we present a structured overview of the reported chemical catalytic systems containing any component derived from a natural product. We discuss the amino acid-based systems, cellulose, saccharides, lignin and lignocellulosic materials, choline-derived species, guanidine and guanidinium salts, and other less explored compounds. Special emphasis has been placed on mechanistic studies providing information about the role of each component in these multifunctional systems.

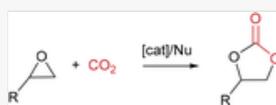
1. Introduction

Carbon dioxide is the product of the aerobic combustion of carbon-containing products. As such, huge amounts of it are generated by human activities such as fuel combustion to obtain energy, for transport and for industrial production (e.g. in the manufacturing of cement). These activities produce anthropogenic emissions of approximately 30 Gt of carbon dioxide annually, which has accumulated in the atmosphere, reaching a concentration of 400 ppm.¹ This increase in the concentration of carbon dioxide, a greenhouse gas, has caused global temperatures to rise and affected the global climate. Although governments began to be concerned about climate change in the 1980s,² only in recent decades has society become aware of the problems associated with global warming. Many social movements, encouraged by media personalities, have called on governments to implement policies to regulate greenhouse gas emissions. As a result, United Nations Secretary-General reports from recent climate summits (Kyoto 1992, Paris 2015 and Chile-Madrid 2019)³ have indicated that carbon dioxide (CO₂) emissions must be reduced by 45% by 2030 and reach net zero by 2050 to limit global warming to 1.5 °C. Achieving this goal requires a combination of efforts in different areas. Firstly, reducing carbon dioxide emissions is critical. However, this issue has been the object of heated debate in developing countries and governments opposed to reform. A second, complementary approach is to capture carbon dioxide emitted in the combustion processes to balance emissions. But this also requires efficient storage and utilization of the captured carbon dioxide. As a consequence of this challenge, research into CO₂ capture and

utilization (CCU) has grown exponentially in the last few years,^{4,5} especially with regard to transforming CO₂ into valuable chemicals⁶⁻¹¹ and fuels.^{12,13} This is a very appealing idea, since carbon dioxide should not be considered as only a by-product of fossil fuel combustion, but also as a potentially cheap and abundant source of carbon for all carbon-based materials. Unfortunately, the carbon in CO₂ is at its most stable valence^{‡(IV)} and CO₂ is a very stable molecule ($\Delta G_f^\circ = -394.228 \text{ kJ/mol}^{-1}$).¹⁴ So, to transform CO₂ into other products, a catalyst and/or a highly reactive co-reactant must be used. Chemical catalysts for CO₂ conversion include a wide variety of materials such as heterogeneous¹⁵⁻¹⁷ and homogeneous metal-based complexes,^{16,18,19} metal-organic frameworks (MOFs),²⁰ nanocatalysts,²¹ ionic liquids (ILs)^{† 22-25} and organocatalysts.²⁶⁻²⁸ Biocatalysts such as enzymes and other cellular components present in micro-organisms have also been used for CO₂ reduction.^{9,29-31} To develop greener chemical processes using sustainable materials, products derived from bio-sources have been used in ~~the~~ different steps involved in carbon dioxide excess remediation. The high functionalities of products such as amino acid salts,³² saccharides,³³ and biopolymers such as cellulose³⁴ and chitin derivatives³⁵ make them ideal ~~for~~ use in carbon dioxide capture. For this reason, they have also increasingly been ~~used~~ utilised in place of more toxic or expensive ~~chemicals~~ products in chemical catalytic systems for carbon dioxide transformation.

One of the most studied reactions ~~is~~ the atom-economical cycloaddition of CO₂ to epoxides to form cyclic carbonates (Scheme 1). Epoxides are highly constrained molecules that react with carbon dioxide in the presence of a Lewis base able to catalyse the ring-opening of an epoxide to allow the insertion of carbon dioxide. Moreover, when an epoxide is activated with a Lewis acid catalyst, the reaction proceeds faster. Several excellent preceding reviews have focused on ~~the~~ different aspects of this reaction. Thus, article reviews reporting the advances in using heterogeneous catalysts,^{15,36} homogeneous catalytic systems,^{37,38} highlighting the possibilities of the synthesis of cyclic carbonates under mild conditions^{39,40} or centring the attention on organocatalysts^{27,41} have been published in the last decades and are reference articles. Recently, bio-based substances have been introduced in many catalytic materials used in this transformation to create cheaper, more benign and more sustainable catalytic systems. They may be the only component in the catalyst or can be combined with other substances. Their role may be as organocatalysts or ligands in metal-based coordination compounds, structural elements in metal-organic frameworks (MOFs) or as a component in ionic liquids (ILs). There are also some publications that have reviewed the use of some bio-inspired systems for CO₂ capture, sequestration and utilization,^{31,42} but a systematic revision of the most recent advances in this particular field is missing. Therefore, in this review, we focus on chemical catalytic systems based on natural products and derivatives used for the reaction of CO₂ with epoxides to form cyclic carbonates for the analysis of potential applications, with special attention to theoretical mechanistic aspects.

Scheme 1



Cycloaddition of CO₂ to ~~epoxides to~~ form cyclic carbonates.

2. Cycloaddition of CO₂ to epoxides

The cycloaddition of CO₂ to epoxides leads to the formation of cyclic carbonates (Scheme 1),⁴¹ which are important products due to their wide range of applications,^{43,44} e.g. as polar aprotic solvents,⁴⁵⁻⁴⁷ electrolytes in lithium-ion batteries,⁴⁸ industrial lubricants,⁴⁹ monomers for polymer synthesis⁵⁰⁻⁵² or as useful intermediates for the preparation of a wide variety of organic chemical products.^{53,54,44,53}

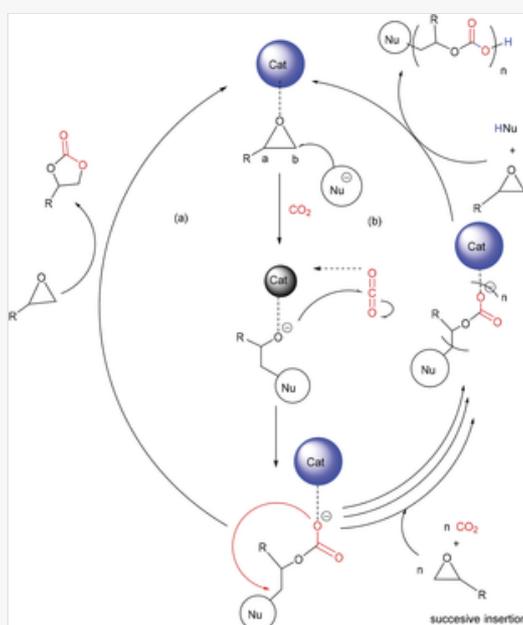
Due to the relatively inert nature of CO₂, this reaction needs a catalyst to take place. As a result of the large number of studies devoted to this reaction, many ~~kinds of~~ homogeneous and heterogeneous catalytic systems have been developed for this transformation. Among them, there are metal-based catalytic systems such as metal halides,⁵⁵ metal-organic complexes,⁵⁶⁻⁶¹ metal-organic frameworks,^{62,63} metal oxides,⁶⁴ ~~transition~~ metal chlorides,⁶⁵ and organocatalysts

such as organic salts,^{26–28,66} ionic liquids^{22,24,25,67} and hydrogen bond donor compounds.^{68–72} Additives to enhance the catalytic activity in binary catalytic systems have also often been used, including halides, quaternary onium salts, organic bases such as 4-dimethylamino-pyridine (DMAP), 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5,7-tri-aza-bicyclo[4.4.0]dec-5-ene (TBD) or other amines such as monoethanolamine (MEOA), diethanolamine (DEOA), triethanolamine (TEOA), triethylamine (TEA), diethylamine (DEA), *N,N*-dimethylaminopyridine (DMAP), pyridine (Py) and tetramethylethylenediamine (TMEDA)^{39,73–77,39,57,74–77} or carbenes.^{78,79} Besides, many authors have been interested in introducing naturally occurring materials as catalysts or as part of binary catalytic systems. Employing natural products or derivatives is, certainly, an advance towards a greener application of catalysis. The results and mechanistic considerations of the application of these bio-based catalytic materials to the cycloaddition of CO₂ to epoxides are discussed in the next sections.

The cycloaddition of carbon dioxide to epoxides requires opening the oxirane ring, inserting CO₂ and closing the ring to form the cyclic carbonate, as illustrated in the mechanism shown in Scheme 2a. Most studies, based on experimental evidence and computations, suggest that the reaction follows this three-step mechanism, **regardless-independently** of the type of catalyst used.^{11,37,39–41,80–82} Catalytic systems that stabilise intermediates and/or decrease reaction barriers will promote the reaction. Since the ring-opening step has the highest barrier, effective catalysts should promote **preferentially,preferentially** this process. Ring-opening can be initiated by a nucleophilic attack at the α or β carbon of an epoxide, so active catalytic systems for this transformation generally involve a Lewis base acting as the nucleophile. In addition, the epoxide can be further activated by interaction with a Lewis acid or an H-bond donor (HBD). These interactions further decrease the barrier of this step so the reaction can proceed faster. In order to achieve this **doubledouble** effect, catalysts are often designed to contain a binary combination of Lewis base/acid or Lewis base/HBD. Both components can also be included in the same molecule, forming what have been called bifunctional systems. Despite this beneficial effect of catalysts, mechanistic studies on different systems have shown that the epoxide ring-opening process continues to have the highest energy barrier, making it the rate-determining step.^{69,83–86} Nevertheless, in some systems the ring-closure step seems to have a higher barrier, which breaks this general rule.^{71,87} Some studies propose a mechanism that involves the activation of CO₂ before the epoxide. In these cases, carbonates or carbamates are formed that may also participate in the ring-opening step. This is the reason for the good activity of catalysts based on amino acid or nucleobases, for example, as will be seen later. The particularities of the mechanisms proposed for **the** different catalysts in this review will be addressed throughout the paper.

Scheme 2

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Generally accepted mechanism for the synthesis of (a) cyclic carbonates by cycloaddition of CO₂ to epoxides and (b) polycarbonates.

The coupling of CO₂ and epoxides may also yield polycarbonates when the insertion of a new epoxide molecule competes with the ring-closing process and an alternate copolymerization of CO₂ with the epoxide takes place (Scheme 2b). In many cases, selectivity seems to rely on a specific balance between the catalyst and cocatalyst and their ratio,²⁷ but it can also depend on the type of solvent, the temperature or the substrate. Most of the catalysts leading to polycarbonates are based on metal complexes. According to the general catalytic cycle proposed for homogeneous metal catalysts, selectivity can be determined in the ‘backbiting’ nucleophile leaving step, to close the cyclic carbonate ring, or lead to successive insertions.

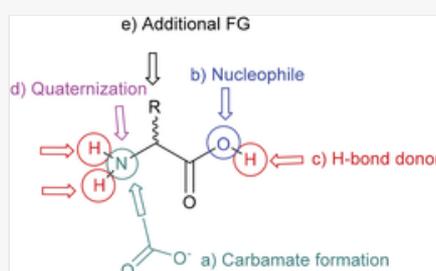
In the following sections, the results obtained for the cycloaddition of CO₂/epoxides using catalytic systems containing some component derived from the natural pool products are discussed presented by organis eding according to the kind of compound category. The most significant results for the cycloaddition of CO₂ to the commonly studied epoxides, mainly propylene oxide (PO), but also styrene oxide (SO), epichlorohydrin (ECH) and allyl glycidyl ether (AGE), are presented in tables. The yields of other carbonates are also commented in the text for some of the more active catalysts.

3. Amino acid-based catalytic systems

Amino acids (AAs) are highly functionalised natural products that have been used extensively as catalysts for organic reactions, and as unmodified organocatalysts or as auxiliaries or ligands for metal complexes. They are considered to be “one of the most versatile class of natural, bio-renewable, and non-toxic raw materials from nature’s toolbox”.⁸⁸ They are often selected as a natural source of chirality.⁸⁹

The versatility of AAs stems from their high degree of functionalization (Fig. 1). Firstly, AAs contain N–H groups that can react with CO₂ to form carbamate–bicarbonate products with low binding energy, which can catalyse the transference of CO₂ to the substrates. Several AA salts have been successfully used in the post-combustion capture of CO₂. The example of the Siemens process is quite remarkable. This process reduces the energy consumption of the monoethanolamine (MEA) CO₂ capture process by 37%.^{90,91} Another functionality that plays a role as a catalyst in the fixation of CO₂ in the carbonates is the ionic carboxylate group –COO[–] which can act as a nucleophile. AAs also include the amino group –NH₂ and hydroxyl –OH to activate the epoxide by forming a hydrogen bond. Furthermore, the amino groups can also be used to introduce halide nucleophiles through quaternisation.⁹² Finally, additional functional groups (FG) can be introduced through the AA skeleton. For example, basic AAs such as histidine contain an additional imidazole group, or an additional carboxylate function can be found in aspartic acid.

Fig. 1



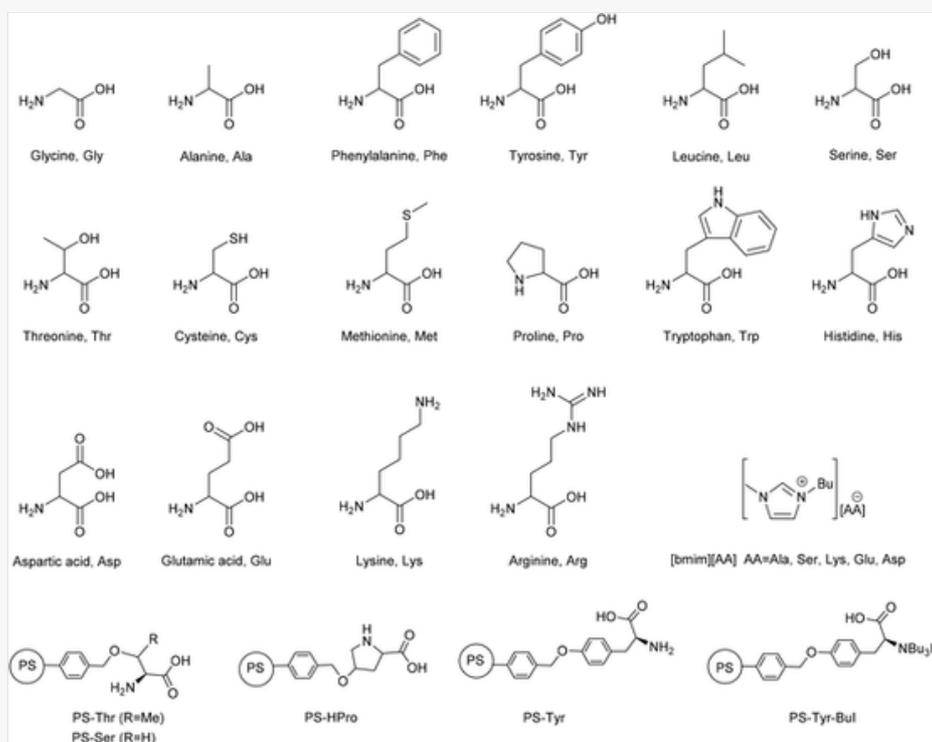
Different functions of amino acids related to their role as catalysts for the cycloaddition of CO₂ to epoxides.

In addition to the intrinsic functionalities of AAs, other functionalities can arise from AAs used in the ionic form. Good examples of this concept are ionic liquids (ILs) formed with ionic AAs (R–C(NH₂)COO[–]) and imidazolium cations widely used as catalysts for this reaction. ILs based on AAs have the advantage of replacing commonly used halides to reduce their environmental impact.

3.1. Amino acid systems

Most of the naturally occurring amino acids (AAs) catalyse the coupling of CO₂ with epoxides, although they require high temperatures, long reaction times and the use of a solvent to produce high yields of cyclic carbonates. The structures of AAs involved in the catalytic systems selected in this review are shown in Fig. 2. The selected results obtained using the AA-containing systems in the cycloaddition of CO₂ to propylene oxide (PO) are reported in Table 1

Fig. 2



Structure of the selected amino acids (AAs) and AA-based systems cited in this work: ionic liquids based [bmim][AA],⁹⁷ cross-linked-polystyrene-supported amino acids PS-AA⁹⁸ and post-functionalised PS-AA-RX (PS-Tyr-Bul).⁹⁹

Table 1

Cycloaddition of CO₂ to propylene oxide catalysed by AAs

Entry	Catalyst ^a	Cocatalyst ^b	Cat/cocat (mol%)	Solvent	T (°C)	P (MPa)	t (h)	Yield (%)	Ref.
1	L-Leu	—	0.6/—	CH ₂ Cl ₂	130	6	48	100	93
2	L-Met	—	0.6/—	CH ₂ Cl ₂	130	6	48	100	93
3	L-Pro	—	0.6/—	CH ₂ Cl ₂	130	6	48	100	93
4	L-Phe	—	0.6/—	CH ₂ Cl ₂	130	6	48	100	93
5	L-Lys	—	0.6/—	CH ₂ Cl ₂	130	6	48	100	93
6	L-His	—	0.6/—	CH ₂ Cl ₂	130	6	48	100	93
7	L-Arg	—	0.6/—	CH ₂ Cl ₂	130	6	48	88	93
8	L-Asp	—	0.6/—	CH ₂ Cl ₂	130	6	48	67	93
9	L-Glu	—	0.6/—	CH ₂ Cl ₂	130	6	48	29	93
10	L-Leu	—	0.8/—	—	130	8	48	63	94
11	L-Pro	—	0.8/—	—	130	8	48	51	94
12	L-His	—	0.8/—	—	130	8	48	100	94

13	L-His	H ₂ O	0.44/12.82	—	120	1.2	3	82 ^c	95
14	HBetI	—	2.5/—	—	140	8	8	98	96
15	QGly	—	2.15/—	—	120	1.2	2	84	92
16	L-His	KI	0.2/0.2	—	120	1	3	98	69
17	L-His	DBU	2/10	—	120	2	2	96 ^c	74
18	—	DBU	—/10	—	120	2	2	85 ^c	74

Table Footnotes

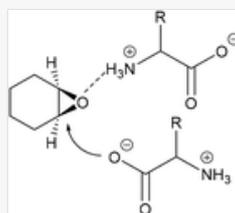
^a Abbreviations in Fig. 2 and Scheme 4, QGly = Gly with MeI under 10 minutes of microwave irradiation. HBetI = IMe₃NCH₂COOH.⁹²

^b DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene.

^c Estimated from conversion and selectivity data.

The initial report by Qi *et al.* on the cycloaddition of CO₂ to propylene oxide used dichloromethane as the solvent and harsh reaction conditions (130 °C and 6 MPa) over a prolonged reaction time (48 h) to obtain yields from 29% to 100% (entries 1–9, Table 1).⁹³ Under these conditions, the best catalysts were leucine (Leu), methionine (Met), proline (Pro), phenylalanine (Phe), histidine (His) and lysine (Lys). The yield was very much dependent on the structure of the AA; basic AAs performed better than acidic ones. So, histidine (His) and arginine (Arg) containing basic additional amino groups (imidazolium and amino, respectively) provided higher yields than aspartic (Asp) or glutamic (Glu) acids. The authors speculate that epoxide activation may take place through the Lewis acid interaction of the ammonium group of the ionic form of AA with the epoxide, and the carboxylate of another AA molecule acts as the nucleophile for the ring-opening of the epoxide, as shown for cyclohexene epoxide (Fig. 3).

Fig. 3



Proposed interactions of AAs with cyclohexene oxide that promote activation and ring-opening of epoxide. Adapted from Qi *et al.*⁹³

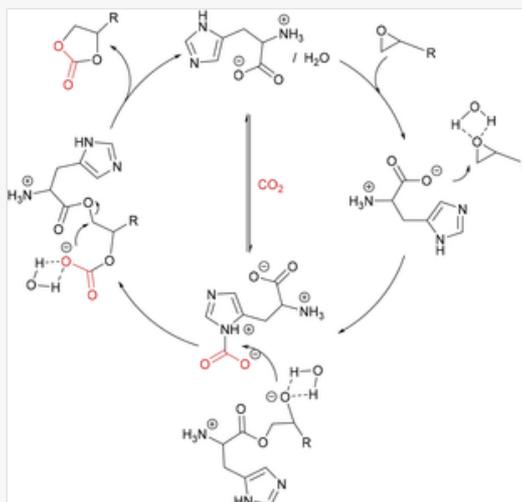
The CO₂ coupling with PO resulted in a substantially decreased yield working under supercritical conditions in the neat substrate for most of the current AAs (yields 5–78%), except when using L-His as the catalyst, which resulted in a 100% yield with no solvent needed (entries 10–12 and entries 1, 3 and 6, Table 1). The diminution of yield when the CO₂ pressure increased (up to 8 MPa) was attributed to the lesser solubility of the catalyst in the supercritical medium.⁹⁴

The combination of one amino acid with an H-bond donor results in a higher catalytic activity under milder reaction conditions than in the absence of HBD. For example, the binary catalytic systems formed with the amino acid pool with the simplest hydrogen bond donor, such as H₂O, produced more active systems for the synthesis of propylene carbonate than in the absence of H₂O.⁹⁵ As observed using AAs as catalysts, the highest conversions were obtained with basic amino acids with an extra amino functionality in the side chain. In the case of L-His, the time for nearly total conversion was reduced from 48 h to 3 h by adding H₂O (L-His : H₂O ratio = 1 : 29) under similar conditions (entries 12 and 13, Table 1).⁹⁵ The content of H₂O was optimised to avoid the hydrolysis of the carbonate product.

Using the binary AA/H₂O system, the authors proposed that the mechanism begins with the activation of the epoxide by H-bond with H₂O followed by ring-opening of the epoxide by a carboxylate group of L-His. In addition, carbon dioxide would react with the N–H of the imidazole of a second L-His molecule to form a carbamate (Scheme 3). The

alcoholate formed would undergo nucleophilic attack on the carbamate salt to insert CO₂ and, finally, ring-closing to form the cyclic carbonate.⁹⁵

Scheme 3



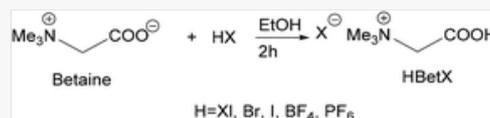
Proposed mechanism for the cycloaddition of CO₂ to epoxides catalysed by the L-His/H₂O binary system. Adapted from Tharun *et al.*⁹⁵

The combination of halide ions as nucleophiles with the HBD properties of the carboxylate in the AA group produced highly active catalytic systems for the cycloaddition of CO₂ to epoxides. Halide ions may be easily be introduced into the AA by the quaternisation of the amino group.

One possibility for quaternisation is adding halohydric acid to form AAHX. For example, L-His·HCl catalysts produced 76–80% yield of propylene carbonate under supercritical CO₂ conditions with a prolonged reaction time.¹⁰⁰ The introduction of the halide in the case of the Gly derivative, trimethylglycine or betaine, achieved by protonation of anhydrous betaine with acids (Scheme 4) was very successful.⁹⁶ Halide derivatives (X = Cl, Br, I) formed the best catalytic systems for the cycloaddition of CO₂ to propylene oxide producing high yields of propylene carbonate (94, 76, and 98% for X = Cl, Br and I, respectively) and were more active than the AA alone (entry 14, Table 1). Styrene oxide and 2-(phenoxy)methyl)oxirane were also converted under the same conditions with high yields (96–99%) using the betaine derivative (X = I). The iodide and bromide derivatives were partially soluble in the reaction media and could partly be separated by centrifugation. The recovered catalyst could be recycled twice without loss of catalytic activity.

Scheme 4

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Preparation of halogen betaine derivatives (HBetX) by protonation of anhydrous betaine with HX.⁹⁶

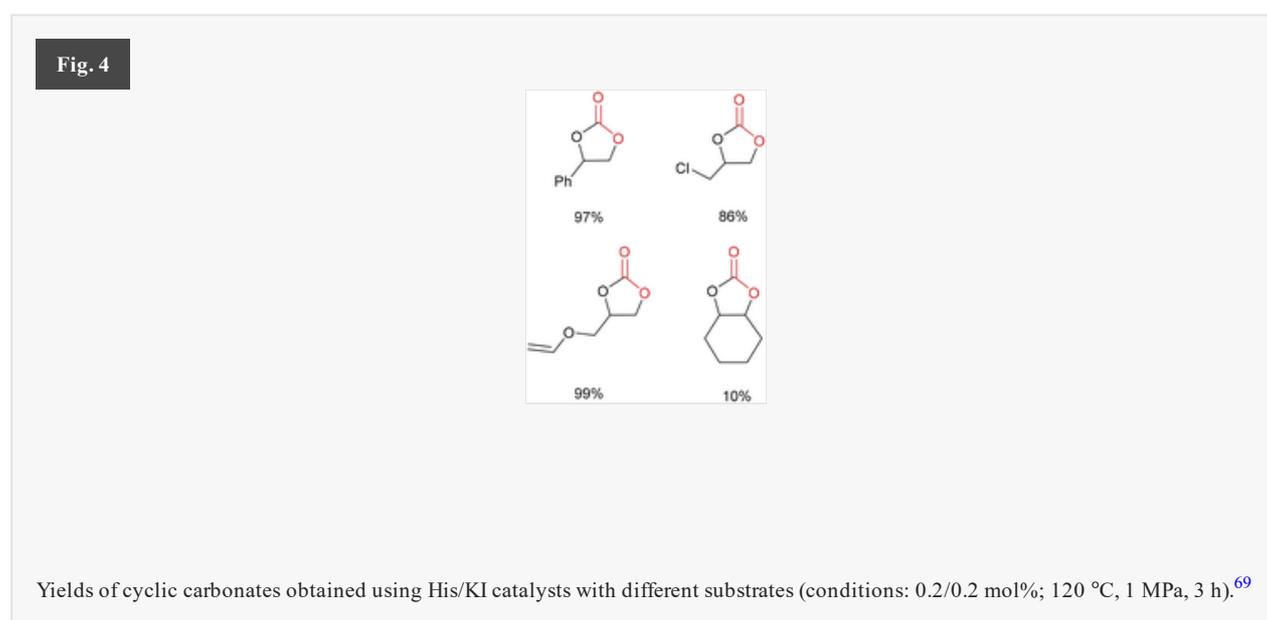
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Another possibility for quaternisation is the reaction of an AA with an alkyl halide RX. Using this method, Park's group prepared quaternised glycine, QGly, by reaction of Gly with MeI under microwave conditions very efficiently in only 10 minutes.⁹² The systems prepared in this way were highly active in the cycloaddition of CO₂ to allyl glycidyl ether (AGE) and terminal monosubstituted epoxides (79–93% yield, entry 15, Table 1). A DFT study was conducted

(at the B3LYP/6-31G(d,p) level) to determine the role of the $-\text{COOH}$ groups, the extra ether oxygen of AGE and the halide ion in this reaction. The results showed that, among the several postulated interactions of reactants, the most energetically favoured established a strong H-bond interaction between the $-\text{COOH}$ group of QGly and the ether oxygen, which enhances the activity of the catalyst. The nucleophilic attack of the halide ion at the β carbon of the epoxide leads to the opening of the ring with a barrier of $33.3 \text{ kcal mol}^{-1}$. The intermediate obtained evolves without further activation barriers to the product complex, that is $13.5 \text{ kcal mol}^{-1}$ more stable than the reactants. The mechanism proposed for this reaction diverges significantly from the well-known three-step reaction due to the absence of secondary reaction barriers.⁹²

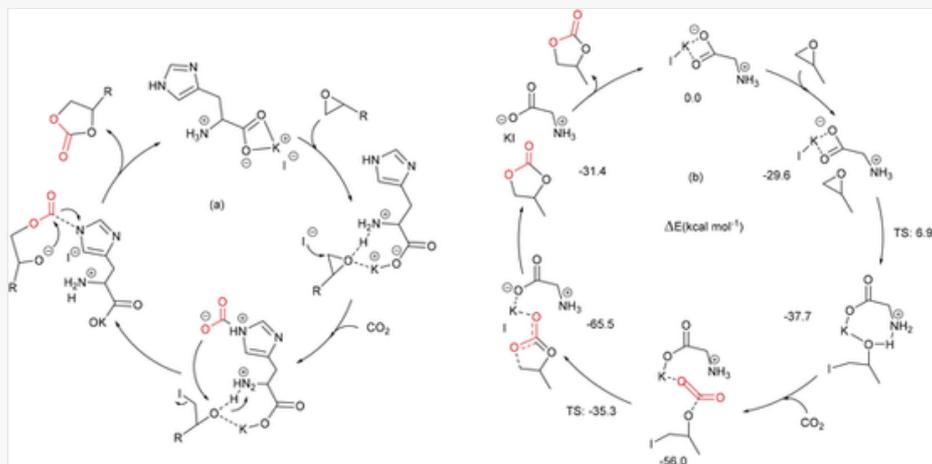
The combination of the acidic and basic hydrogen bonding groups with the halide ions of simple alkali metal salts MX (M = Li, Na, and K; X = Cl, Br, and I) resulted in active binary catalytic systems for the cycloaddition of PO under mild conditions ($120 \text{ }^\circ\text{C}$, 1 MPa) in 3 h with low catalyst loading.⁶⁹ The most effective binary catalytic systems contained KI with basic AAs such as His/KI (entry 16, Table 1). In a related work, Yang *et al.* proved the high stability of AA/KI catalytic systems, namely L-Trp/KI, for the cycloaddition of CO_2 to PO to form propylene carbonate. After carbonate separation by distillation, the catalytic system was reused five times without loss of activity.¹⁰¹ The catalytic activity of the different KX salts followed the order $\text{Cl} < \text{Br} < \text{I}$ corresponding to the increasing nucleophilicity and leaving group ability.⁶⁹ This confirmed the role of these anions in the opening of the epoxide ring. Other terminal epoxides were transformed into cyclic carbonates with high yields under the same conditions except for cyclohexene oxide (Fig. 4).



The authors proposed that the AAs' zwitterionic form activated the epoxide through an H-bond with the quaternised group while the additional basic moiety, imidazole in the case of the His, activated CO_2 to form the carbamate salt. The observation that the conversion obtained with protected His was smaller supports this hypothesis. To further confirm the approach, a computational study was performed to determine the reaction mechanism for the glycine-KI system and obtain the energy profile of the reaction pathway. DFT calculations were performed using the B3LYP functional and a mixed basis set (6-311++G(d,p) for all atoms except iodine, for which LANL2DZ was used). The results showed that the K^+ ion interacts both with the $-\text{COO}^-$ group of the zwitterionic AA and with the epoxide oxygen, while I^- attacks the β carbon of the epoxide, opening the ring (Scheme 5). This is the rate-determining step with a barrier of $36.5 \text{ kcal mol}^{-1}$. In the next step, the epoxide oxygen attacks the CO_2 carbon that is incorporated between glycine- K^+ and the open epoxide- I^- moieties. Eventually, the cycle is closed and the catalytic system is recovered.⁶⁹ The comparatively high barriers obtained in this work can be due to the use of a model system instead of the real one to perform the computational study. Nevertheless, the results can be considered meaningful to determine the reaction mechanism.

Scheme 5

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Proposed mechanism for His/KI catalysed cycloaddition of CO₂ to epoxides (a) based on the reaction profile obtained by DFT calculations for Gly/KI (b). Adapted from Roshan *et al.*⁶⁹

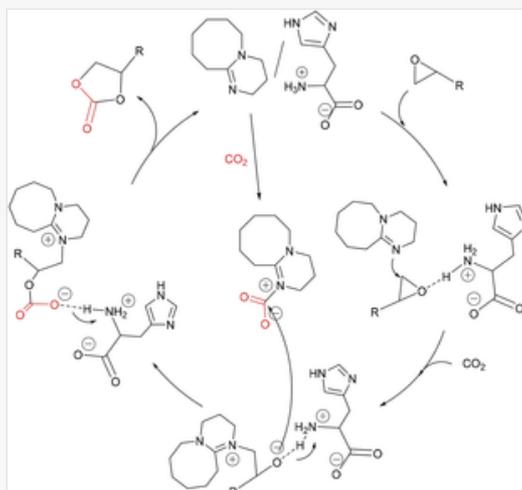
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To eliminate halides from the catalytic materials, different organic bases (DBU, MEOA, DEOA, TEOA, TEA, MTBD, DEA, DABCO, TBD, DMAP, Py, and TMEDA) were used as a cocatalyst in binary systems in combination with AAs (Gly, Thr, Pro, Tyr, His, Lys, Asp, and Trp, Fig. 2).⁷⁴ Under the conditions studied, the cycloaddition of CO₂ to propylene oxide with the combination of DBU/AAs reached conversions in the 86–97% range. The best results were obtained with the combination of a strong base such as DBU ($pK_a = 24.33$ ¹⁰²) and L-His, which increased the yield by approximately 10% obtained using only DBU as the catalyst (entries 17 and 18, Table 1).⁷⁴ In this work, the interaction of the epoxide with the ammonium zwitterionic form of the AA was detected by a shift in the NH stretching frequency of infrared spectra (IR). For example, this band for free L-His appeared at 3015.2 cm⁻¹ and shifted to 3016.9, 3017.4 and 3031.2 cm⁻¹ in the presence of 2,2-dimethyloxirane, 1,2-epoxihexane and styrene oxide, respectively, due to H-bond formation.⁷⁴ Apart from the activation of the epoxide, the base would act to open the epoxide ring and also capture CO₂, thereby forming the carbamate salt and transferring it to the alkoxide species (Scheme 6).⁷⁴ The fact that the different pK_a values of the bases do not correlate with the conversion observed indicates that other groups present in the AAs, such as -OH, may also participate in the activation of the epoxide. The hindrance of the bases may also affect the catalytic activity as well.

Scheme 6

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Proposed mechanism for the L-His/DBU catalysed cycloaddition of CO₂ to epoxides. Adapted from Qi *et al.*⁷⁴

3.2. Amino acid-based ionic liquids and deep eutectic solvents

Ionic liquids have proved to be one of the best catalytic systems for the cycloaddition of CO₂ to epoxides.^{22,24,25,67} ILs based on imidazolium cations containing Lewis acid cocatalysts notably increased the activity in the cycloaddition of CO₂ to epoxides, while at the same time facilitating the separation and recycling of the catalysts. In general, the anions of the IL salts are halides which have potent toxicity. To replace the halides, ionic liquids containing AAs (AA-ILs) were prepared and tested as catalysts for cyclic carbonate synthesis. ILs based on natural AAs not only decrease the toxicity of the ILs, a subject of constant debate in the scientific community, but also include a highly functionalised component in the IL.⁸⁸

Wu *et al.* reported the use of AA-ILs based on the 1-butyl-3-methylimidazolium cation [bmim]⁺ and amino acid anions as a catalyst for the synthesis of several organic carbonates from CO₂ and epoxides ([bmim][AA], Fig. 2).⁹⁷ Under comparative reaction conditions, the system with [bmim][Lys] achieved the highest yield. This was attributed to the presence of an extra amino group (entries 1–4, Table 2). Nevertheless, to achieve a 98% yield, a higher temperature (150 °C) and catalyst loading were required (3 mmol%) (entry 5, Table 2).⁹⁷ TOFs of up to 80 h⁻¹ at 48% isolated yield (entry 6, Table 2) were reported using [bmim][Asp] ionic liquid for the CO₂/epychlorohydrine cycloaddition.¹⁰³ The system was reused five times, separating the carbonate product by means of vacuum distillation, without loss of activity. Similar activities were obtained for terminal epoxides such as styrene oxide, propylene oxide, 1,2-epoxyhexane and 1,2-epoxyoctane. For these AA-ILs systems, it was suggested that the activation resulted from the interaction of the epoxide with imidazole cations and H-bond with the amino group of AAs, while the carboxylate anion would open the epoxide ring. The additional amino group present in the Lys-based system would react with CO₂ to form carbamates that may also have participated in the ring-opening step.⁹⁷

Table 2

Cycloaddition of CO₂ to epoxides catalysed by AA-based ILs (AA-ILs) and DES

Entry	Epoxide ^a	Catalyst ^b	Cocatalyst	Cat/cocat (mol%)	T (°C)	P (MPa)	t (h)	Yield (%)	Recycling (cycles)	Ref.
1	PO	[bmim][Ala]	—	1/—	130	4	8	33	—	97
2	PO	[bmim][Ser]	—	1/—	130	4	8	20	—	97
3	PO	[bmim][Lys]	—	1/—	130	4	8	40	—	97
4	PO	[bmim][Glu]	—	1/—	130	4	8	35	—	97
5	PO	[bmim][Ala]	—	3/—	150	4	12	98	—	97
6	EPC	[bmim][Asp]	—	0.3/—	130	0.5	2	48	5	103
7	SO	L-Pro _{4,4} Br	DBU	1/1	90	0.1	24	83	—	75
8	EPH	L-Pro _{4,4} Br	NEt ₃	1/1	90	1	24	82	5	75
9	SO	His-MeI	—	0.28/—	120	0.1	6	95	4	88
10	PO	L-Pro/PA	—	2.1/—	130	1.2	5	13.7	—	104
11	PO	L-Pro/PA	ZnBr ₂	2.1/0.3	130	1.2	5	92.6	9 (150 °C)	104

12	PO	L-Pro/—	ZnBr ₂	2.1/0.3	130	1.2	5	24.7	—	104
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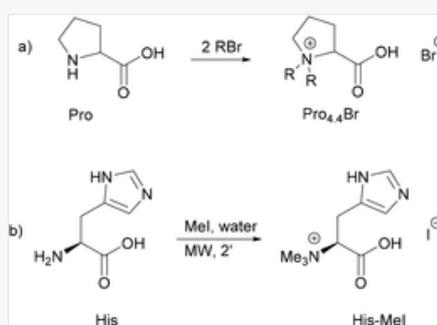
Table Footnotes

^aPO = propylene oxide, EPC = epichlorohydrin, SO = styrene oxide, and EPH = 1,2-epoxyhexane.

^bAbbreviations from Fig. 2 and Scheme 7, L-Pro_{4,4}Br = L-Pro/BuBr and PA = propanedioic acid.

ILs were also prepared using the strategy of quaternisation of the AA with an alkyl halide. For example, L-Pro ionic liquid derivatives were prepared by the reaction of an AA with 1-bromobutane in anhydrous acetonitrile under reflux for 48 h (Scheme 7a).⁷⁵ An approximately 80% yield of styrene and hexylene carbonate were obtained with L-proline/BrBu in combination with a base (NEt₃, DBU or DMAP) at 80 °C (entries 7 and 8, Table 2). The catalytic system L-proline/BrBu/NEt₃ was recycled 5 times. The optimisation of the synthesis of these types of AA-ILs was achieved by carrying out the reaction under microwave irradiation for only two minutes (Scheme 7b).⁸⁸ A high yield of propylene carbonate was obtained with His/HI or MeI (entry 9, Table 2). The catalyst was recycled four times with a small decrease in conversion.⁸⁸

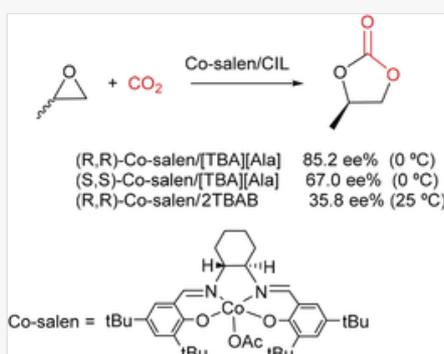
Scheme 7



Preparation of ionic liquids (a) Pro_{4,4}Br from L-Pro⁷⁵ and (b) His-MeI assisted with microwave irradiation (MW).⁸⁸

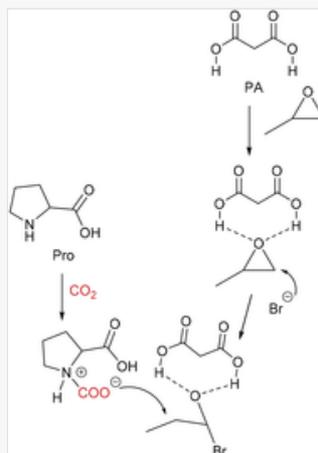
AA-based ILs were used as chiral auxiliaries (CILs) and cocatalysts for the asymmetric cycloaddition of CO₂ to epoxides in combination with a Co(III) chiral catalyst (*R,R*)-Co-salen (Scheme 8).¹⁰⁵ CILs were prepared by the reaction of tetrabutylammonium bromide (TBAB) with AA to form [TBA][AA], where [AA][−] was the anionic form of the corresponding AAs. The use of CILs increased the enantioselectivity obtained with the cobalt/TBAB catalytic system for the cycloaddition of CO₂ to propylene oxide. The best enantioselectivity (80% ee) was obtained with [TBA][L-Ala] at 0 °C and 0.7 MPa, although under these conditions the yield was low (10%). At higher yields, the enantiomeric excess decreased. Combinatory studies using both enantiomers, (*R,R*)- and (*S,S*)-Co-salen, with the chiral ionic liquid showed a synergic effect since the same absolute configuration produced the highest ee while the opposite produced lower enantioselectivity (Scheme 8).¹⁰⁵ Similar results were obtained when using CILs derived from tartaric and lactic acids.

Scheme 8



Amino acids have also been used as components of deep eutectic solvents¹⁰⁴ (DES), which have been reported as a reaction medium for the catalytic formation of cyclic carbonates from carbon dioxide and epoxides. The deep eutectic mixtures were formed by a combination of the AAs (L-Pro, L-Ala, L-Gly), acting as hydrogen-bond acceptors and a dicarboxylic acid (oxalic acid, propanedioic acid and succinic acid) as a hydrogen-bond donor (HBD) in a 1 : 2 ratio.¹⁰⁴ The catalytic activity of these DES in the fixation of CO₂ to propylene oxide was low (entry 10, Table 2), but adding ZnBr₂ or ZnCl₂ increased it substantially. The best result (92.6% yield in PC) was obtained with L-Pro/propanedioic acid (PA) and ZnBr₂ (entry 11, Table 2). Dicarboxylic acid was necessary to achieve high yield (entry 12, Table 2). The authors proposed that the activation of the epoxide resulted from H-bond donor interaction with the diacid, while the CO₂ reacted with the amino acid (Scheme 9). The catalytic system was recycled nine times with a low decrease in carbonate yield.

Scheme 9



Key steps of the proposed mechanism for the fixation of CO₂ in propylene oxide catalysed by L-Pro/PA-ZnBr₂.¹⁰⁴

3.3. Amino acid supported systems

Divinylbenzene cross-linked polystyrene was functionalised covalently with AAs containing the –OH group (Thr, Tyr, HPro, Ser, Fig. 2) to form nanometer particles (PS-AA, Fig. 2) thermally stable up to 370 °C.⁹⁸ PS-AA materials showed significantly high activity in the cycloaddition of CO₂ to propylene oxide under supercritical conditions without solvent or cocatalyst.⁹⁸ For example, the propylene carbonate yield obtained with catalyst L-Tyr increased by approximately 60% at half reaction time under the same conditions by supporting this AA on the polymer (entries 1 and 2, Table 3). The authors attributed this increase in activity to changes in physical properties and the specific structure of the polymeric supported materials. PS-Tyr and PS-Thr were separated from the catalytic suspension by filtration, rinsed with acetone and dried to be re-used in five consecutive runs without loss of activity. High yields were also obtained with other epoxides.

Table 3

Cycloaddition of CO₂ to epoxides catalysed by AA supported catalysts^a

Entry	Epox ^a	Catalyst ^b	Catalyst (mol%)	T (°C)	P (MPa)	t (h)	Yield (%)	Recycling (cycles)	Ref.
1	PO	Tyr	0.8	130	9	48	36	5	98
2	PO	PS-Tyr	0.6	130	9	24	93	5	98
3	PO	PS-Tyr-BuI	0.75	120	1.2	6	98.6	5	99
4	AGE	PS-Tyr	0.75	120	1.2	6	88.3	5	99
5	AGE	PS-Tyr-BuI	0.75	120	1.2	6	99.3	4	99

Table Footnotes

^aPO = propylene oxide, AGE = allyl glycidyl ether, and PS = polystyrene.

^bAbbreviations from Fig. 2.

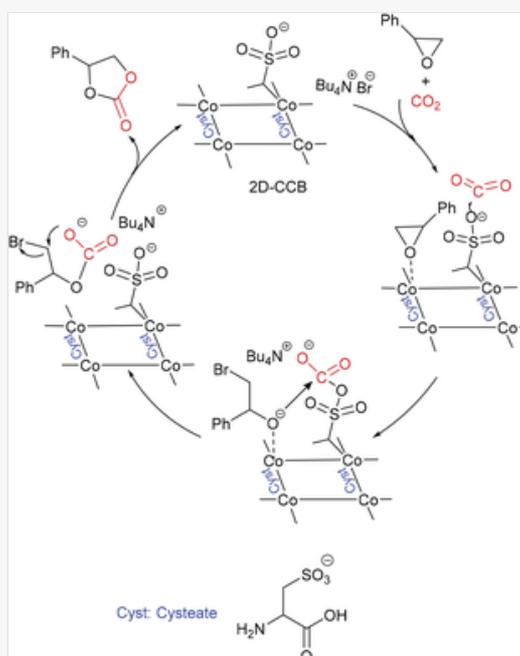
The catalytic activity of the PS-AA materials was increased through their post-functionalisation with alkyl halides RX (PS-AA-RX, Fig. 2) as reported by Park's group.⁹⁹ Propylene carbonate was obtained with a 98.6% yield under mild conditions than with the unfunctionalised material (entry 3 vs. 2, Table 3). The increase in yield was attributed to the introduction of the halide, which acted as nucleophile and facilitated the ring-opening of the epoxide. This catalyst was effective for a series of terminal epoxides. In the case of the substrate allyl glycidyl ether (AGE), the conversion and yield improved by approximately 10% with the functionalisation. The catalytic material was able to be separated by filtration and re-used three times, although a decrease of about 21% in conversion and yield was observed in the last run.⁹⁹

3.4. Amino acid-based metal–organic frameworks (MOF)

After the first examples in which it was demonstrated that MOFs could work as active catalysts for the cycloaddition of CO₂ to epoxides,^{106,107} considerable effort was made to develop more sustainable MOFs by introducing ligands derived from the natural pool products (bio-MOFs).^{63,108}

A combination of AA derivatives and bipyridine ligands was used to form a MOF with cobalt. L-Cysteic acid, a product formed during the metabolism of cysteine by oxidation of the thiol group to sulphonate, was chosen as a spacer for the construction of Co–bipyridine metal–organic frameworks (MOFs) with a 2D grid structure (2D-CCB, Scheme 10).¹⁰⁹ The conjunction of a known active cobalt centre with the sulphonate group of L-cysteic acid in the same structure would combine the capacity of the cobalt centres to activate the epoxide with the ability of the sulphonate groups to activate CO₂.¹⁰⁹

Scheme 10

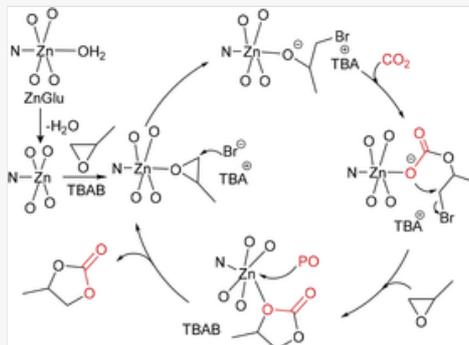


Representation of the MOF 2D-CCB including the L-cysteic acid fragment and proposed catalytic cycle for the cycloaddition of CO₂ to epoxides¹⁰⁹ with this material. Adapted from Kathalikkattil *et al.*¹⁰⁹

The observed conversion of styrene oxide with 2D-CCD together with TBAB¹⁰⁹ (89.5%) exceeded the conversion with TBAB or 2D-CCB separately (entries 1–3, Table 4). When the material was prepared by microwave irradiation (2D-CCB(M)) instead of the classical solvothermal method, the conversion increased to 91.1% (entry 4, Table 4). When a 3D-CCD analogous MOF without sulphonate groups was used, the conversion decreased (entry 5, Table 4), confirming the participation of the sulphonate group in the reaction. The authors proposed a mechanism in which the

Co centres in the MOF activate the epoxide and the Br⁻ participates in the ring-opening of the epoxide (Scheme 10) (Scheme 11). The free oxygen of the sulphonate group then activated the carbon of the CO₂, forming an R-S(O₂)O-CO₂ species to transfer it to the haloalkoxylate formed. Ring closure would selectively produce the cyclic carbonate.¹⁰⁹ The catalytic material was recycled and re-used four times with a slight decrease in conversion in the first two runs (0.9–2.7% decrease) which was attributed to the blocking of the active sites evidenced by changes in the XRD pattern.¹¹⁰

Scheme 11



Mechanism of CO₂/PO cycloaddition using Zn-Glu-MOF proposed based on DFT calculations. Adapted from Kathalikkattil *et al.*¹¹⁰

Table 4

Cycloaddition of CO₂ to styrene oxide (SO) and propylene oxide (PO) catalysed by AA containing MOF materials

Entry	Epoxide ^a	Catalyst ^b	Cocat	Catalyst/cocat (mol%)	T (°C)	P (MPa)	t (h)	Conv (%)	Recycling (cycles reported)	Ref.
1	SO	2D-CCB	—	0.4/—	100	0.1	12	18.5	—	109
2	SO	TBAB	—	0.4/—	100	0.1	12	39.2	—	109
3	SO	2D-CCB	TBAB	0.4/0.4	100	0.1	12	89.5	—	109
4	SO	2D-CCB(M)	TBAB	0.4/0.4	100	0.1	12	91.1	4	109
5	SO	3D-CCB	TBAB	0.4/0.4	100	0.1	12	65.9	—	109
6	PO	Zn-Glu-MOF	TBAB	0.47/0.94	80	1.2	6	>99	4	110

Table Footnotes

^aPO = propylene oxide and SO = styrene oxide.

^bAbbreviations from Scheme 10, 2D-CCB(M) = 2D-CCB under microwave irradiation.

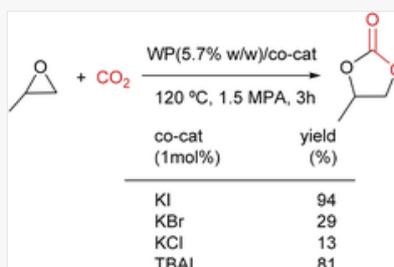
To prevent all sources of synthetic ligands, a Zn-glutamate-based bio-MOF containing only naturally occurring L-glutamic acid, {[Zn(H₂O)(Glu)]·H₂O}_n (Zn-Glu-MOF), was prepared in aqueous media by Park's group.¹¹⁰ The Zn-Glu-MOF was able to absorb CO₂ at high pressures. The combination of Zn-Glu-MOF with TBAB at a 1 : 2 ratio provided high conversion in the CO₂/PO cycloaddition, with an average TOF of 35 h⁻¹ (entry 6, Table 4), similar to the values reported for other MOFs. The material was separated and recycled four times with a slight decrease in conversion observed after the second run. According to the XDR diffractogram, the recycled material retained its structure after the catalytic reaction. Less than 3 ppm of zinc leaching was detected by ICP-OES analysis. A mechanistic cycle was proposed based on DFT calculations (Scheme 11).¹¹⁰ The Zn centre of this MOF is hexacoordinated, with one of this coordinating sites occupied by a water molecule. The initial hypothesis for the mechanistic study was that when the catalyst is heated, the water dissociates, generating an active centre. The MOF

topology was explored using TOPOT Pro software. The reaction mechanism was determined using experimental inferences, previous reports and DFT calculations performed in this work at the M06/lacvp*** level. For DFT calculations, a simplified model with only 28 atoms of the ZnGlu MOF was used, constraining six carbon atoms in fixed positions to model the MOF skeleton. The results show a reaction mechanism similar to the classical three-step one already described. In this case, the oxygen atom of the epoxide coordinates to the Zn atom through the vacancy left by the eliminated water molecule. This is the first step in the reaction. Next, the ring is opened by the nucleophilic Br⁻ anion attack. CO₂, physically bonded to the catalyst, is then inserted between the epoxide oxygen and Zn to form the intermediate that forms the cyclic carbonate product by ring closure. The energetic profile of this path shows that this last step has a free energy barrier of 17.0 kcal mol⁻¹, although the authors of the work state that the rate-determining step is the epoxide ring-opening, with a free energy barrier of 14.3 kcal mol⁻¹.¹¹⁰

3.5. Other related AA-based systems

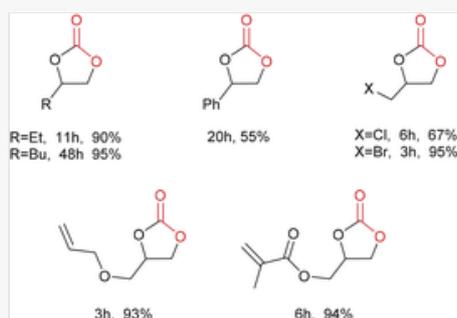
Wool, a natural protein fibre composed mostly of keratin containing 18 different AAs, was used in a binary catalytic system for the cycloaddition of CO₂ to propylene oxide.¹¹¹ The best yield of propylene carbonate (94.1%) was obtained using wool in combination with KI (Scheme 12). This binary system was recycled five times with a slight drop in the activity. This catalytic material was effective for a wide range of substrates providing good to high yields except for cyclohexene oxide, which only produced traces of the carbonate (Fig. 5).

Scheme 12



Cycloaddition of CO₂ to propylene oxide catalysed by wool powder (WP)/cocatalyst.¹¹¹

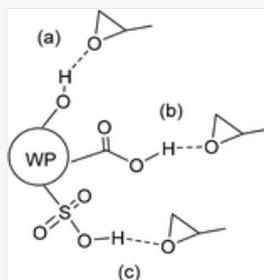
Fig. 5



Yields of cyclic carbonates obtained using WP/KI catalysts with different substrates (conditions: WP/KI ratio to epoxide 5.7/5.7 wt%; 120 °C, 1.5 MPa, time indicated).¹¹¹

Analysis by IR of the wool material showed signals at 1730 cm⁻¹, which are attributed to carboxylation of the -OH groups on the surface of wool. XPS spectra indicate that carbamate was formed by the reaction of CO₂ with the amino surface groups. Based on XPS and FTIR spectra it was proposed that epoxide activation could take place by the hydrogen bond formed by the amide, hydroxyl, carboxyl groups, sulfonic acid or amine groups on the surface of wool (Fig. 6).

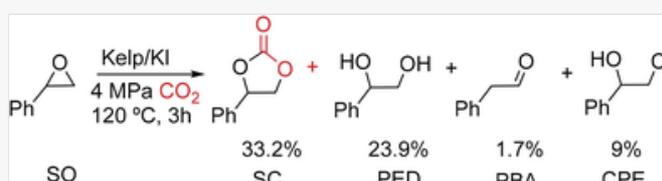
Fig. 6



Possibilities of activation of the epoxide with wool powder (WP) by interaction with (a) $-OH$, (b) $-COOH$ and (c) $-SO_3H$ groups on the surface. Adapted from Chang *et al.*¹¹¹

AAs are present in the form of proteins together with halide salts in many plants such as seaweeds. The direct use **as catalysts** of seaweeds containing proteins (in 14–50%) **as catalysts** and high loading of metal halides **were was** proposed for the synthesis of cyclic carbonates to avoid the step of isolation and purification of the components. This approach has additional benefits of sustainability and abundance of the catalytic material.¹¹² Two common seaweeds were selected: kelp (*Laminaria digitata*), which has a high iodide content, and dulse (*Palmaria palmata*) for comparison. Apart from AA, both seaweeds contain polysaccharides such as cellulose, alginate, fucoidan and carrageenan that may also act as HBD to promote the reaction. The addition of KI was necessary to obtain the activity. Selectivity in the carbonate was moderate: 33.2% yield and 49% selectivity using the Kelp/KI catalytic system (Scheme 13). The main by-product was the corresponding diol, 1-phenylethane-1,2-diol (PED), but variable quantities of phenylacetaldehyde (PAA) and a chlorinated compound, 2-chloro-1-phenylethan-1-ol (CPE), were also formed, probably due to the high chlorinated salt content (Scheme 13). Attempts to reuse the catalytic material resulted in the loss of the catalytic activity, which was attributed to the degradation of the organic compounds in the seaweeds during the reaction.

Scheme 13



Formation of styrene carbonate (SC), 1-phenylethane-1,2-diol (PED), phenylacetaldehyde (PAA) and 2-chloro-1-phenylethan-1-ol (CPE) using the Kelp seaweed/KI catalytic system for the cycloaddition of CO_2 to styrene oxide (SO).¹¹²

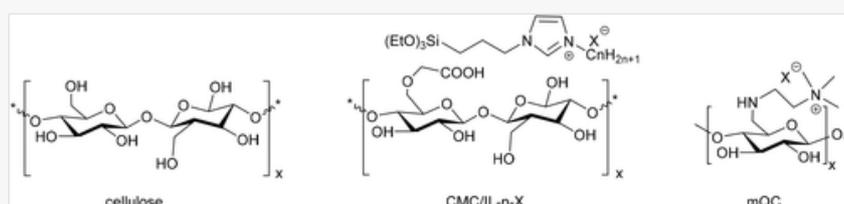
4. Catalysts related to cellulose, lignin, chitosan and saccharides

Several studies show that cellulose, lignin, chitosan and saccharide derivatives can be used as effective metal-free catalysts for the cycloaddition reaction of CO_2 with epoxides under mild conditions to produce carbonates.

4.1. Cellulose-based catalysts

Cellulose (Fig. 7) is a well-known biopolymer characterised by a broad network of ordered intermolecular and intramolecular hydrogen bonds with abundant hydroxyl groups that can act as hydrogen bond donors (HBD). It is also readily available, inexpensive, biocompatible and stable. Cellulose is a potentially renewable biopolymer for generating new functional materials.¹¹³

Fig. 7



One of the first studies on cellulose-based catalysts for the cycloaddition reaction of CO₂ and epoxides was reported by Liang *et al.*¹¹⁴ Their study demonstrated the importance of hydrogen bonding and the synergistic effect produced by the cellulose/KI system in the CO₂/epoxide cycloaddition. The results show the effect of the cellulose/KI composition, since the yield of propylene carbonate when only KI was used as the catalyst under the reported conditions without cellulose was about 2%. The addition of cellulose increased the yield up to total conversion when the percentage by weight of cellulose/KI was 14.7/7.3 wt% (entry 1, Table 5). The yield of propylene carbonate was also negligible when only cellulose was used to promote the reaction, indicating an excellent synergic effect of cellulose and KI for catalysing the reaction.

Table 5

Cycloaddition of CO₂ to epoxides catalysed by bio-polymer-based catalytic materials

Entry	Epox a	Catalyst ^b	Cocat	Catalyst/cocat (mol%)	T (°C)	P (MPa)	t (h)	Yield (%)	Recycling (cycles reported)	Ref.
1	PO	Cellulose	KI	14.7/7.3 wt%	110	2	1.5	100	5	114
2	PO	Cellulose	IL-4-I	1.2/1.2	110	1.8	2	81 ^c	—	115
3	PO	CMC	IL-4-I	1.2/1.2	110	1.8	2	99 ^c	5	115
4	PO	HBimCl-Nb-HCMC	—	17 wt%/—	130	1.5	3	96 ^c	5	117
5	PO	mQC-1.I	—	0.4/—	120	1.2	3	97	6	116
6	PO	Cellulose	DBU	1.8/27.1 wt%	120	2.0	2	92 ^c	4	76
7	PO	—	DBU	—/27.1 wt%	120	2.0	2	79 ^c	—	76
8	PO	EHLignin	KI	0.67 ^d /2.01	140	2	12	93	5	118
9	PGE	Lignin-ChCl-PABA	TBAB	6.66 wt/10 mol%	110	1.0	3	99	5	119
10	PO	CS-emimBr	—	1/—	120	2	4	96	—	120
11	PO	CS-BuPPh ₃ Br	—	1.5/—	120	2.5	4	95 ^e 96.3	5	121
12	PO	CS-NR ₃ Cl	—	1.7/—	140	4	6	98	5	122
13	PO	QCS	—	9.3 wt%/—	120	1.17	6	86	5	123
14	PO	CS-TPPS	TBAI	1.72/1.72 wt%	75	1	6	66	—	124
15	SO	CuPc@CS	TBAB	6.9 wt/1 mol%	80	0.1	4	95	5	125
16	PO	Zn-CS	bmimBr	0.035/0.21	110	1.5	1	95	— ⁵	126
17	PO	ZY- or GO-CS CS-GO	TBAB	3 wt/0.426 mol%	100	1.0	6	61	— ⁵	127, 146
18	PO	Chitin	KI	5/5 wt%	100	2.8	2	97	—	128
19	PO	β-CD	KI	8.6 wt/2.5 mol%	120	6	4	98	5	129
20	PO	Bis-β-CD	KI	0.14/1.25	120	4	2	94	—	130
21	PO	Q-bis-β-CD (<i>n</i> = 6, R = C ₄ H ₉ , X = I)	—	0.14/—	110	2	4	99	5 for EPC (n=2)	130

22	PO	β -CD	TBAB	0.25/0.125	130	3	5	100	5	127 149
23	PO	β -CD	—	1.5/—	130	3	10	29.8 ^e ^d	—	131
24	PO	[DBUH][PFPhO]	—	1.5/—	130	3	10	90 ^c	—	131
25	PO	[DBUH][PFPhO]@CD	—	1.5/—	130	3	10	97	4	131
26	PO	SCB	KI	8.6 wt%/2.5 mol%	120	2	6	93	—	130 151
27	SO	LS-DIL	TBAB	8.3 wt%/9 mol%	90	1	5	94	6	131 152

Table Footnotes

^aPO = propylene oxide, SO = styrene oxide, PGE = phenyl glycidyl ether, and EPC = epichlorohydrine.

^bCMC = carboxymethyl cellulose, -Nb- = NbCl₅, IL-4-I = 1-butyl-3-triethoxysilylpropyl imidazolium iodide, CMIL-4-I = carboxymethyl cellulose/IL-4-I, and HbimCl = 1-hydroxypropyl-3-*n*-butylimidazolium chloride, EHLignin = enzymatic hydrolytic lignin, ChCl = choline chloride, CS = chitosan, QCS = quaternised chitosan, AGE = allyl glycidyl ether, CS-TPPS = *meso*-tetrakis(4-sulfonatophenyl)porphyrin, ZY = zeolite, GO = graphene oxide, β -CD = β -cyclodextrine, EPC = epichlorohydrin, SCB = sugarcane bagasse, and LS-DIL = Luffa sponge-based catalytic system (Scheme 18).

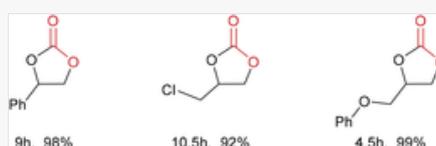
^cEstimated from conversion and selectivity data.

^dActive OH groups.

^eTo 1,2-diol.

Since it is known that the two -OH groups of the 1,2-diols can form seven-membered ring species with propylene oxide by hydrogen-bonding that enhance activity, the existence of numerous hydroxyl groups on the vicinal carbons of cellulose should be the main reason for cellulose's high efficiency in accelerating some reactions. The cellulose/KI system provided high yields for other monosubstituted carbonates under the same reaction conditions but at extended times (Fig. 8) proving that it constitutes a very active, selective, stable, and recyclable catalytic system for the cycloaddition reaction of CO₂ and terminal epoxides to produce cyclic carbonates.¹¹⁴

Fig. 8



Yields of cyclic carbonates obtained using cellulose/KI catalysts with different substrates (conditions: cellulose/KI ratio to epoxide 14.7/7.3 wt%; 110 °C, 2 MPa, time indicated).¹¹⁴

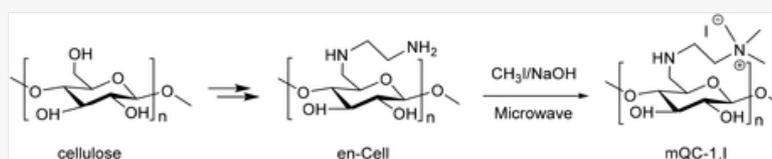
Cellulose derivatives have also been used to heterogenise ILs, which facilitates product separation and recycling. With this in mind, Park and co-workers¹¹⁵ prepared carboxymethyl cellulose (CMC) in which **carboxymethyl groups (the -CH₂COOH fragments)** are bound to some hydroxyl groups of the monomers that form the cellulose backbone. CMC was used as a support for ILs, which are well-known catalysts for carbonate formation through the epoxide and CO₂ reaction. However, it was found that CMC not only **is was** the support, but also played **sed** a role in the catalytic reaction. Because of the presence of the functional hydroxyl and carboxyl groups, CMC was able to contribute to the activation of the nucleophilic attack, playing a bifunctional role in cooperation with the ionic liquid promoting the cycloaddition reaction of epoxides with carbon dioxide. Imidazolium-based ionic liquids non-covalently immobilised on carboxymethyl cellulose *via* a simple co-dispersing method have been used as heterogeneous catalysts (CMC/IL-*n*-X, Fig. 7) in the cycloaddition reaction of propylene oxide with CO₂. No activity was observed when CMC alone was used as the catalyst. The fact that the experiment conducted with CMC/ILs resulted in better activity than the corresponding catalytic experiment with cellulose/ionic liquid demonstrates the role played by the carboxyl moieties in the reaction. The best results using CMC/IL-*n*-X systems achieved >99% yield in a reaction time of 2 h (entry 3, Table

5). Density Functional Theory studies were performed to determine the effect of the carboxyl groups present in the support in the catalytic reaction at the mechanistic level.¹¹⁵ To do this, the structures of the reaction intermediates were sought, assuming the classical three-step mechanism. The system was modeled by three anhydroglucose units with one $-CH_2COOH$ group together with propylene oxide, CO_2 and a chloride anion, and the geometries were optimised at the B3LYP/6-31G(d,p) level.¹¹⁵ The results showed that, while in the reactant complex the epoxide oxygen interacts with one of the OH groups of the CMC, in the open-ring intermediate the interaction is established between the carbonyl oxygen of the carbonate and the H atom of the carboxyl group. This delocalises the negative charge of the intermediate and it is stabilised, which explains the enhanced catalytic activity of CMC when compared with methylcellulose.

Later, [Hou Wu et al.](#) reported a heterogenised catalytic system based on carboxymethyl cellulose (CMC) supporting imidazolium-based ILs with a Lewis acid applied for the synthesis of various cyclic carbonates under solvent-free conditions.¹¹⁷ The protonated carboxymethyl cellulose (HCMC) supporting the hydroxyl group functionalised ionic liquid (1-hydroxypropyl-3-*n*-butylimidazolium chloride, HbimCl) and $NbCl_5$ as a Lewis acid (HbimCl-Nb-HCMC) provided the best catalytic results and excellent resistance to leaching (entry 4, [Table 5](#)). The catalytic performance has been attributed to a strong synergistic effect between HBimCl and the Lewis acid promoter. The HBimCl-Nb-HCMC catalyst was recovered by simple centrifugation after the reaction. It was reused five times without any loss of activity in a batch reactor. Interestingly, the system was active in a continuous fixed bed reactor for more than 100 h on stream, which demonstrates the robustness of the catalytic system and the applicability of the catalyst as a heterogeneous catalyst for synthesizing cyclic carbonates.¹¹⁷

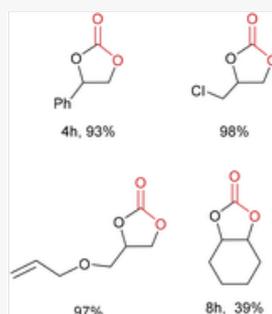
Quaternised celluloses (QCs) containing an ionic nitrogen moiety and hydroxyl groups are a class of ionic celluloses that have been overlooked as potentially biocompatible and safe materials for a range of applications ([Scheme 14](#)).¹³² An excellent catalytic system for the cycloaddition reaction of CO_2 with epoxides was reported by [Park's group et al.](#)¹¹⁶ It was prepared from an ethylene diamine-functionalised cellulose (en-cell) through microwave quaternisation (mQCs). A series of mQCs with different alkyl chains and anions was synthesised and characterised by several techniques such as solid-state ^{13}C NMR, FT-IR, XPS, and EA. The system is efficient under solvent-free conditions and low catalytic loading, achieving an excellent yield of propylene carbonate (97%, entry 5, [Table 5](#)). This catalytic material was applied for the transformation of common terminal epoxides providing high yields of the corresponding cyclic carbonates except for cyclohexene oxide ([Fig. 9](#)).

Scheme 14



Synthesis of microwave quaternised celluloses (mQCs) using ethylene diamine-functionalised derivatives (en-cell).¹¹⁶

Fig. 9



Yields of cyclic carbonates obtained using mQC-1.1 ([Scheme 14](#)) catalysts with different substrates (conditions: mQC-1.1 to epoxide 0.4 mol%; 120 °C, 1.2 MPa, 3 h except other time indicated).¹¹⁶

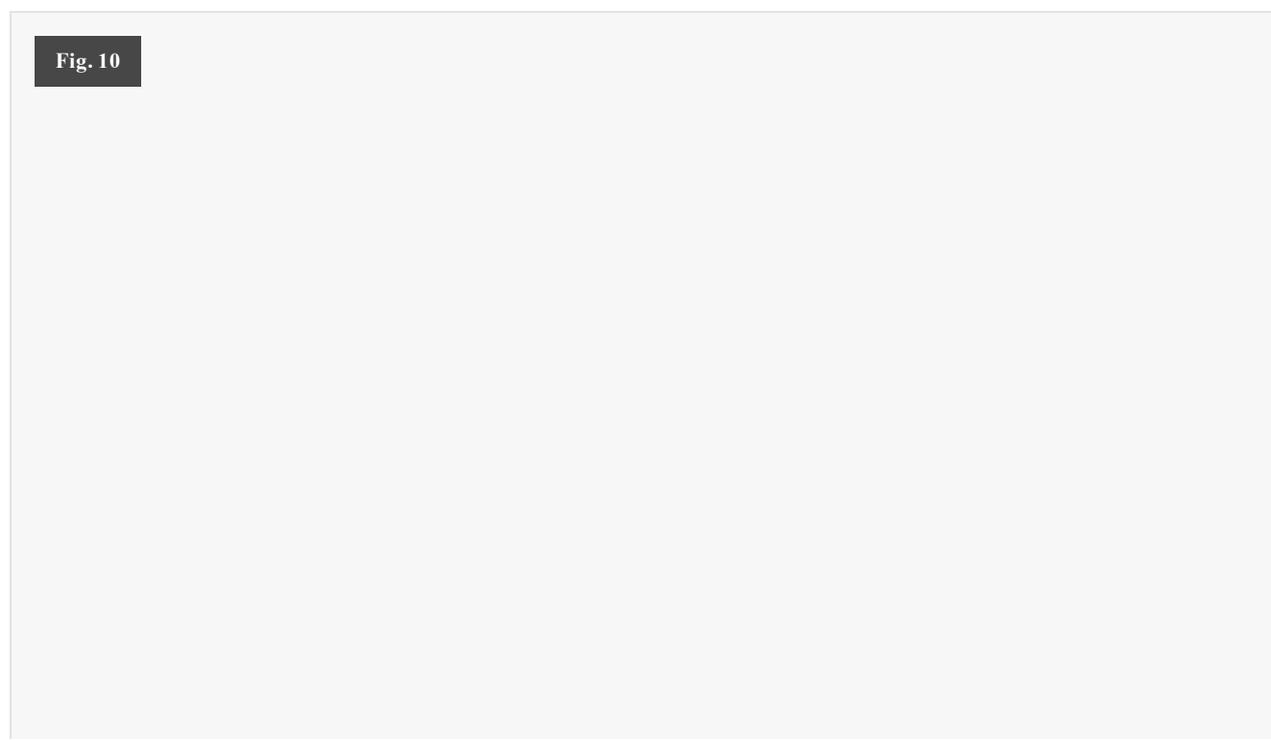
The role of the vicinal hydroxyl groups in promoting the catalysis of cycloaddition was thoroughly investigated using hydroxyl-protected cellulose derivatives. The results conclusively confirmed the possibility of seven-membered ring formation at the catalyst–reagent solid–liquid interface, as previously reported.¹¹⁴ Based on these results, a plausible mechanism was proposed, in which all the functional moieties of mQCs operate synergistically. The rapid initiation of the quaternisation and the mQCs' high surface areas enhancing the catalytic activity were attributed to the microwave pulses.¹¹⁶

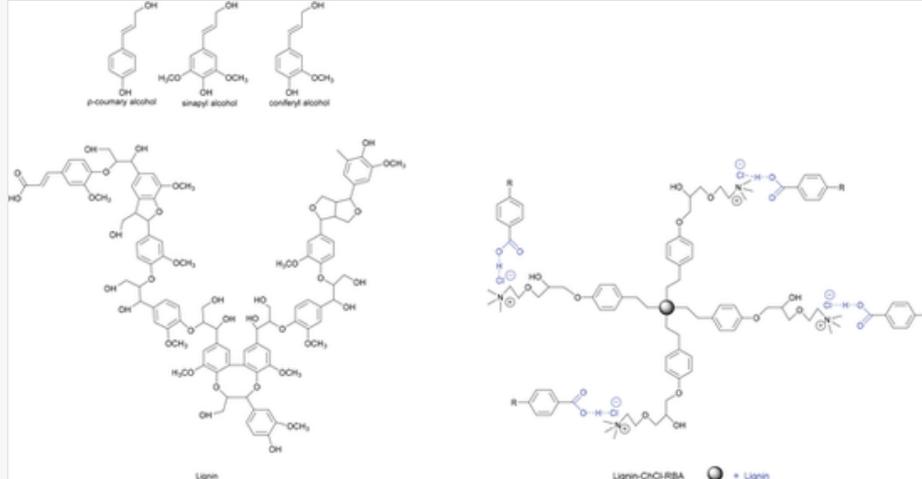
Seeking to develop catalysts that were both halide-free and metal-free, Zhang-Sun *et al.* applied a combination of several HBDs (cellulose, chitosan, glycerine, PEG600, β -cyclodextrin, *etc.*) with organic bases such as DBU, DMAP, and DABCO.⁷⁶ They analysed the use of cellulose combined with the superbase DBU in detail. After optimisation of the reaction conditions, the system showed excellent results for the reaction of CO₂ with mono-substituted and disubstituted epoxides (entries 6 and 7, Table 5). The catalysts were able to be reused with high activity and selectivity. Based on previous reports and the results of this study, a catalytic cycle for the hydrogen bond-assisted ring-opening of epoxide and the DBU-induced activation of CO₂ was proposed following a mechanism similar to the one shown in Scheme 6. As it has been mentioned, cellulose is known to act as an HBD, promoting the ring-opening of epoxides. DBU can also act as a nucleophile and activate CO₂ by coordination, forming a zwitterionic adduct. The synergetic roles played by both cellulose and DBU could favour the reaction.

4.2. Lignin-based catalysts

This section focuses on the application of lignin as a catalyst for CO₂ valorisation to form carbonates as a sustainable method for the use of “carbon-neutral” resources. Lignin constitutes 15–30% of lignocellulosic biomass and contains a cross-linked racemic macromolecule formed by methoxylated alcohols (Fig. 10).¹¹⁸ The treatment and valorisation of lignin as a sustainable resource to produce valuable chemicals is currently the subject of extensive study as, due to the complexity of its composition, lignin recovery is one of the major challenges for the use of this biomass.¹³³ Lignin can be obtained from biomass by enzymatic hydrolysis, but it requires a pre-treatment of the lignocellulose biomass to enhance the hydrolysis by enzymes. Among the many treatments developed, ILs have been studied, since they have been efficiently used for biomass pre-treatment.¹³⁴ One of the most efficient strategies involves biomass dissolution using a minimal amount of ILs in a mixed solvent (*N*-methylpyrrolidone (NMP)/1-ethyl-3-methyl imidazolium acetate), which results in cellulose regeneration and efficient enzymatic hydrolysis of the pre-treated sample to produce the enzymatic hydrolytic lignin (EHL).¹³⁵ To find out more about its structural composition, the lignin obtained by means of this procedure was treated with dioxaphospholane as a phosphorylation reagent for subsequent ³¹P NMR spectroscopic characterization to determine the number of active OH groups (aromatic, aliphatic, and carboxylic) as well as the *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) ratio in lignin. The presence of these hydroxy group functionalities determines the application of these lignin materials as catalysts.¹¹⁸

Fig. 10





Lignin structure¹¹⁸ and lignin supported choline chloride (ChCl) benzoic acid derivatives (RBA) (lignin–ChCl–RBA, adapted from Xiong *et al.*¹¹⁹).

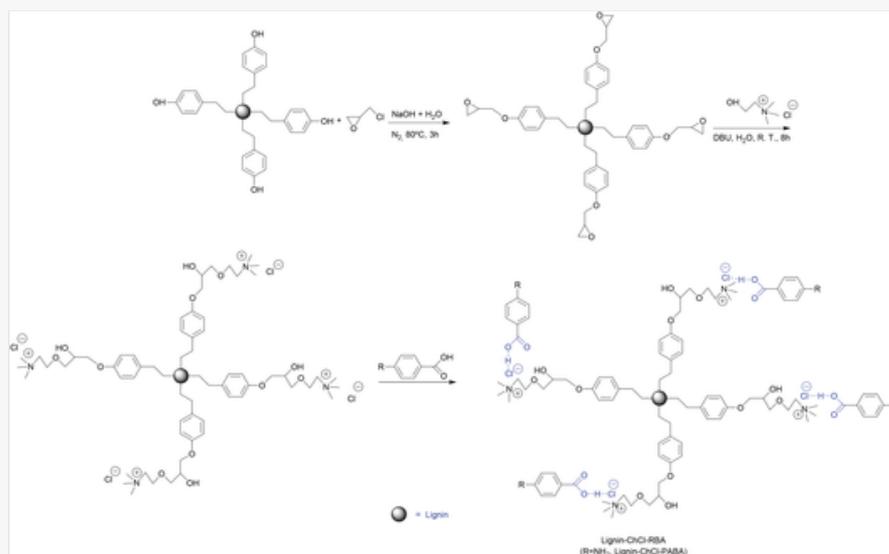
As discussed above, the cooperative effect between a hydroxy or a carboxylic acid group and a nucleophilic reagent makes for an efficient catalytic system.¹³⁶ It has been reported that sulphonated lignin, for instance, has been used as a catalyst for the dehydration of fructose to obtain 5-hydroxymethylfurfural in ionic liquids.¹³⁷ Only a few works address the use of these type of lignin materials as catalysts for the CO₂/epoxide cycloaddition. An interesting catalytic system formed by EHL and KI has been reported to achieve 93% yield in the chemical fixation of carbon dioxide with propylene oxide to form propylene carbonate (entry 8, Table 5).¹¹⁸ This system has been studied in detail and compared with other halogenated catalytic systems, showing the previously discussed effect of the nucleophilicity of halides. Given that the number of –OH active groups is known for this lignin, it was found that the best molar ratio of KI to the active –OH groups was 3 : 1. Using KI at this ratio, the reaction temperature, CO₂ pressure and reaction time were optimised. However, under the best reaction conditions, the enzymatic hydrolytic lignin/KI system still required a high temperature (140 °C). Screening for this catalytic system was applied to different terminal epoxides. It is important to note that the system was also active for the cycloaddition of CO₂ with styrene oxide, a less active substrate, providing a yield of 87%. When cyclohexene oxide was used, only a 20% yield (*cis*-product) of the corresponding carbonate was obtained. The difficulty in making this substrate react is due to the structural steric hindrance of the bicyclic carbonate. The separation and recycling of the catalysts was completed by simple filtration at the end of the reaction, since lignin is insoluble in the formed propylene carbonate. The cocatalyst KI, however, is partially soluble and only a part can be separated together with lignin. Distillation of the formed cyclic carbonate allows the soluble part to be recovered, which can then be integrated into the recycled system to associate with lignin for the next run. Using this approach, five successive cycles could be performed without a significant drop in the yield of the reaction, which demonstrates the good stability and reusability of the catalyst throughout the reaction runs.

The application of lignin-based catalysts in the CO₂ cycloaddition to epoxides to obtain cyclic carbonates was also the subject of a patent in 2019.¹³⁸ The patent describes a method for synthesizing cyclic carbonates with lignin as the catalyst and metal salt and quaternary ammonium salt as promoters resulting in an efficient and sustainable technology with high activity and selectivity, mild conditions and recyclability through easy separation.

The catalytic properties of lignin as HBD can be also combined with its characteristics as a biodegradable support. It was used to attach a deep eutectic solvent system formed by choline chloride (ChCl) and benzoic acid derivatives (RBA), which were used as a heterogeneous recyclable materials to catalyse the cycloaddition of CO₂ with terminal epoxides (Scheme 15).¹¹⁹ High yields (90–99%) of a variety of terminal cyclic carbonates including mono and

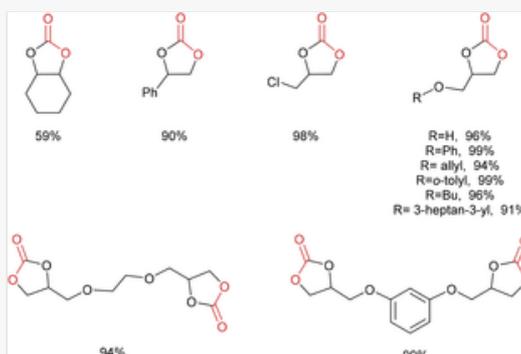
bis(carbonates) were obtained, lignin-ChCl-PABA (PABA = *p*-aminobenzoic acid) being the best catalytic material. Even for the disubstituted cyclohexene oxide the yield was good (entry 9, Table 5 and Fig. 11). The system was stable under catalytic conditions and was reused in five cycles (84% yield after five cycles).

Scheme 15



Synthesis of lignin supported choline chloride (ChCl) benzoic acid derivatives (lignin-ChCl-RBA). Adapted from Xiong *et al.*¹¹⁹

Fig. 11

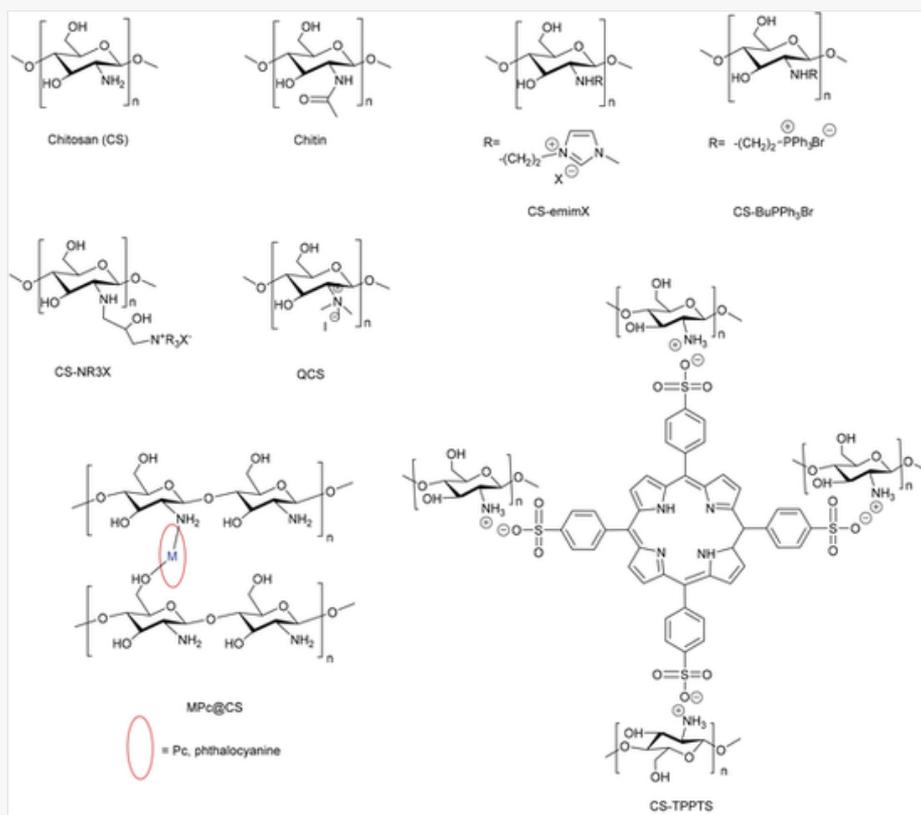


Yields of cyclic carbonates obtained using lignin-ChCl-RBA/TBAB (Scheme 15) catalysts with different substrates (conditions: lignin-ChCl-RBA/TBAB ratio to epoxide 6.6 wt%/10 mol%; 110 °C, 1 MPa, 3 h).

4.3. Chitosan- and chitin-based catalysts

Chitosan (CS) is obtained through the deacetylation of natural chitin, the second most abundant biopolymer found on Earth after cellulose (Fig. 12). It has been the focus of increasing interest as a sustainable, biocompatible, biodegradable and non-toxic material. Chitosan can be considered a natural cationic polymer because of the presence of amino groups on the polymer backbone and with many accessible basic surface sites provided by its macroporous network and large surface area. In fact, due to the amino group and the two hydroxyl groups of chitosan's repeating hexosaminide moiety, it can act as a multifunctional catalyst in the cycloaddition reaction, by means of hydrogen bond assisted epoxide ring-opening and by nucleophilic tertiary nitrogen-induced activation of CO₂. This multifunctionality means it can act not only as an organocatalyst, but also as a macrochelating ligand for metal catalysts and as a support for nanoparticles.¹³⁹ This is why chitosan, like cellulose derivatives, has also been used for IL heterogenisation. So, chitosan as an IL-catalyst support enhances the activity of the reaction while simultaneously allowing catalyst recycling. The quaternisation of chitosan (QCS) is also possible, leading to well-known materials with applications in many fields, especially in the field of biomedicine.¹⁴⁰ Examples of these different possible applications of chitosan and chitin to obtain catalysts for the reaction of CO₂ with epoxides are described in this section.

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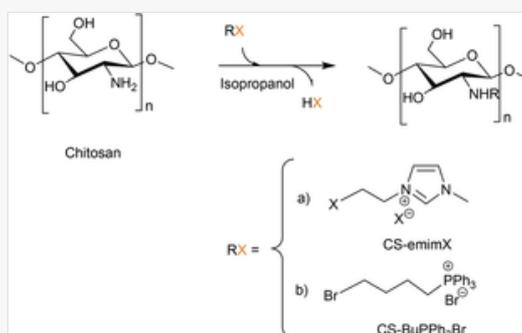
Chitosan (CS) and chitin based catalytic systems: based on chitosan imidazolium ILs (CS-emimX)¹²⁰ and phosphonium IL (CS-BuPPh₃Br),¹²¹ quaternised chitosan (CS-NR₃X¹²² and QCS),¹²³ chitosan based *meso*-tetrakis(4-sulfonatophenyl)porphyrin (CS-TPPS)^{124,141} and metallophthalocyanine modified chitosan (MPc@CS).¹²⁵

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Chitosan-IL catalysts were prepared by chemically supporting 1-ethyl-3-methyl imidazolium halide catalysts in chitosan and functionalising their amine groups (CS-emimX, X = Cl and Br, Scheme 16).¹²⁰

Scheme 16



Chitosan/ionic liquid catalysts: (a) based on imidazolium ILs¹²⁰ and (b) based on phosphonium IL.¹²¹

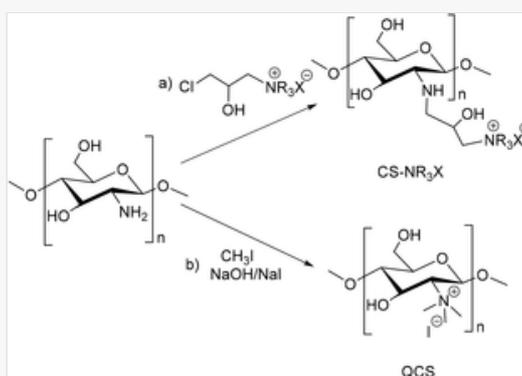
The results obtained for this reaction show that the CS-emimBr catalyst achieved up to 96% yield comparable to the activity of homogeneous emimBr (entry 10, Table 5).¹²⁰ However, a low conversion was obtained in the presence of chitosan or imidazole alone, indicating that the bifunctional synergic effect of the hydroxyl groups and the tertiary amine groups in chitosan promote the activity of the catalytic reaction. The reaction mechanism suggested in this work is similar to the three-step one mechanism proposed for other systems, with the particularity that CO₂ reacts with the

tertiary amine of the support (imidazolium cation), forming carbamate. This one is the species that reacts with β -haloalcoholate to produce the alkyl carbonate anion that yields the cyclic carbonate after the ring-closing step. The nature of the interaction of chitosan with epoxide was further studied utilizing DFT calculations performed at the B3PW91/6-31++G(d,p) level. The structure of the initial complex formed by one unit of chitosan with an epoxide molecule was determined. It shows H-bond interactions between both hydroxyl groups of chitosan and oxygen of the epoxide, supporting the mechanistic hypothesis suggested by this group.¹²⁰

The same strategy of functionalising the amine group of the hexosaminide fragment was used to graft an active quaternary phosphonium ionic liquid (1-butyl-triphenylphosphonium bromide) onto chitosan.¹²¹ The catalyst CS-BuPPh₃Br provided a better PC yield (96.36.3%, entry 11, Table 5) than its homogeneous analogue BuPPh₃Br (85.2%) under the same conditions. It was suggested that the hydroxyl group played an active role in the activation of the epoxide since the -OH derivative HOBuPPh₃Br also produced a high PC yield (98%). What is more, the yield was also very high using a mixture of the ionic liquid BuPPh₃Br and chitosan (CS/BuPPh₃Br). This led the authors to propose that CS was not a passive inert support, but that it participated in the activation of the epoxide through the polarisation of the latter by H-bond donor interaction with the -OH groups of CS, electronic interaction with the [BuPh₃P]⁺ fragment, and nucleophilic attack by bromide anion to open the epoxide ring. The supported CS-BuPPh₃Br system was stable after the catalytic reaction according to TG and FT-IR and was recycled and reused for five runs without an apparent decrease in PC yield or selectivity. A series of terminal epoxides was also transformed to cyclic carbonates with high yields.

Quaternary ammonium salts (such as Bu₄NBr, Et₄NBr, etc.) are currently used as homogeneous catalysts for the industrial preparation of cyclic carbonates.¹⁴² The synthesis of a series of functionalised biopolymer supported quaternary ammonium salts in chitosan (abbreviated as CS-NR₃X) has been reported and they are used as catalysts for the cycloaddition reaction of epoxides with CO₂ (Scheme 17a).¹²² The catalytic system was studied and optimised for the CO₂/PO cycloaddition without a cocatalyst and a solvent. Chitosan is believed to play a role in the enhancement of propylene carbonate formation, although it is not an active catalyst for this reaction. Once the reaction conditions were optimised, several cyclic carbonates were obtained with high yields and selectivity using CS-NMe₃X as the catalyst. Propylene oxide was found to be the most reactive epoxide (entry 12, Table 5), while styrene oxide exhibited relatively low activity. The CS-NMe₃Cl catalyst was recovered by filtration after the reaction and recycled five times without loss of activity or selectivity, proving the thermal stability of the modified chitosan and consequently the potential application of the catalytic system.

Scheme 17



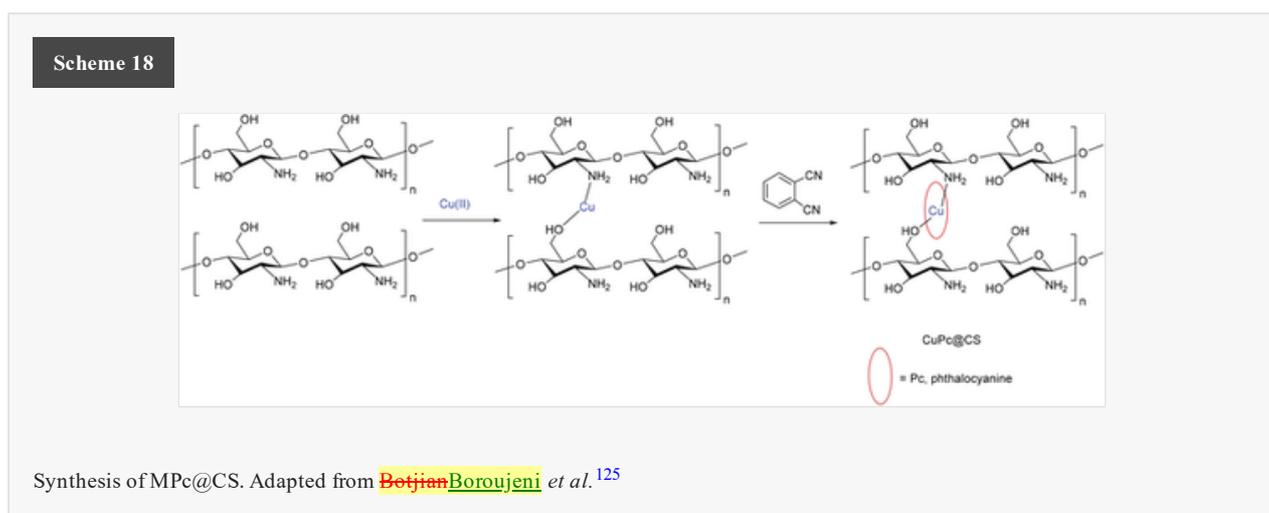
Preparation of quaternary ammonium salt chitosan derived by (a) a covalent bond (CS-NR₃X)¹²² and (b) direct quaternisation of chitosan QCS.¹²³

The direct quaternisation on the primary amine group present on the chitosan led to a cationic biopolymer (QCS, Scheme 17b) different from the covalent tethering of a quaternised species onto the chitosan backbone. This catalyst has been used for synthesising cyclic carbonates from different epoxides (for example, entry 13, Table 5).¹²³ The scope of the catalyst applied to several epoxide substrates showed the efficacy for the monosubstituted terminal epoxides with practically total selectivity in all cases. The presence of an electron-withdrawing CH₂-Cl group in the epoxide decreased the activity. For styrene oxide, the conversion was slightly lower than that for other monosubstituted terminal

epoxides. As expected, the lowest activity was observed in the case of cyclohexene oxide. The catalyst was separated and effectively used for up to five cycles with limited loss of activity. The synthesis of the quaternised chitosan materials (QCS, Scheme 17b) required the use of 1-methyl-2-pyrrolidinone (NMP) as the solvent for prolonged reaction times (36 h) because it had the limitation of the low solubility of chitosan in this medium. The reaction time was drastically reduced to three minutes by applying microwave irradiation at 70 W.¹⁴³ Furthermore, the quaternised chitosan catalysts prepared in this manner showed slightly increased activity compared to those prepared by the conventional method.

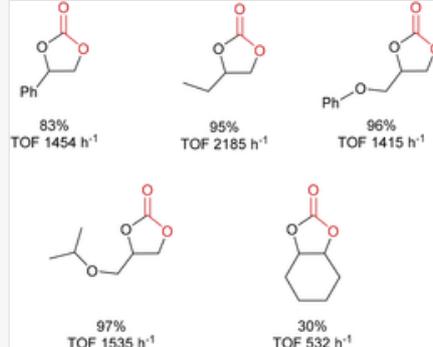
A different approach related to the modification of chitosan **the preparation of an is the** ionic complex **preparation** of chitosan with *meso*-tetrakis(4-sulfonatophenyl)porphyrin by self-assembly through interactions between the positive protonated amino group of chitosan and negatively charged sulphonate groups of porphyrin (CS-TPPS, Fig. 12).¹⁴¹ The catalytic activity of porphyrins in CO₂ conversion to carbonates is well known.^{144,145} As such, the chitosan modification with porphyrins provides an efficient catalytic system for CO₂ capture and conversion. The CS-TPPS material with TBAI was applied as the heterogeneous catalyst for the cycloaddition reaction between CO₂ and propylene oxide to produce cyclic propylene carbonate with a good yield (66%, entry 14, Table 5), which is double the yield achieved with CS/TBAI under the same conditions.¹²⁴

The amine functionalities of chitosan also allowed to support metal-based catalysts such as metal phthalocyanines¹²⁵ and zinc chloride-based ionic liquids.¹²⁶ A series of Cu, Co and Ni containing metal phthalocyanines was prepared for the cycloaddition of CO₂ with epoxides (MPc@CS, Fig. 12).¹²⁵ The synthetic pathway included a first step consisting of the suspension of the M(II) metal salt in chitosan. In the second step, metal phthalocyanine was formed *in situ* using a deep eutectic solvent (choline chloride/urea = 2/1) (Scheme 18). These materials catalysed the fixation of CO₂ to epoxides to obtain carbonates under mild conditions. The best results were obtained with the Cu(II) derivative. For instance, styrene carbonate was obtained in high yield (95%) after four hours at 80 °C (entry 15, Table 5). The catalyst was recycled five times without detectable leaching of Cu(II).



Zinc chloride was supported in CS (Zn-CS) by refluxing both materials in ethanol for 24 h. Evidence of Zn(II) interaction with the hydroxyl groups of chitosan was obtained by the changes in the -OH stretching IR frequency and a decrease in the Zn_{2p3} binding energy observed by XPS of the supported material.¹²⁶ The catalytic materials were prepared by adding the supported Zn-CS to the IL. Imidazolium- and pyridinium-based IL produced high yields of propylene carbonate (75–99%) with high averaged TOF (up to 2717 h⁻¹, entry 16, Table 5). The yield dropped to 50% when PVP was used as the support. Other cyclic carbonates were obtained at a higher rate (TOF 500–1500 h⁻¹, Fig. 13). The system was recycled for five runs, adding fresh IL in each cycle, with a slight loss of activity.

Fig. 13



Yields of cyclic carbonates obtained using Zn-CS/bmimBr catalysts with different substrates (conditions: Zn-CS/bmimBr molar ratio to epoxide 0.035/0.21 mol%; 110 °C, 1.5 MPa, 1 h).¹²⁶

Chitosan has not only been used as an active support for CO₂ conversion catalysts, but also been used in composite materials. As such, Sobral and co-workers reported the preparation of a zeolite–chitosan composite (ZY–CS) by means of solvent exchange with acetone from a gel containing zeolite and chitosan in an aqueous solution. A powder of the composite ZY–CS was obtained after calcination at 400 °C for 2 h.¹²⁷ Evidence for the formation of the composite was established using different techniques. In infrared spectroscopy, the bands corresponding to N–H and C–O–C of CS were observed in the 1600–1650 cm⁻¹ and 1000–1100 cm⁻¹ regions. The XRD diffractogram predominantly showed the zeolite peaks, but the appearance of a new peak proved the formation of a new material. The thermogravimetric analysis of the ZY–CS material showed a behaviour similar to pure chitosan. The authors proposed that the composite was formed by the electrostatic interaction between the negatively charged sites of zeolite (SiO⁻) and the positively charged sites of chitosan (NH₃⁺). The modification of zeolite resulted in increased adsorption capacity of CO₂ (1.7 mmol g⁻¹) compared to pure zeolite (1.17 mmol CO₂ per g) or CS (0.2 mmol CO₂ per g). The catalytic system formed with the composite ZY–CS and TBAB produced 61% of propylene carbonate in 6 h (entry 17, Table 5), while under the same conditions, the combination of chitosan and TBAB transformed only 31%. The best performance of this catalytic system was obtained in the cycloaddition of CO₂ to epichlorohydrin (99.5% yield).

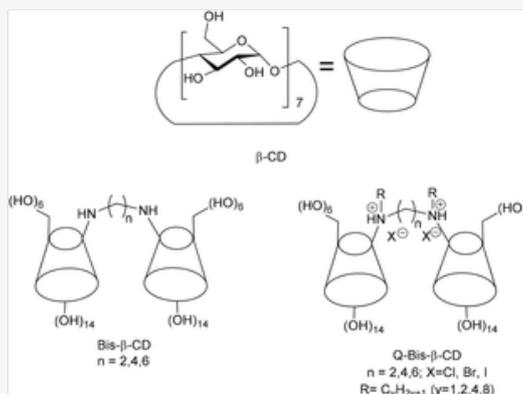
The same group prepared a nanocomposite film combining chitosan with graphene oxide (CS–GO). The X-ray diffraction pattern showed that CS was introduced into graphene oxide. Furthermore characterisation by means of TEM images revealed that the biopolymer was uniformly coated on the surface of the graphene sheets.¹⁴⁶ The yield of cyclic propylene carbonate obtained with CS–GO/TBAB was similar to the yield obtained with the zeolite/chitosan-based catalyst. The catalyst was able to be recycled for up to five runs with a 4% loss in yield.

Recently, it has been reported that the natural chitin biopolymer (Fig. 12), the precursor of chitosan by basic deacetylation, can be used directly as a support for catalysts for the cycloaddition of CO₂ to epoxides. A series of chitin anchored potassium halide catalytic systems in combination with small amounts of DBU was tested as catalysts for the synthesis of propylene carbonate.¹²⁸ The best result (97% yield of styrene carbonate) was obtained with the chitin/KI system (entry 18, Table 5), which is comparable with the result obtained using deacetylated biopolymer CS/KI. The yield of carbonate increased with the addition of small amounts of DBU (0.15–0.25 mol%), especially evident in the case of more demanding substrates such as 1,2-epoxihexane and cyclohexene oxide (99% and 82% yield, respectively). The separation of the catalyst by filtration allowed it to be reused for up to seven cycles without apparent loss of activity although fresh DBU had to be added in every cycle.

4.4. β-Cyclodextrin-based catalysts

β -Cyclodextrins (β -CD, Fig. 14) are a family of cyclic oligosaccharides frequently characterised as a doughnut-shaped truncated cone. β -Cyclodextrins are stable and readily available and contain abundant hydroxyl groups to act as a natural hydrogen bond donor.¹⁴⁷ It has been reported that the β -CD catalysed reactions take place by supramolecular interactions through non-covalent bonding such as epoxide activation forming a cyclodextrin–epoxide complex.¹⁴⁸

Fig. 14

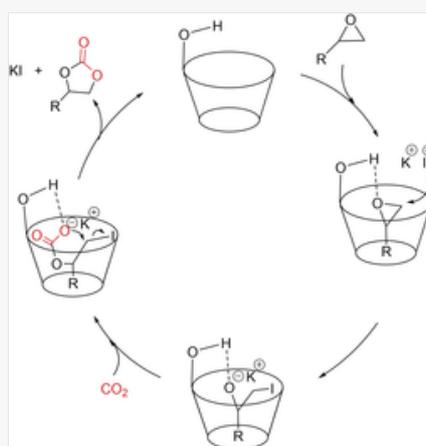


β -Cyclodextrins (β -CD) based catalytic systems:¹²⁹ amino-bridged bis- β -cyclodextrins (bis- β -CD) and quaternised amino-functional Q-bis- β -CD compounds. Adapted from Peng *et al.*¹³⁰

Despite the interest in cyclodextrins as HBD, little research has focused on their use as a catalyst in the synthesis of cyclic carbonates. In general, they are used in combination with alkali halide or quaternary ammonium salts. The first report, in 2008, describes the use of a binary system of β -CD and potassium halide for cyclic carbonate formation through the coupling reaction of CO_2 with epoxides.¹²⁹ As a benchmark reaction, the cycloaddition of propylene oxide to CO_2 to produce propylene carbonate was studied using various catalysts. The order of activity was observed to be $\text{KI} > \text{KBr} > \text{KCl}$ (entry 19, Table 5), which is consistent with the leaving ability and nucleophilicity of these halide anions, as previously discussed. Using potassium iodide and after the optimisation of the reaction conditions, including temperature and reaction time, the catalyst recyclability was studied for the benchmark reaction, maintaining the activity in the propylene cyclic carbonate for five cycles and demonstrating the stability of the catalyst. Screening of terminal epoxides as substrates showed that cyclic carbonates were obtained with yields of about 93–99%. Less activity was found for epichlorohydrin and styrene oxide, which required longer times although the yields were about 93%. Much less activity was found for cyclohexene oxide as a substrate.

A reaction mechanism was suggested based on previous reports in the literature¹⁴⁸ and the results obtained in this work (Scheme 19) starting with epoxy activation through hydrogen bonding to form the cyclodextrin–epoxide inclusion complex followed by the iodide anion attack at the carbon atom of the activated epoxide and ring-opening reaction. The alkyl carbonate anion is stabilised by hydrogen bonding and cyclic carbonates are formed by intramolecular reaction, leading to catalyst regeneration.

Scheme 19



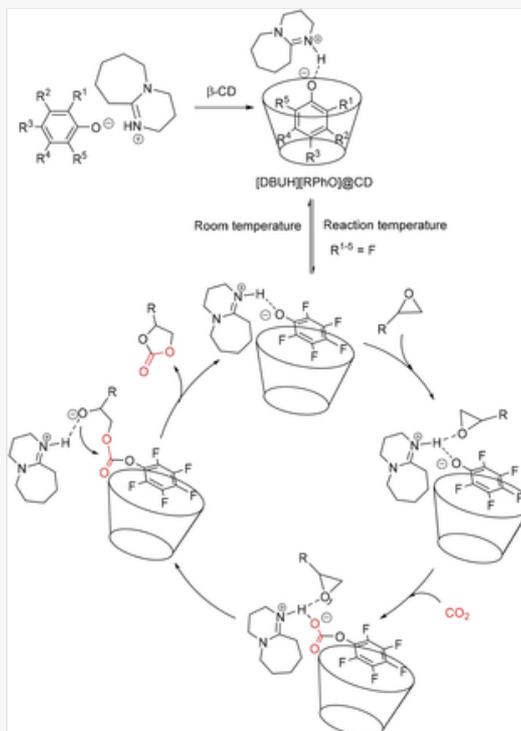
In 2019, Peng *et al.* reported a very high performance catalyst for this reaction consisting of amino-bridged bis-β-cyclodextrins (bis-β-CD, Fig. 14).¹³⁰ Under optimised conditions, the bis-β-CD/KI catalytic system provided excellent yield (94%) in 2 h and was highly selective to propylene carbonate (99%), although used at a temperature above 100 °C (entry 20, Table 5).

Based on the excellent results obtained using bis-β-CD ($n = 2$) with potassium iodide as a cocatalyst, in the same work, a modification was introduced to obtain related haloalkane quaternised Q-bis-β-CDs (Fig. 14).¹³⁰ These systems can act as a single catalyst without the addition of the cocatalyst KI. The trends in CO₂ pressure and other reaction parameter effects were similar to those observed for the catalytic system containing bis-β-CD ($n = 2$)/KI. As such, the catalytic reaction was performed under the same reaction conditions. To explore the potentiality of both bis-β-CDs/KI and bifunctional haloalkane Q-bis-β-CD, these catalysts were used in the cycloaddition reactions of CO₂ with several epoxides as substrates. These systems were extremely efficient for a variety of substrates, including those with electron-withdrawing and electron-donating substituents, providing the corresponding cyclic carbonates in good yields and with excellent selectivity (see for example the results for PO in entry 21, Table 5). The reusability of the bifunctional catalyst Q-bis-β-CD ($n = 2$, X = I; R = -C₄H₉) was investigated for epichlorohydrin as substrate under optimised reaction conditions, showing that the catalyst could be reused at least five times without a considerable decrease in the yield or selectivity.

The preparation of catalytic systems using β-cyclodextrin combined with quaternary ammonium salts as cocatalyst for the synthesis of cyclic carbonates from CO₂ and epoxides was also reported in 2019.¹⁴⁹ The systematic optimisation of the reaction conditions, including temperature, time, CO₂ pressure and the mole ratio of reactants for the β-CD/tetrabutylammonium bromide (TBAB) catalyst, lead to a 100% yield of cyclic propylene carbonate (entry 22, Table 5). Screening of the performance of the catalytic system β-CD/TBAB for a variety of epoxides as substrates provided good to excellent yield and high selectivity (>99%). The system was recycled without a significant decrease in the activity after five cycles. A mechanistic proposal was included based on the reaction results and literature.¹⁴⁹

Inclusion complexes of DBU-based phenolates with β-CD have also been developed to be used as recyclable catalysts for the cycloaddition of carbon dioxide with epoxide without additional solvents or additives.¹³¹ Organic bases such as DBU, MTBD, TBD, and DABCO are considered to be environmentally friendly in the CO₂ conversion to cyclic carbonates since the presence of halide anions is not required,^{74,76,77} although the recovery of the catalyst is difficult for these homogeneous systems. The idea was therefore to develop heterogeneous catalytic systems through the inclusion in β-cyclodextrins as phenolate salts. After synthesising the salts by neutralizing phenol derivatives with DBU, the corresponding phenolates were included in the β-CD through the hydrogen bond interaction in aqueous solution (Scheme 20). Careful FT-IR and ¹H NMR together with ¹⁹F NMR and ¹³C NMR characterisation of the system provided the evidence for the formation of the inclusion complex [DBUH][PFPhO]@β-CD.

Scheme 20



β -Cyclodextrins inclusion complexes with DBU phenolate ([DBUH][RPhO]@ β -CD) and proposed mechanism for the cycloaddition of epoxide and CO₂ catalysed by [DBUH][PFPhO]@ β -CD.¹³¹

The cycloaddition reaction of propylene oxide with CO₂ to produce propylene carbonate was used as a model reaction to optimise the reaction conditions and evaluate the catalytic activity of these catalysts. First, DBU-based phenolates were studied and it was found that the salt [DBUH][PFPhO] formed with DBU and 2,3,4,5,6-pentafluorophenol (the one with the lowest pK_a value) showed the highest catalytic activity. The best catalysts used in this work increased the activity and selectivity compared to only β -CD (entries 23–25, Table 5). All catalysts were highly selective to cyclic carbonates (98%) except β -CD, which has 1,2-propanediol as its main by-product. Screening the scope of the catalysts showed their applicability to a series of epoxides as substrates with high activities in the formation of cyclic carbonates following the usual trend: higher steric hindrance as for 1,2-epoxyhexane and 1,2-epoxycyclohexane required longer reaction times. The recyclability of the catalyst was studied for [DBUH][PFPhO]@ β -CD which provided the best catalytic performance. The catalyst was recovered by filtration, followed by washing with ethyl ether and vacuum drying. The catalyst could be reused up to four times with high product selectivity and a slight decrease in conversion. The catalyst characterization and the results obtained suggest a rational mechanism in which β -cyclodextrin plays a crucial role in immobilizing the catalytically active species, which improves recyclability (Scheme 20).

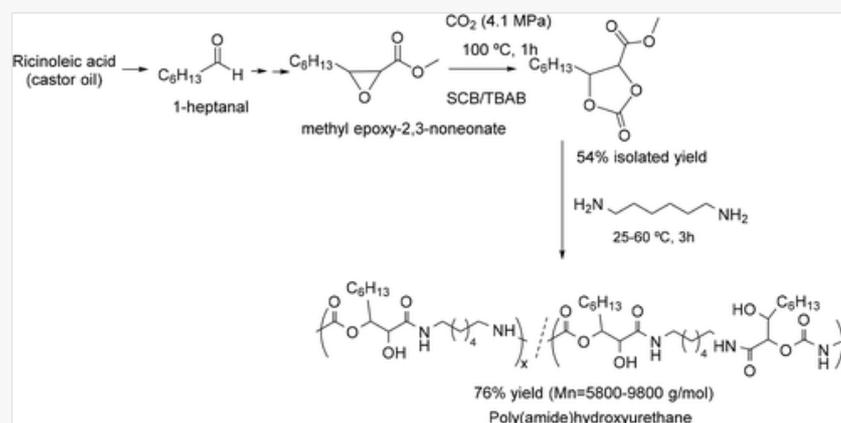
Although comparing the catalytic performance among the catalytic systems is difficult because of the different reaction conditions, the results of several catalytic systems based on biopolymers for the coupling reaction of CO₂ with propylene oxide¹³⁰ have been compiled and illustrate the excellent performance of the systems based on functionalised β -cyclodextrins.

4.5. Lignocellulosic materials

Lignocellulosic biomass is considered the most abundant and bio-renewable biomass on earth and is mainly composed of three biopolymers: cellulose (40–60%), hemicellulose (15–30%) and lignin (15–30%), which are interconnected in a complex matrix within the structure of plants.¹⁵⁰ Lignocellulosic materials obtained from vegetal plant residues ~~in~~ of sugarcane bagasse (SCB) can be used directly in combination with halide containing nucleophiles as catalysts for the synthesis of carbonates from epoxides and carbon dioxide.^{51,151} Propylene carbonate was obtained with high yield (93%) and selectivity (99%) by using a binary SCB/KI system (entry 26, Table 5).¹⁵¹ The vegetal plant waste was simply dewaxed before use and it could be separated and reused in five cycles. The reaction was scaled up to a 500 mmol (29 g) of propylene oxide, obtaining an 81% yield of carbonate with 99% selectivity. Other terminal epoxides were successfully obtained by using this procedure (82–96% yield).

The application to a sustainable route to non-isocyanate polyurethanes (NIPUs) from five-membered cyclic carbonates and amines was developed using the plant waste from SCB in combination with an ammonium salt, TBAB, as a catalyst for the CO₂ fixation step.⁵¹ Methyl epoxy-2,3-noneonate was obtained from 1-heptanal, a by-product of castor oil (Scheme 21). From this activated internal epoxide, the corresponding cyclic carbonate was obtained with a good isolated yield (54%) using an SCB/TBAB catalytic system at 100 °C, 4.1 MPa of CO₂, 2.5 wt% SCB and 5 mol% TBAB in 1 h. It is worth noting that using only TBAB under the same conditions it required 6 h to obtain the same yield. The system was reused up to six cycles before the yield decayed. Polymerization of the cyclic carbonate by reaction with 1,6-diaminohexane produced the poly(amide-hydroxyurethane) (PAHU, Scheme 21) in high yield (76%) at mild temperatures (25–60 °C) with moderate molecular weight ($M_n = 5800\text{--}9800\text{ g mol}^{-1}$).

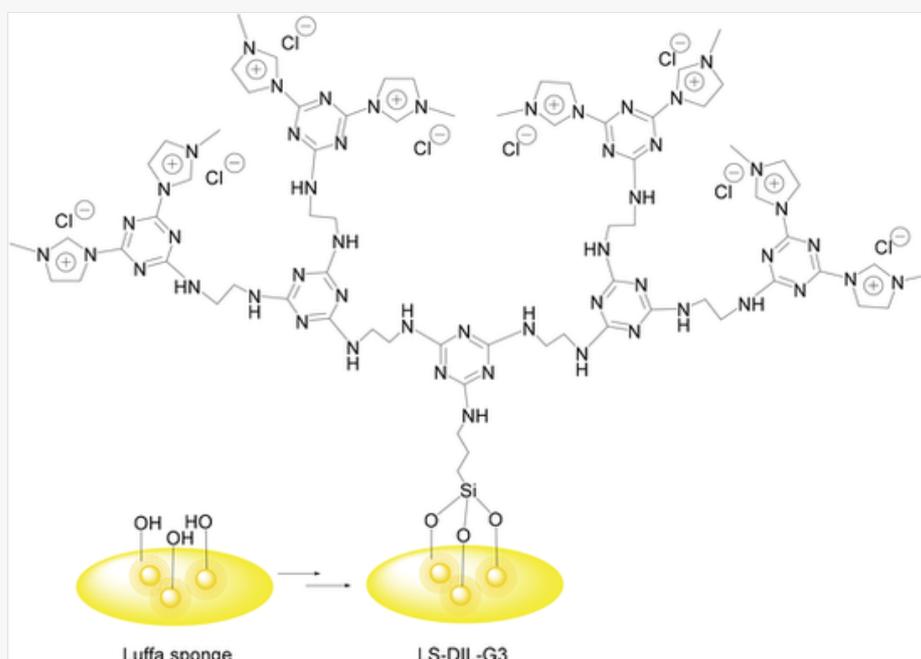
Scheme 21



Preparation of poly(amide)hydroxyurethane (PAHU) from 1-heptanal obtained from castor-oil.⁵¹

Highly functionalised biopolymers can be used as supports as well. Luffa sponge, a lignocellulosic material, is a cheap, biodegradable, abundant and renewable material source with a fibrous porous structure that has been used as a support for imidazolium-based ILs.¹⁵² Imidazolium moieties were incorporated into ionic dendritic structures (LS-DIL, Scheme 22). LS-DIL of the third dendritic generation in combination with TBAB was active as a catalyst for the synthesis of cyclic carbonates with high yields (84–99%) from terminal epoxides. For example, styrene carbonate was obtained with a 94% yield (>99% selectivity) and the system was reused up to six runs (entry 27, Table 5). The isolated yield was still high (78%) under these conditions on a multi-gram scale (80 mmol, 9.6 g of styrene oxide).

Scheme 22



Imidazolium dendritic ILs supported on Luffa sponge (LS-DIL). Adapted from Lai *et al.*¹⁵²

5. Other catalytic materials in the cycloaddition of CO₂ to epoxides

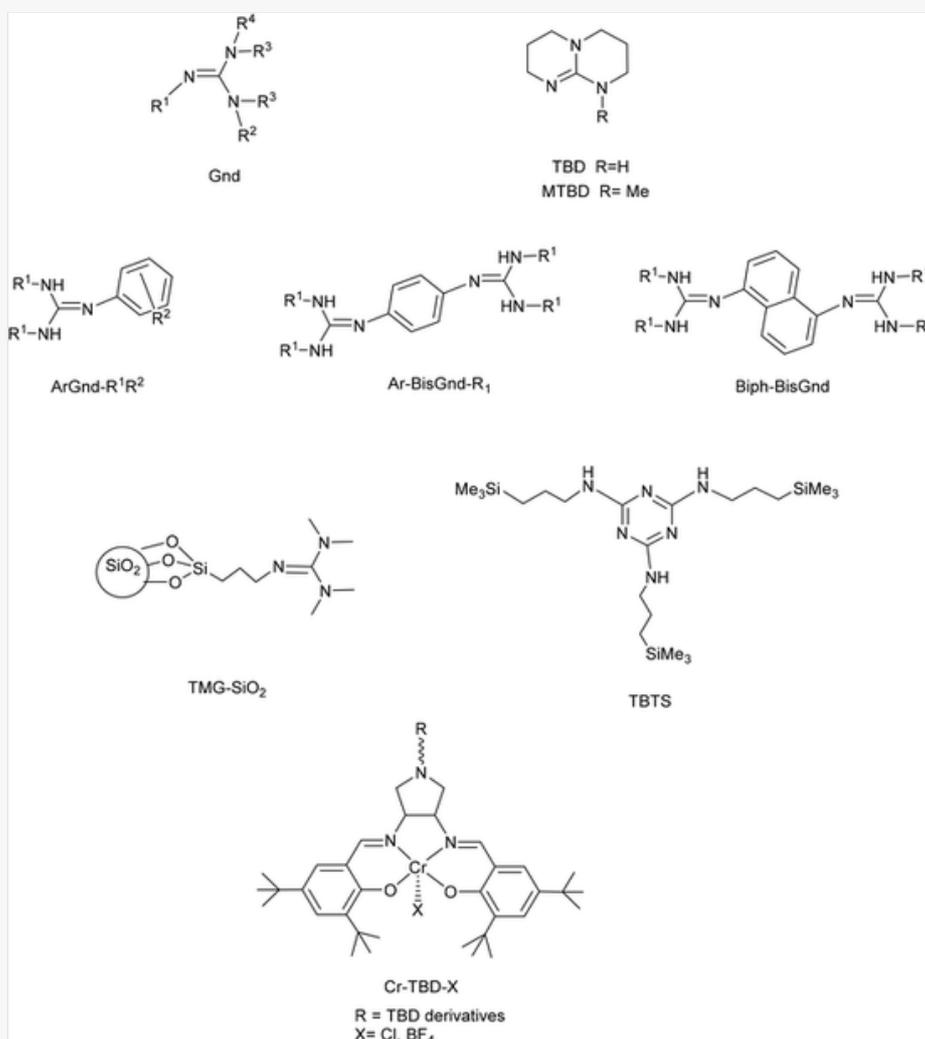
5.1. Nucleobases or nitrogenous bases

Like amino acids, nucleobases are very versatile natural products that can be useful in many fields of chemistry, on their own, or as building blocks for more complex structures. The characteristics that make them so attractive include their reduced size, their rigid structure and their multiple binding sites. Moreover, they can establish interactions through $\pi\cdots\pi$ stacking and/or hydrogen bonds. In the particular field of catalysing the cycloaddition of CO₂ to epoxides, guanidines and adenines have been the most frequently used, acting as nucleophilic centres and forming part of homogeneous as well as heterogeneous catalysts.⁴²⁺

5.1.1. Guanidine systems

Guanidines (Gnd), of the general formula $R^1N=C(NR^2R^3)(NR^4R^5)$ ($R^{1-5} = H, \text{alkyl, aryl, and Gnd}$, Fig. 15), in their neutral, cationic (guanidinium) or anionic (guanidinate) forms, are present in many natural products and have been used widely in chemistry due, among other factors, to their tunable structural and electronic properties. Research into the use of guanidines as catalysts for obtaining cyclic carbonates from CO₂ and epoxides began in the early years of the 21st century. A recent review⁴² compiles the most significant research on the use of guanidines and guanidinium salts as catalysts for this purpose and other reactions for CO₂ capture and activation. The publication summarises the characteristic performance and, in some cases, the proposed mechanism of reaction of many systems in relation to the aim of obtaining cyclic carbonates from reaction with epoxides. The following is a list of these systems, grouped by type, along with their most significant characteristics, including data about their best performance (Table 6), and their structure (Fig. 15). The proposed mechanisms of reaction are summarised afterwards.

Fig. 15



Guanidine (Gnd) based catalytic systems: *N*-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD),¹⁵³ mono- (ArGnd) and bis(guanidines) (Ar-BisGnd, Biph-BisGnd),¹⁵⁵ supported guanidine based catalytic systems TBD, TMG-SiO₂,¹⁵⁹ TBTS,¹⁶⁰ chromium(III) complexes with TBD modified ligands(Cr-TBD-X).¹⁵⁴

Table 6

Cycloaddition of CO₂ to epoxides catalysed by guanidine-based catalytic materials

Entry	Epox ^a	Catalyst ^b	Cocat	Catalyst/cocat (mol%)	<i>T</i> (°C)	<i>P</i> (MPa)	<i>t</i> (h)	Yield (%)	Recycling (cycles reported)	Ref.
1	SO	Bis-Gnd- ⁱ Pr	TBAI	1/2	70	0.1	24	88		155
2	PO	TBD-SiO ₂	—	6.4 wt%/—	150	2	20	99.5 ^c	(solvent DCM)	156 and 157
3	PO	TMG-SiO ₂	—	1.6 wt%/—	130	5.0	8	90 ^c	4 (solvent toluene)	159
4	PO	TBTS-PMO	—	4 wt%/—	100	0.55	10	40 ^d	1 (solvent, DMF)	160
5	SO	TMG-PPh	—	0.1/—	100	0.7	20	90 ^d	—	161
6	PO	Cr-TBD-Cl	—	0.02/—	80	2	1	42.4 ^d	—	154
7	PO	HBGCl	—	1.5/—	110	4.5	3	100	—	162
8	PO	HBGBr	ZnBr ₂	0.22/0.028	100	4.0	1	100	—	163
9	PO	GndHCl	ZnI ₂	2.9/5.8	100	1	1.5	94	3	164
10	PO	BrTBD-PEG	—	1/—	120	1	3	>99	—	165
11	PO	BrGnd-PEG	—	0.5/—	110	2	4	99	4	165
12	PO	TMG-C ₂ H ₄ -NH ₂ -Br	—	0.5/—	130	2.0	2	94.6	—	166
13	PO	TBDHCl	—	1/—	140	1	2	86	—	167
14	PO	TBDHBr	—	1/—	80	8	20	88	—	168
15	PO	(TMGH) ₃ NbO ₅	—	3/—	130	3.0	5	86 ^c	—	169
16	PO	COP-123	—	4.83/—	100	0.1	48	98 ^c	—	170

Table Footnotes

^aSO = styrene oxide and PO = propylene oxide.

^bAbbreviation from Fig. 15–18, TMG-PPh = TMG on polyphenylene polymers.

^cEstimated from conversion and selectivity data.

^dConversion.

The guanidine *N*-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, Fig. 15) was one of the first compounds of this kind used in this reaction as a homogeneous catalyst. The reaction was slow, but the catalyst was easily recovered and could be reused.¹⁵³

Improved efficiency resulted using aromatic mono- and bis(guanidines) ((Ar-Gnd-R¹R², Ar-BisGnd-R¹, and Biph-BisGnd, Fig. 15) in binary catalytic systems (guanidine/cocatalyst).¹⁵⁵ These catalysts were designed for use under mild reaction conditions, due to the activation of the epoxide through the formation of multiple H bonds between the N-H groups of the catalyst and the oxygen atom of the epoxide. Reactions were performed at 70 °C and 0.1 MPa of CO₂, with the proportion of the catalyst (mono- or bis(guanidines)) necessary to keep the number of N-H bonds constant, and using TBAI as the most effective cocatalyst.¹⁵⁵ In reactions with styrene oxide, the yield was lower when using monoguanidines (58–74%) than when using bis(guanidines) (62–92%) (see, for example, entry 1, Table 6).

Selectivities in all cases were around 99%. The reaction yields were similar for all terminal epoxides. For internal and/or disubstituted epoxides, however, the temperature had to be increased to 85 °C. In some cases, the pressure had to be increased up to 2.0 MPa to obtain high conversions. By comparing to other catalytic systems it was concluded that, in general, guanidines that were unable to form H bonds did not perform as well as guanidines with NH groups, but their catalytic performance was also worse than catalysts with hydroxyl groups.

5.1.2. Supported guanidine-catalytic systems

Some efficient catalysts have been obtained when guanidines were tethered covalently to silica modified by aminoalkyl silanes. A simple bicyclic guanidine such as TBD (Fig. 15) was used to functionalise amino-modified silica supports (TBD-SiO₂).^{156,157} These materials exhibited better performance than other amino-functionalised catalysts (entry 2, Table 6). The crucial role of the silanol functional groups formed was revealed by test reactions performed with the modified catalysts. Another approach was used to covalently bond TBD moieties to a porous MCM-41 siliceous support by covering the surface with the oxirane groups through the reaction of the Si-OH groups with 3-trimethoxysilylpropoxymethyloxirane. TBD was covalently bonded by the reaction of the amino group with epoxides under mild conditions.¹⁵⁸ The cycloaddition of CO₂ to styrene oxide to form styrene carbonate took place at a lower rate with the MCM-41-TBD catalyst than with the homogeneous TBD catalyst.¹⁵³ In a subsequent work, 1,1,3,3-tetramethylguanidine (TMG) was also bonded covalently to silica (TMG-SiO₂, Fig. 15).¹⁵⁹ Under optimal conditions, the results were satisfactory (results for PO in entry 3, Table 6) with the advantage that the catalyst was easily recovered and reused at least four times with a loss of catalytic activity of about 20%.

Melamine tri-silsesquioxane (TBTS, Fig. 15) was used to act as bridge in a periodic mesoporous organosilica (PMO) catalyst.¹⁶⁰ The conversion for the reaction of PO obtained using this catalyst was around 40% (TOF reported 836 h⁻¹, entry 4, Table 6) and it had the benefit of being recycled without any loss of activity. The mechanism of this reaction was studied using a computational model, as described later.

Supporting TMG (Fig. 15) on porous polyphenylene polymers resulted in effective catalysts for the cycloaddition of CO₂ to epoxides (TMG-PPh) to yield the corresponding cyclic carbonates in a reaction without solvent.¹⁶¹ The support did not affect the reactivity, but a spacer (-CH₂) between the TMG group and the polymer backbone had a beneficial effect. Although the yield was low for disubstituted cyclohexene oxide (30% in 20 h) it was high for epichlorohydrin (100% in 4 h) with 100% selectivity in all cases. Conditions and results for SO are included in Table 6 (entry 5).

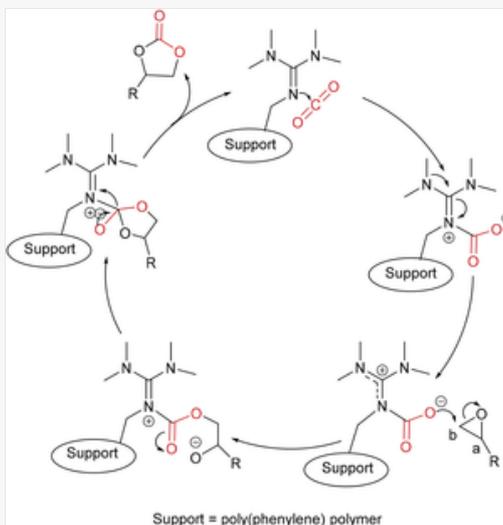
5.1.3. Guanidines as part of metallic complexes

TBD (Fig. 15) was also used to design bifunctional catalysts containing pyrrolidine Cr(III)salenX (Cr-TBD), which combines an electrophilic centre (the metal ion) and the nucleophile TBD.¹⁵⁴ The catalytic activity of the chloride derivative (Cr-TBD-Cl, Fig. 15) was quite high (TOF 2120 h⁻¹, entry 6, Table 6). **The analogous** Related cobalt complexes led to the selective formation of polycarbonates.¹⁷¹

The first step in the reaction mechanism for the guanidine-based catalysts is generally agreed to be the interaction between guanidine and CO₂ to form a carboxylate^{153,156} or a carbamate^{157,159,160} zwitterion that attacks the epoxide and opens the ring that eventually incorporates CO₂ and forms a cyclic carbonate. This is shown in the catalytic cycle proposed by Maya *et al.*¹⁶¹ (Scheme 23) which begins with the adsorption and activation of CO₂ on the Lewis basic sites N=C. In this case, the carbamate so formed attacks the less substituted β carbon of the epoxide forming an O-C bond, which leads to the opening of a three-membered epoxide ring to form a cyclic carbonate. These hypotheses are backed up by the study conducted by Prasetyanto *et al.*^{160,144} using a model (as mentioned earlier) employing DFT calculations. The results suggest that the carbamate formed is stabilised by an intramolecular H-bond forming a pseudo cyclic carbamate intermediate.

Scheme 23

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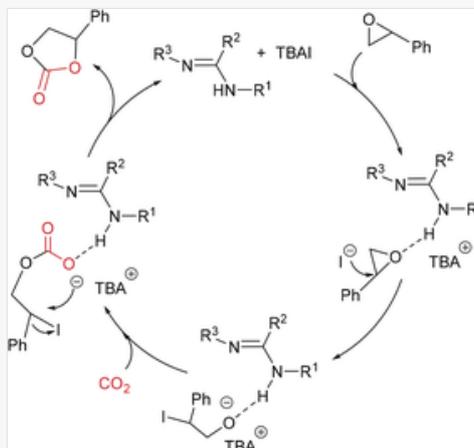
Proposed mechanism of TMG supported on polyphenylene polymers (TMG-PPh). Adapted from Maya *et al.*¹⁶¹

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The only discrepancy with this generally accepted hypothesis was proposed in the earlier mentioned work by Mesías-Salazar *et al.*,¹⁵⁵ in which the mechanism was studied using NMR measurements. The formation of a hydrogen bond between guanidine and epoxide was observed. Surprisingly, however, the nucleophilic attack of an halide on an epoxide that leads to the ring-opening was only observed when CO₂ was present. The proposed mechanism for the reaction of styrene oxide with CO₂ with a generic guanidine and TBAI as the cocatalyst is shown in Scheme 24.

Scheme 24

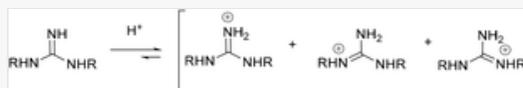


Proposed mechanism of styrene carbonate using aromatic guanidine/TBAB as catalysts. Adapted from Mesías-Salazar *et al.*¹⁵⁵

5.1.4. Guanidinium salt-based catalysts

Guanidinium salts are easily prepared and modified from the commercially available and relatively inexpensive reagents and show adequate stability for air, water and temperature. The strong basicity of the guanidinium cation, together with its several resonant species (Scheme 25) makes it very useful in the field of CO₂ conversion. In fact, ILs of guanidinium salts, without any additional components, can promote the addition of CO₂ to epoxides by using ion-pair interactions and hydrogen bonding. The anion activates an epoxide to undergo the cycle opening, while the bulky cation stabilises the oxy-anion.

Scheme 25

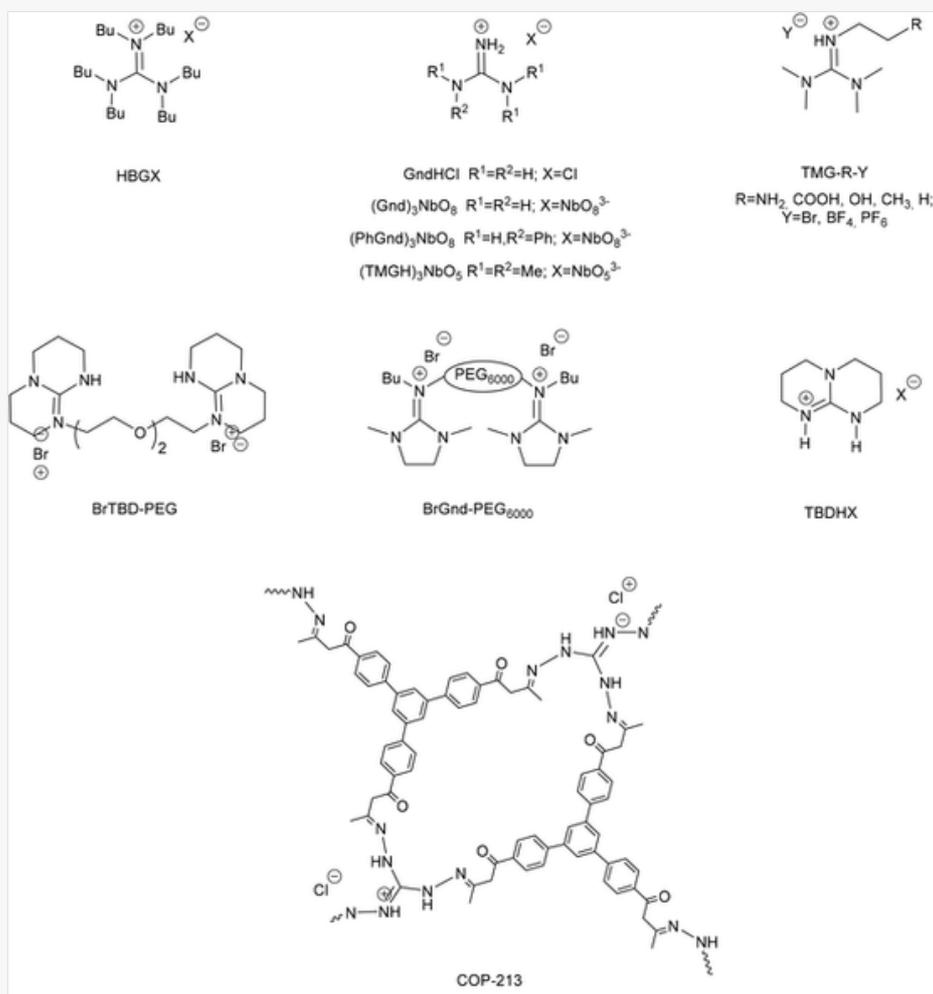


Resonance of the guanidinium ion in guanidinium salts.

Hexaalkylguanidinium chloride-based ILs were used as homogeneous catalysts (HBGX, Fig. 16) and as silica-supported heterogeneous catalysts (HBGX–SiO₂) to make them easily recyclable. Hexabutylguanidinium chloride (HBGX, X = Cl, Fig. 16) showed the best performance under mild conditions (entry 7, Table 6).¹⁶² The silica-supported material provided also high yields of other monosubstituted cyclic carbonates and good yield of cyclohexene carbonate (Fig. 17).

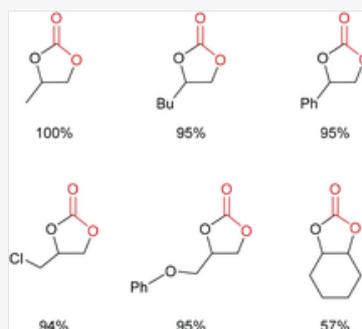
Fig. 16

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Guanidinium salt-based catalytic systems.

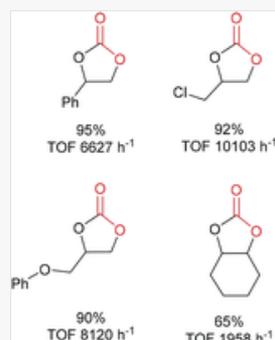
Fig. 17



Yields of cyclic carbonates obtained using HBGX-SiO₂ catalysts with different substrates (conditions: HBGX-SiO₂ molar ratio to epoxide 1.5 mol%; 110 °C, 4.5 MPa, 4 h).¹⁶²

Hexaalkylguanidinium salts were also combined with ZnBr₂ to form binary systems.¹⁶³ In this study, the best performance at 100 °C (TOF, 3571 h⁻¹, entry 8, Table 6) was shown by hexabutylguanidinium bromide/ZnBr₂ (Fig. 16, HBGX, X = Br). For this system, the optimised TOF for propylene carbonate production was 8670 h⁻¹ at 140 °C. The TOFs for other epoxides were also high (Fig. 18).

Fig. 18



Yields and TOFs of cyclic carbonates obtained using HBGBr/ZnBr₂ catalysts with different substrates (conditions: 100 °C, 4.0 MPa, 1 h).¹⁶³

Another binary system composed of guanidine hydrochloride and zinc(II) iodide (Fig. 16) was also used as an efficient solvent-free heterogeneous catalytic system¹⁶⁴ with good yields and selectivity (entry 9, Table 6).

A series of polyethylene glycol (PEG)-functionalised basic ionic liquids was also explored as efficient and recyclable catalysts. The examples prepared with a TBD core salt and (BrTBDBr-PEG, Fig. 16)¹⁶⁵ and hexaalkylguanidinium bromide covalently tethered to PEG₆₀₀₀ (BrGnd-PEG, Fig. 16)¹⁷² showed the best catalytic activity for different substrates (results for PO in entries 10 and 11, Table 6). The ionic liquid BrGnd-PEG was separated after the catalytic reaction by extraction with diethyl ether and reused in five runs with a loss of only 9% in yield. Analysis by ionic chromatography of the filtrate after catalyst separation showed minor leaching of 60 ppm of bromide, thus proving the stability of the catalyst.

The study of a series of functionalised guanidinium-based ionic liquids (TMG-R-Y, Fig. 16), used without any cocatalyst or solvent, indicated that the functional R groups played an important role in the catalytic efficiency since the yields varied from 62% to 95%.¹⁶⁶ The best performance in the cycloaddition of CO₂ to propylene oxide was obtained for the ionic liquid with R = NH₂ and X = Br (TMG-NH₂-Br, entry 12, Table 6).

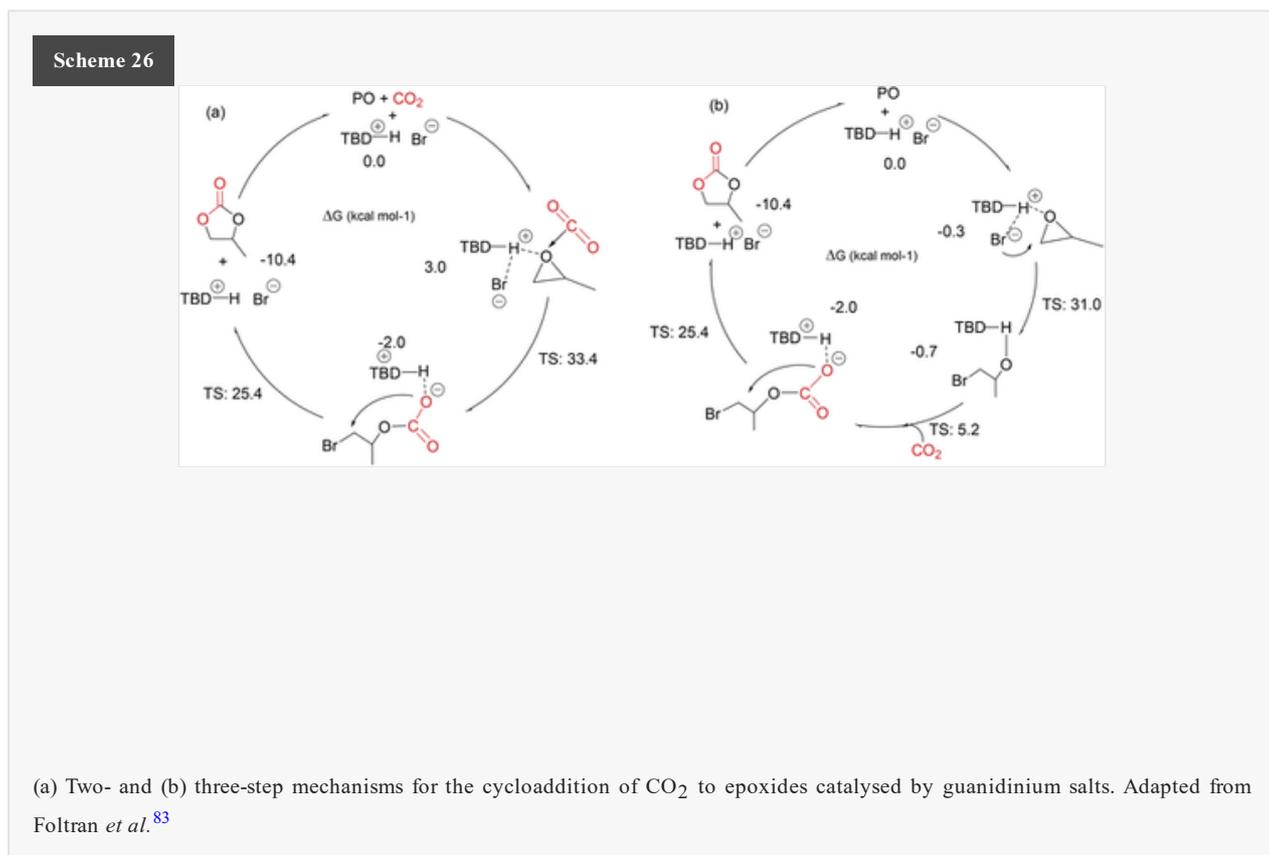
The mechanisms proposed in these studies based on experimental evidence differs in the species that interacts with the guanidinium cation. While in some cases the epoxide was proposed to be the reactant that forms a complex by

interaction through its oxygen atom,¹⁶² other studies suggest that the initial interaction takes place between one of the amine groups and CO₂ to form a carbamoyl that generates an H bond with the epoxide, which activates it and subsequently opens the ring by the nucleophilic attack of the anion of the guanidinium salt.¹⁶⁵ Liu *et al.*¹⁶⁴ suggested that the guanidinium salt plays a double role, activating both CO₂ and epoxide.

In 2010, Yang *et al.*¹⁶⁷ studied the activity of a guanidinium salt derived from TBD, TBDHCl as well as other ionic liquids (Fig. 16). TBDHCl was one of the best among the ILs tested in terms of efficiency (86% yield, entry 13, Table 6) probably due to the capability of the cation to stabilise the ring-opened epoxide intermediate, supposedly formed during the reaction mechanism, and the high nucleophilicity and good leaving ability of the anion.

Later, Foltran *et al.*¹⁶⁸ studied the influence of different anions of TBDHX salts (X⁻ = Cl⁻, Br⁻, and RCOO⁻; R = CH₃, CF₃, and C₁₁H₂₃) on their catalytic performance, showing that in some cases they presented yields better than or similar to other tetrabutylammonium and imidazolium salts. The highest yields were obtained with TBDHBr (81–88%) (entry 14, Table 6). Similar to other salts (*i.e.*, tetraalkylammonium salts), the bromide counter-anion showed much higher yields than chloride (21%), probably because the stabilization of the TBDH⁺-X⁻-AH pair is higher in the case of X = Cl than for X = Br and decreases the presence of free Cl⁻ anions. Moreover, the carboxylate anions showed very low conversion rates (from 0 to 10%), probably due to having lower nucleophilicity than halides.

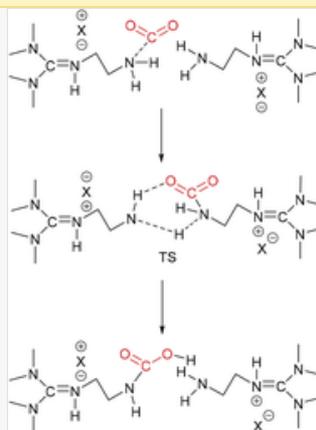
To better understand the mechanism of the guanidinium salt catalysed reaction, the same group performed a computational study at the CAM-B3LYP/6-31G(d,p) level,⁸³ comparing two- and three-step reaction paths for TBDH⁺-X⁻ (X⁻ = Cl⁻ and Br⁻, Scheme 26 for X⁻ = Br⁻). In the two-step path (Scheme 26a), the first process was the formation of an epoxide ring-opened intermediate, produced by simultaneous coordination of CO₂, epoxide and catalyst. In the three-step mechanism (Scheme 26b), the epoxide is first activated by the nucleophilic attack of the IL anion that opens the ring. The intermediate formed is stabilised by an H-bond created between the oxygen epoxide and the guanidinium cation. In the second step, the H-O interaction is broken by the electrophilic attack of carbon of CO₂ at the oxygen of the epoxide, forming a C-O bond. The last step, common to both mechanisms, corresponds to the carbonate ring closure and regeneration of the guanidinium salt. The reaction profiles obtained show that in both cases the rate-determining step is the epoxide ring-opening, with a barrier of $\Delta G = 33.4$ kcal mol⁻¹ in the first case and 31.0 kcal mol⁻¹ in the second case for the bromide salt. Although the barriers obtained are too large, indicating that these results are not precise enough at a qualitative level, the energetic difference between the mechanisms together with the smaller probability of a tri-molecular event indicates that the most probable mechanism of this reaction follows a three-step path.



A later work, performed at the B3LYP level (optimising geometries with the 6-31G(d,p) basis set and refining energies with the 6-311+G(2d,2p) set),^{84,173} reported the mechanism of the reaction of CO₂ with epoxide catalysed by several functionalised guanidinium-based ILs (specifically, TMG-R-Y, with R = -NH₂, -COOH, -OH, -CH₃ and -H; and Y = Br, BF₄ and PF₆, Fig. 16). It was confirmed that in all cases the reaction followed the three-step path described in previous works. In these cases, the opening of the epoxide ring was also the rate-determining step with energy barriers in the range of 19–23 kcal mol⁻¹. Nevertheless, when R = C₂H₄NH₂ (TMG-C₂H₄NH₂-Y ILs), *i.e.* the catalysts that perform the best, the mechanism exhibits a significant difference: the reaction begins with the formation of carbamic acid by the reaction of the primary amine with CO₂ *via* a tri-molecular complex formed by CO₂ and two TMG-C₂H₄NH₂-Y molecules (Fig. 19). The carbamic acid-functionalised IL is the species that reacts with an epoxide. The ring-opening barrier of this path is only 18.24 kcal mol⁻¹, explaining the best performance of this catalyst. The involvement of two catalyst molecules has also been investigated for the other IL, but the decrease in the energy barrier of the rate-determining step in those cases is not significant. The comparison of the reaction profiles for different anions and cations led to the conclusion that more acidic functional groups in the cation and stronger ability of nucleophilic attack of the anion are desirable to increase the catalytic activity.

Fig. 19

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The formation, *via* a trimolecular complex, of carbamic acid that reacts with an epoxide in the reaction catalysed by TMG-C₂H₄NH₂-Y.^{84,173}

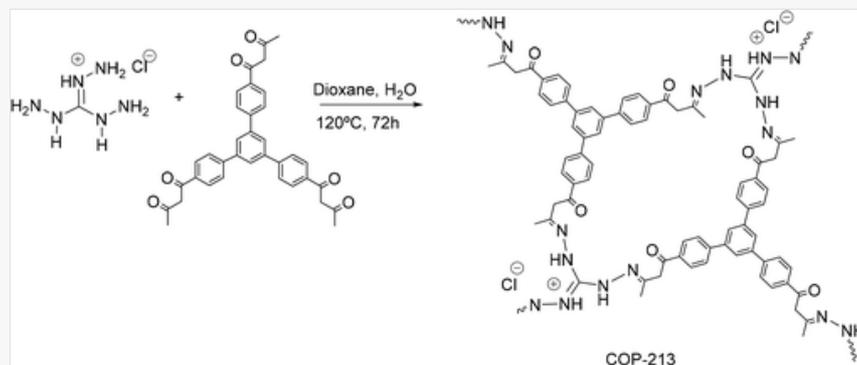
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In pursuit of a halogen-free reusable catalyst with good catalytic performance under solvent-free and mild temperature and pressure conditions, and in short reaction times, Lewis basic peroxoniobate salts of amidine and guanidine were synthesised ((Gnd)₃NbO₈, (PhGnd)₃NbO₈, (TMGH)₃NbO₈, Fig. 16).¹⁶⁹ The yields oscillated between 50.6 and 91.7%, and the selectivities between 86.5 and 94.0% (entry 15, Table 6). The catalytic efficiency increased in the order of the conjugate basicity of the cations. Guanidinium salts were less active than the amidine salts.

In a more recent work, triguanidinium halides together with β-ketoenols as components of a covalent organic polymer (COP-213, Fig. 16 and Scheme 27) have been employed to obtain cyclic carbonates by reaction of CO₂ with epoxides.¹⁷⁰ The bulkiness of the guanidinium cation was expected to make the counter-anion more nucleophilic, resulting in an active catalyst.

Scheme 27



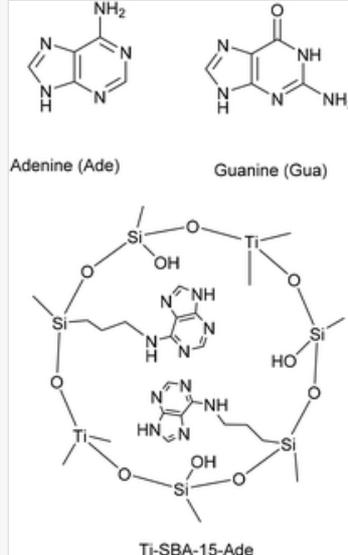
Preparation of the β -ketoenol derivative of guanidinium salt COP-213.¹⁷⁰

Several factors that potentially influence the catalytic performance were studied. After confirming that the physical mixtures of the components of COP-213 showed negligible catalytic activity, the best conditions for the reaction with COP-213 were sought. The results showed that the chloride ions showed the highest activity. The substrates PO, ECH and epibromohydrin (EBH) showed excellent selectivities (>99%) and conversion rates (92–99%), with low TONs (between 19 and 20 for PO, entry 16, Table 6). Hard and less reactive substrates (such as 1,2-epoxybutane, 1,3-butadiene monoepoxide, and 1,2-epoxyhexane) showed high selectivity (>99%), but much lower conversion rates (20–53%).¹⁷⁰

5.1.5. Adenine-based catalytic systems

Among the nucleobases, adenine (Ade, Fig. 20) has also been widely employed as a component of discrete metal complexes, coordination polymers or MOFs with transition metals with many different uses in a variety of chemical applications (drug delivery, sensing, gas adsorption, selective separation of gases, *etc.*). Adenine's ability to coordinate with metals and form network architectures is due to the specific characteristics of its structure: it is quite rigid, presents five potential coordination sites (two imidazole, two pyrimidine N atoms and a secondary amino group), and can adopt tautomeric neutral or protonated forms upon coordination with metals.

Fig. 20

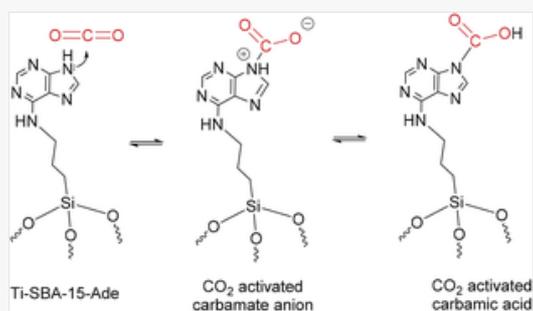


Nucleobases adenine (Ade) and guanine (Gua) structures and catalytic systems: mesoporous silica SBA-15 modified with adenine (Ti-SBA-15-Ade).^{174,175}

For the specific aim of synthesising cyclic carbonates from CO₂ and epoxides, adenine alone shows catalytic activity and selectivity in a homogeneous catalytic process (36.6% of conversion and 89.6% selectivity for chloropropene carbonate),¹⁷⁴ probably due to its many coordination sites. However, recently, Ade has also been used to develop sustainable heterogeneous catalysts by incorporating it into different types of supports.

Srivastava *et al.* modified mesoporous silica SBA-15, incorporating Ti or Al and adenine or guanine (Fig. 20) as well as other non-natural alkyl amines, in the search for an effective heterogeneous catalyst for cyclic carbonate formation that could be used without a cocatalyst or solvent under mild temperature and pressure conditions.^{174,175} The conversion and selectivity of SBA-15 were in fact very low. However, both parameters increased when a Lewis acid (Ti and Al) and a Lewis base (adenine and guanine) were incorporated into the SBA-15 structure (see as an example mesoporous Ti-SBA-15-Ade structure in Fig. 20). The nature of the active sites in the synthesised catalyst was analysed using *in situ* IR spectroscopy of adsorbed CO₂.^{174,175}

The authors found that only nucleobase-modified catalysts showed a large concentration of activated CO₂, which increased with CO₂ pressure and decreased with temperature. CO₂ was activated mainly with the amine groups to form surface carbamate, which in the case of primary and secondary amines were in equilibrium with the carbamic acid species (Scheme 28). In tertiary amines (like imidazole), carbamic acid does not exist, making carbamate more stable and ultimately less prone to react with an epoxide. The balance between the strength of binding of CO₂ (greater in the primary amines than in the secondary and tertiary amines) and the stability of carbamate *vs.* carbamic acid show that the secondary amines (adenine first followed by guanine) are the most effective catalysts of the series of modified Ti/Al-SBA-15 tested. This indicates that the density of medium strength basic sites is a crucial parameter in the design of solid catalysts for the cycloaddition reaction. Acidic functionalities were provided by Lewis acid Ti⁴⁺ and Al³⁺ incorporated into SAB-15. Their most important role was to increase the surface concentration of the epoxide molecules to enhance the catalytic activity. Epoxide conversion was observed to increase with an increase in the Ti content, but only up to a Si/Ti value of 40. M-SBA-15-nucleobase catalysts were highly active and selective with a variety of epoxides of different sizes and structures even in the absence of any solvent (see the result for PO in entry 1, Table 7).¹⁷⁴ Nevertheless, it was found that solvents prolonged the catalyst life. The recycled catalyst was not deactivated even after the tenth cycle, presumably because the solvent removes the carbonaceous deposits from the catalyst surface and keeps it clean.



Schematic representation of the activation of CO₂ with a secondary amine in mesoporous silica SBA-15 modified with the adenine catalytic system (Ti-SBA-15-Ade).^{174,175}

Table 7

Cycloaddition of CO₂ to epoxides catalysed by miscellaneous catalytic materials

Entry	Epox ^a	Catalyst ^b	Cocat	Catalyst/cocat (mol%)	T (°C)	P (MPa)	t (h)	Yield (%)	Recycling (cycles reported)	Ref.
1	PO	Ti-SBA-15-Ade (Si/Ti = 40)	—	9.5 wt/0.5 mol% (Ade)	120	0.69	6	95.3 ^c	10 (MeCN)	169 174
2	PO	PNU-Zn	TBAB	0.6/0.3	80	0.4	8	91	5	85
3	SO	ChCl	—	1.66/—	120	1.5	23	66 ^c	—	176
4	SO	HEA16Cl	—	1.66/—	120	1.5	23	62 ^c	—	176
5	SO	CTAB	—	1.66/—	120	1.5	23	73 ^c	—	176
6	PO	ChCl	—	1/—	110	2.45 ^d	10	85	—	177
7	PO	PS-ChCl	KI	60 wt/4.2 mol%	85	1	12	99	—	178
8	PO	ChCl/2urea	—	1/—	110	2.45 ^d	10	99	—	177
9	PO	ChCl/2urea@MS	—	0.5/—	110	1.74 ^d	6	96	5	177
10	PO	ChCl/PEG ₂₀₀	—	2.1/—	130	1.2	5	94.6	5 (150 °C, 0.8 MPa)	179
11	PO	ChI/2NHS	—	6/—	60	1.0	1	92	—	180
12	PO	ChI/PEG ₂₀₀	—	6/—	60	1.0	1	91	—	180
13	PO	ChI/2NHS	—	6/—	30	1.0	10	96	5	180
14	CHO	ChI/2NHS	—	6/—	70	1.0	10	72	—	180
15	EPC	[Ch][His]	TBAI	5/5	80	1.0	2	97 ^c	5	181
16	PO	Lecithin	KI	1.25/1.25	100	2	4	97.7	—	86
17	PO	Betaine	KI	1.25/1.25	100	2	4	11.8	—	86
18	EPH	AscA	TBAB	1/2	40.	0.1	23	94	—	71
19	PO	AscA	TBAB	2/4	rt. ^e	0.5	23	82	—	71

Table Footnotes

^aPO = propylene oxide, SO = styrene oxide, CHO = cyclohexene oxide, EPC = epichlorohydrin, and EPH = 1,2-epoxyhexane.

^b Abbreviations from [Instruction: Please add "and Fig. 21"] Fig. 20, PNU-ZN = $[\text{Zn}_2(\text{H}_2\text{O})(\text{stdb})_2(5\text{H-Ade})(9\text{H-Ade})_2]_n$, Ch = choline [Instruction: Please, add here "MS = molecular sieves,"], PS-ChCl = polymer-supported ChCl, NHS = *N*-hydroxysuccinimide, AscA = ascorbic acid.

^c Estimated from conversion and selectivity data.

^d Ratio of CO_2 /substrate.

^e r.t. = room temperature.

Another class of heterogeneous catalysts has been obtained by incorporating adenine into MOFs. Specifically, Rachuri *et al.* synthesised two adenine-based Zn(II)/Cd(II) metal MOFs, namely $[\text{Zn}_2(\text{H}_2\text{O})(\text{stdb})_2(5\text{H-Ade})(9\text{H-Ade})_2]_n$ (PNU-Zn) and $[\text{Cd}_2(\text{Hstdb})(\text{stdb})(8\text{H-Ade})(\text{Ade})]_n$ (PNU-Cd), (stdb = 4,4'-stilbenedicarboxylate) that showed the catalytic activity comparable to or even higher than other previously reported MOFs.⁸⁵ Like the type of catalysts described above, the metal centres constituted the Lewis acidic sites, while adenine provided the basic amine functional groups and dicarboxylate (stdb) was an auxiliary ligand.

Crystalline PNU-M has a 2D coordination framework in which protonated adenine links the metal atoms to form chains. These chains are connected by strong $\pi \cdots \pi$ interactions between the heterocyclic rings of Ade and by coordination through the carboxylate oxygen atoms. The inter- and intramolecular C-H \cdots O and C-H \cdots N interactions between the adenine and stdb ligands also form a three-dimensional (3D) framework.⁸⁵ Both MOFs exhibited basic sites that adsorb CO_2 , probably due to binding interactions with the nitrogen atom of adenine (both free N atoms and in amino groups) and oxygen atoms of the carboxylate groups.⁸⁵

The catalytic activity of PNU-M (yields and selectivity) with and without TBAB as the cocatalyst were compared with the performance of separated and combined components of MOFs. Under optimal reaction conditions, TOFs of up to 140 h^{-1} were obtained with high selectivities of cyclic carbonates (entry 2, Table 7). These results are comparable to or better than those of other previously reported MOFs. The yield for styrene oxide was lower, and much lower for cyclohexene oxide, probably due to the larger size of these epoxides, which prevents them from approaching the reactive sites on the surface of MOFs. These catalysts exhibited good conversion rates and selectivities up to five cycles without loss of their structural stability.

In the same work,⁸⁵ the mechanism of the reaction of CO_2 with epichlorohydrin (ECH) to form a cyclic carbonate catalysed by PNU-Zn and cocatalysed by TBAB was studied using DFT calculations performed at the M06 level using a mixed basis set (6-31G(d) for H, C, N, O and C, and LanL2DZ with effective core potentials for Zn and Br^-). A model formed by 73 atoms was used to represent the catalyst and only the Br-anion of the cocatalyst was considered. The mechanism was similar to that obtained for the previously studied amino acid-based MOF.⁸⁷ However, the barriers were significantly smaller in this case, $7.6 \text{ kcal mol}^{-1}$ for the epoxide ring-opening step (the rate-determining step) and $4.1 \text{ kcal mol}^{-1}$ for CO_2 insertion. The transition state of the ring closure was not reported, but the intermediate obtained after this step was only $2.5 \text{ kcal mol}^{-1}$ less energetic than the preceding one.

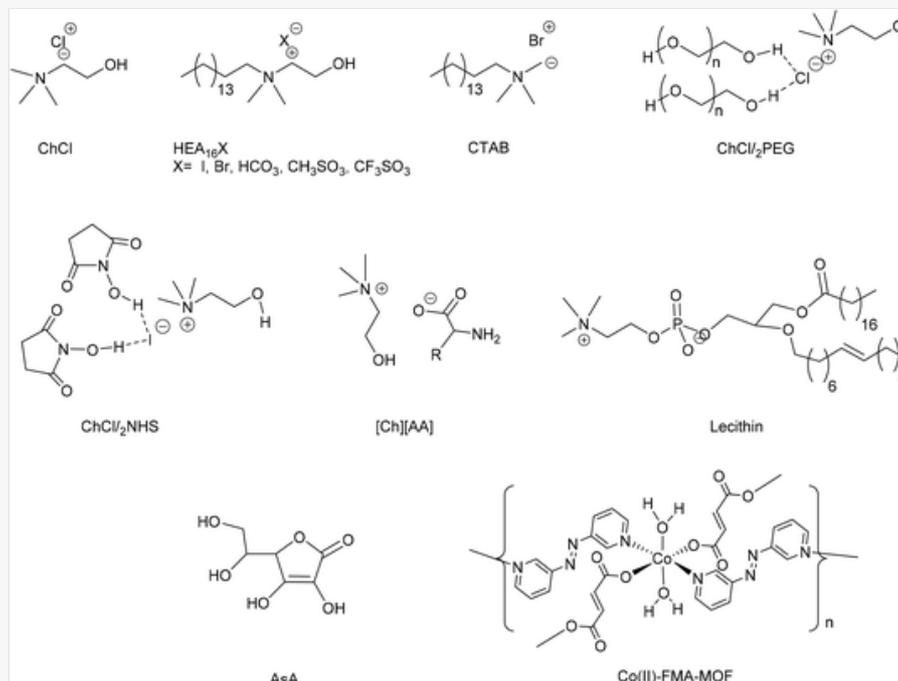
Recently adenine has been introduced into a manganese-based MOF, Mn-MOF-74, without altering its crystal structure, but increasing its basicity and catalytic activity in the fixation of CO_2 into epoxides.¹⁸² The catalytic material formed by Ade-Mn-MOF-74 and TBAB produced a high yield of terminal monosubstituted cyclic carbonates (about 98–99%). The system did not show evidence for decomposition after seven runs and the yield decreased only slightly.

5.2. Choline-based catalytic materials

Choline, 2-hydroxyethyltrimethyl ammonium chloride, (ChCl, Fig. 21) is considered an essential nutrient present in foods such as eggs and meats.¹⁸³ Choline salts refer to a choline cation containing an undefined anion. They are used as sustainable ionic liquids in many transformations¹⁸⁴ and also as deep eutectic solvents for carbon dioxide capture¹⁸⁵ and as catalysts for CO_2 transformation.^{176,177}

Fig. 21

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Choline (ChCl)-based ammonium salts used in the cycloaddition of CO₂ to epoxides (HEA16X),¹⁷⁶ PEG-ChCl/PEG deep eutectic solvent. Adapted from Wu *et al.*¹⁷⁹ Deep eutectic solvent choline-based (ChI/2NHS).¹⁸⁰ Choline-amino acid ionic liquids [Ch][AA],¹⁸¹ lecithin,⁸⁶ ascorbic acid (AsA)⁷¹ and Co(II)-FMA-MOF.¹⁸⁷

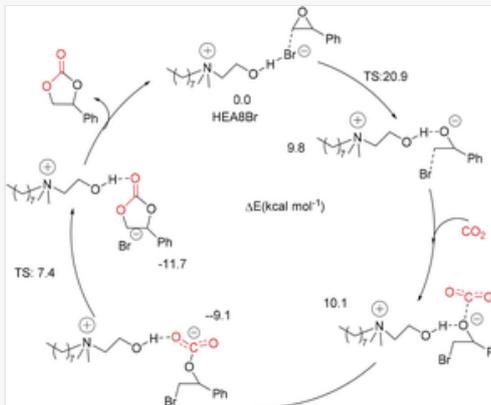
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Choline chloride or iodide catalyses the chemical fixation of CO₂ in carbonates with moderate yields.¹⁷⁶ Thus, it has been modified to increase the conversion and support it to form catalytic materials that are easy to separate.¹⁷⁶ Since choline-based catalytic materials can be considered hydroxyl-functionalised quaternary ammonium salts, their catalytic activity has been compared with other quaternary ammonium salts. In the cycloaddition of CO₂ to styrene oxide, the yield obtained using choline chloride (ChCl) was similar to that of other hydroxyl-functionalised quaternary ammonium salts with longer chains (62% for a side chain C₁₆H₃₃⁺, HEA16X, Fig. 21) compared to 66% for CH₃⁺ in ChCl and non-hydroxyl-functionalised salts (73% for cetyltrimethylammonium bromide, CTAB, Fig. 21) (entries 3–6, Table 7).¹⁷⁶ Choline iodide, ChI, was more active, producing 99% yield after 6 h at 85 °C and 1 MPa CO₂ pressure in EtOH.¹⁷⁸ Interestingly, no conversion in the cycloaddition of CO₂ to 1,2-epoxibutane was obtained with the ChX derivatives (X = Cl, Br, and I) in the absence of solvent. Nevertheless, increasing the steric bulk of the ammonium substituent increased the yield to 96% for the butyl derivative.¹⁸⁶ The authors speculate that this effect may be attributed to the stronger nucleophilicity of halides as the electrostatic interaction with the ammonium cation decreased, or to a simple increase in the solubility. The system was recycled six times with a yield loss of 24% attributed to the partial decomposition of the catalyst during the separation process.

DFT calculations performed for choline salt-based catalysts showed that in the first step of the reaction the hydroxyl group of a choline salt interacts with the anion during the nucleophilic attack of the latter on an epoxide. The hydrogen bond between the hydroxyl group and the epoxide only is formed once the nucleophilic attack has taken place and the epoxide ring has been opened. The stabilisation that the –OH group of choline provides to the initial intermediate and transition state of the reaction seems to be responsible for the high conversion rate and high cyclic carbonate selectivity observed (Scheme 29, for HEA8Br).¹⁷⁶

Scheme 29



Energetic profile of the mechanism for the cycloaddition reaction of CO₂ with SO catalysed by a model choline salt, HEA8Br. Adapted from *Carvalho Rocha et al.*¹⁷⁶

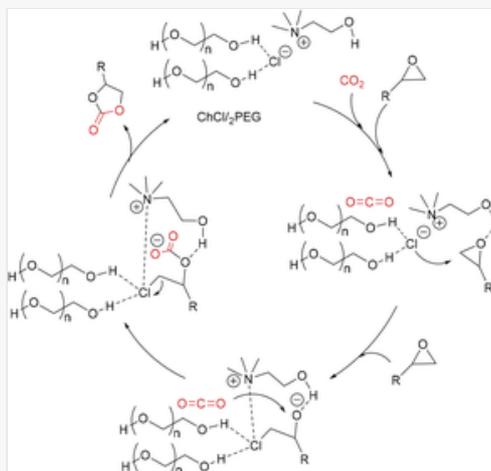
The choline iodide system was heterogenised by grafting it onto Merrifield resin with functionalised benzyl chloride to form polymer-supported choline, PS–ChCl.¹⁷⁸ In combination with KI, this catalytic system produced a 99% yield of propylene carbonate under mild conditions (entry 7, Table 7). The system was recycled and a decrease in yield was observed, which was attributed to the loss of KI, since high yield was restored after the addition of the salt.

Deep eutectic solvents based on choline halides were prepared with different materials as hydrogen bond donors to be used as catalysts for carbon dioxide fixation. The mixture of ChCl with urea in a 1 : 2 ratio (ChCl/2urea) has a melting point (12 °C) below the melting points of the pure components, exhibiting a deep eutectic behaviour. Using ChCl/2urea as a catalyst for the cycloaddition of CO₂ to propylene oxide, a 99% yield of propylene carbonate was obtained (entry 8, Table 7), while under these conditions, ChCl provided lower yield and selectivity (85%, entry 6, Table 7).¹⁷⁷ Furthermore, to form an easily separable catalytic material, ChCl/2urea was supported on molecular sieves (ChCl/2urea@MS). The optimisation of the reaction conditions resulted in a 96% yield of propylene carbonate (entry 9, Table 7). This system was recycled for up to five runs without loss of yield.¹⁷⁷

Polyethylene glycols (PEG) of different lengths were used as HBD for the preparation of DES based on choline (ChCl/PEG).¹⁷⁹ The conversion using the deep eutectic solvent ChCl/PEG (entry 10, Table 7) exceeded the value obtained with ChCl by only 30–60%. The shorter PEG chains produced a higher yield of cyclic propylene carbonate, which was attributed to the mass-transfer limitation in polymers with longer chain length. The combination of PEG₂₀₀ ($M_w = 200$) with choline increased the thermal stability compared to PEG₂₀₀ although it was lower than the thermal stability of choline. Nevertheless, the catalyst could be recycled under optimised conditions with only a 3.5% decrease in yield. Terminal monosubstituted epoxides were converted in the corresponding cyclic carbonates in high yields (75–99%), while for disubstituted epoxides such as cyclohexene oxide the yield decreased (46%).

As for the role of each component in the catalytic activity, the authors proposed, in disagreement with previous DFT calculations cited,¹⁷⁶ that the hydroxyl group of choline activated the epoxide by H-bond interaction and the PEG adsorbed carbon dioxide, increasing its solubility in the reaction medium. The chloride ion of choline opens the epoxide ring, acting as a nucleophile. After the insertion of the adsorbed carbon dioxide and intramolecular cyclisation, the carbonate formed is released to reinitiate the cycle (Scheme 30).¹⁷⁹

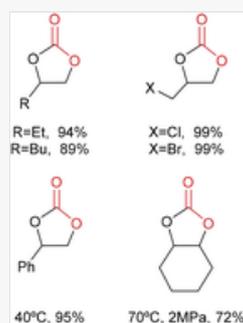
Scheme 30



Proposed mechanism for the cycloaddition of CO₂ to epoxides catalysed by the PEG/ChCl deep eutectic solvent. Adapted from Wu *et al.*¹⁷⁹

In a study presented in 2019 by Liu and coworkers, the influence of the halide of ChX was assessed using a deep eutectic solvent formed by choline halides and *N*-hydroxysuccinimide (ChX/2NHS, molar ratio 1 : 2, Fig. 21). As observed with other halide containing catalytic systems, the catalytic activity of ChX/2NHS increased in the order X = Cl < Br < I (entry 11, Table 7).¹⁸⁰ This behaviour was attributed not only to the obvious higher nucleophilicity of iodide, but also to its higher availability from the ChI system due to the H-bond interaction with NHS. The system was active at a mild temperature (60 °C), providing a 92% yield of cyclic carbonate in 1 h. Similar behaviour was observed for the ChI/PEG₂₀₀ catalytic system (entry 12, Table 7). ChI/2NHS was active even at 30 °C, producing a 91% yield of propylene carbonate after 10 h (entry 13, Table 7). Under these conditions, the system was stable and could be recycled for the production of propylene carbonate at similar initial rates for five cycles. Other monosubstituted epoxides were carbonated to obtain high yields under mild conditions (Fig. 22). Remarkably, even a more hindered substrate such as cyclohexene oxide was transformed to obtain a 72% yield under mild conditions (entry 14, Table 7).

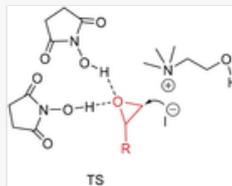
Fig. 22



Yields of cyclic carbonates obtained using ChI/2NHS catalysts (conditions: 30 °C, 1.0 MPa, 10 h or otherwise stated).¹⁸⁰

Infrared spectroscopic studies with ChI/2NHS catalytic solvent system confirmed the physical adsorption of carbon dioxide by the appearance of new bands in the 2130–1930 cm⁻¹ region in the presence of a gas. In the ¹H NMR spectrum, the signals corresponding to the hydroxyl protons of ChI and NHS disappeared when an epoxide was added.¹⁸⁰ The fact that the ring-opening of epoxide is often the rate-determining step prompted the authors to propose that the most probable intermediate in the catalytic cycle was formed by the H-interaction of NHS with epoxide (Fig. 23).

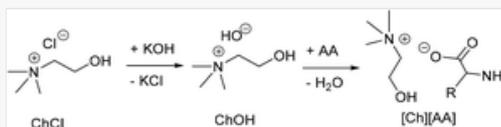
Fig. 23



Deep eutectic solvent choline-based (ChI/2NHS) proposed transition state (TS).¹⁸⁰

Highly sustainable ionic liquids are obtained using the combination of amino acids and choline.¹⁸¹ Apart from the possibility of acting as an HBD due to the hydroxyl group of the choline, the amino group in AA may probably activate carbon dioxide. With this idea in mind, Saptal and Bhanage and Saptal reported the preparation of a series of [Ch][AA] ionic liquids (AA = Gly, Trp, Ala, Pro, His, 4-OH-Pro (4-hydroxyproline), Ser, Tyr, and Val (valine) by replacing the chloride ion in choline by reaction with potassium hydroxide. Choline hydroxide formed in this manner readily reacted with the corresponding AA to form [Ch][AA] (Scheme 31). The combination of [Ch][AA] with ammonium salts formed a deep eutectic mixture which was active in the fixation of CO₂ in epoxides at mild temperature. The best catalytic system was with histidine and TBAI as the cocatalyst, [Ch][His]/TBAI. Under optimised conditions, epichlorohydrin was transformed to the corresponding cyclic carbonate with 97% yield in 2 h (entry 15, Table 7). At atmospheric pressure, high conversion rates were obtained with terminal and cyclic epoxides after 30 h of reaction time. The catalytic system was recycled five times without apparent loss of activity when the reaction was run at 1 MPa for 2 h although a decrease in conversion took place when the reaction lasted for 30 h at atmospheric pressure.

Scheme 31



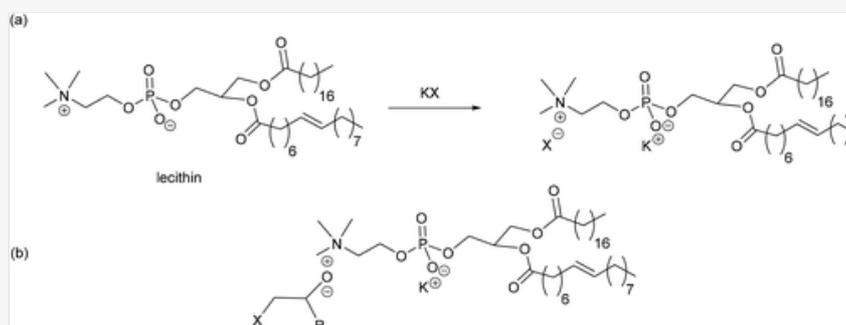
Preparation of choline-amino acid ionic liquids.¹⁸¹

To analyse the role of each component, reference infrared experiments of ChCl with epichlorohydrin were performed. The spectra showed a shift of 6 cm⁻¹ in the -OH stretching frequency of choline after the addition of epichlorohydrin, which led the authors to propose that the activation of epoxide took place by H-bond interaction with choline.¹⁸¹

5.3. Lecithin-based catalytic systems

A biocompatible lecithin-based catalyst (Fig. 21) formed by combination with potassium halides was used as a catalyst for the cycloaddition of CO₂ to epoxides.⁸⁶ The increased solubility of lecithin in the epoxide substrate may account for the good activity that the lecithin/KI catalytic system showed for the cycloaddition of CO₂ to PO compared to the betaine/KI system under the same conditions (entries 16 and 17, Table 7). The authors proposed that the main reason for the observed synergic effect was the formation of a quaternary ammonium halide by the interaction of the zwitterionic structure of lecithin and potassium halides (Scheme 32).

Scheme 32



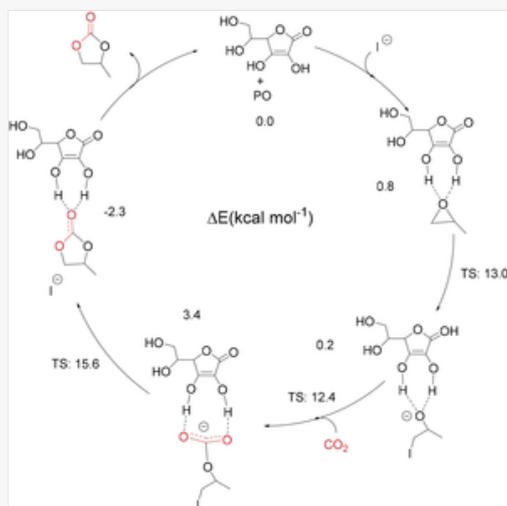
5.4. Carboxylic-based catalytic materials

Among the natural HBD carboxylic-based materials reported such as lactic acid, glucose and ascorbic acid (AscA, [Fig. 21](#)), ascorbic acid has exhibited the best performance as a catalyst for CO₂/epoxide cycloaddition.⁷¹ One of the best results was obtained for the reaction of epichlorohydrin with CO₂, which showed a good degree of conversion at room temperature, becoming almost quantitative at 40 °C and atmospheric pressure (94% yield with a TON of 67 and a TOF of 2.9 h⁻¹, entry 18, [Table 7](#)). Propylene carbonate was also obtained in high yield (82%, entry 19, [Table 7](#)). In general, epoxides with larger side chains afforded lower yields. In all cases, the presence of water in the reaction environment only marginally decreased the conversion, pointing to the resilience of the catalytic system. The high activity of ascorbic acid is attributed to the presence of the enediol hydroxyl groups and the ethyldiol side chains.

To gain a deeper insight into the reaction mechanism, the profile of the free energy change along the reaction path was obtained at the B3LYP level for the reaction of propylene oxide with CO₂, using the 6-31+G** basis set for geometry optimisation and a combined 6-31+G**/triple- ζ basis set for energy calculations with added 3D dispersion corrections. Following the well-known three-step mechanism ([Scheme 33](#)), epoxide is activated by H-bonding of its oxygen atom with the enediol groups of ascorbic acid. The epoxide ring-opening occurs by the nucleophilic attack of iodide at the β carbon of the epoxide, resulting in a 13.0 kcal mol⁻¹ barrier. CO₂ is activated by the interaction between one of its oxygen atom and hydrogen of one of the hydroxyl groups of the side chain, yielding an energetic barrier for the CO₂ insertion step of 12.4 kcal mol⁻¹. The rate-determining step is the ring-closure process, with a 15.6 kcal mol⁻¹ barrier. This low value is consistent with low temperatures needed for the reaction to occur.⁷¹

Scheme 33

Figure Replacement Requested



Energetic profile of the mechanism for the cycloaddition reaction of CO₂ with PO catalysed by ascorbic acid. Adapted from Arayachukiat *et al.*⁷¹

Replacement Image: Scheme33.jpg

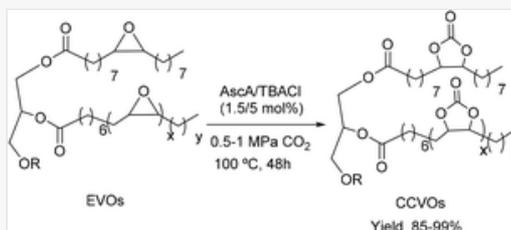
Replacement Instruction: Replace image requested

The ascorbic acid-based catalytic system was used for the synthesis of carbonates derived from mono- and polyunsaturated epoxidised fatty acid esters (EFAEs, [Table 8](#)) and epoxidised vegetable oils (EVOs, [Scheme 34](#)).¹⁸⁸ The carbonated fatty acid esters (CCFAE) and carbonated vegetable oil (CCVO) were obtained using ascorbic acid as a catalyst in the presence of quaternary ammonium salts under mild conditions (80–100 °C and 0.5–1.0 MPa CO₂ pressure, [Scheme 34](#) for CCVOs). The carbonation of methyl oleate with a combination of ascorbic acid/TBAX showed that the Cl salt (TBAC) was highly selective to cyclic carbonate, while TBAI and TBAB selectivity for this

product was low (19 and 74% respectively, entries 1–3, Table 8). Nevertheless, the conversion obtained with TBAC was lower (69% versus 98–99% with TBAB and TBAI) as expected due to the lower leaving group ability of the chloride anion. The same reason was put forward by the authors to justify that the *cis* : *trans* ratio of the product was similar to the starting material, indicating that the reaction stemmed from an S_N2 mechanism, unlike the case of TBAB and TBAI. The effect of increased loading of acid was detrimental to conversion, which was attributed to the protonation of the zwitterionic intermediates.

Scheme 34

Figure Replacement Requested



Cycloaddition of CO_2 to epoxidised vegetal oils (EVOs) using ascorbic acid/TBACl catalytic systems to form the corresponding cyclic carbonates (CVOs).¹⁸⁸

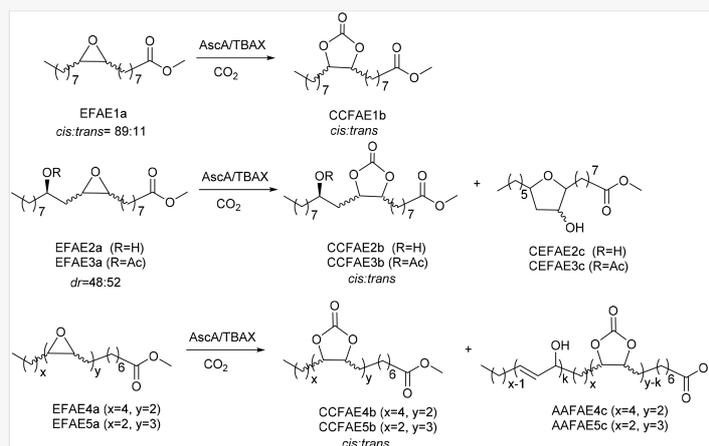
Replacement Image: Scheme34.jpg

Replacement Instruction: Replace image requested

Table 8

Cycloaddition of CO_2 to epoxidised fatty acid esters (EFAEs) catalysed by ascorbic acid (AscA)/TBAX (X = Cl, Br, and I) catalytic system

Figure Replacement Requested



Replacement Image: Table8_Scheme.jpg

Replacement Instruction: Replace image requested

Entry	Epox (<i>cis</i> :	X	AscA/TBAX	T	P	t	Yield	Sel b/c	b <i>cis</i> :	Ref.
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	<i>trans</i>	(TBAX)	(mol%)	(°C)	(MPa)	(h)	(%)	(%)	<i>trans</i>	
1	EFAE1a (89 : 11)	Cl	1.5/5	100	0.5	24	68 ^a	99/—	85 : 15	188
2	EFAE1a (89 : 11)	Br	1.5/5	100	0.5	24	72	74/—	24 : 76	188
3	EFAE1a (89 : 11)	I	1.5/5	100	0.5	24	19	19/—	17 : 83	188
4	EFAE2a (dr:48 : 52)	Cl	1.5/5	100	0.5	48	68	71/29	18 : 82	188
5	EFAE3a (dr:48 : 52)	Cl	1.5/5	100	0.5	48	95	>99/—	82 : 18	188
6	EAFE4a	Cl	1.5/3	100	1.0	48	85	94/6	91 : 9	188
7	EAFE5a	Cl	4.5/15	80	1.0	48	75	93/7	91 : 9	188

Table Footnotes

^aEstimated from conversion and selectivity data.

Other EFAEs such as those derived from methyl ricinoleate (EFAE2a and 3a, Table 8) were carbonated with a total conversion to cyclic carbonate after 48 h and with selectivities ranging from 71 to 99% (entries 4 and 5, Table 8). In the case of epoxide from methyl ricinoleate, 29% cyclic ether (CEFAE2, Table 8) was formed by the intramolecular reaction of the alcohol group with epoxide.¹⁸⁸

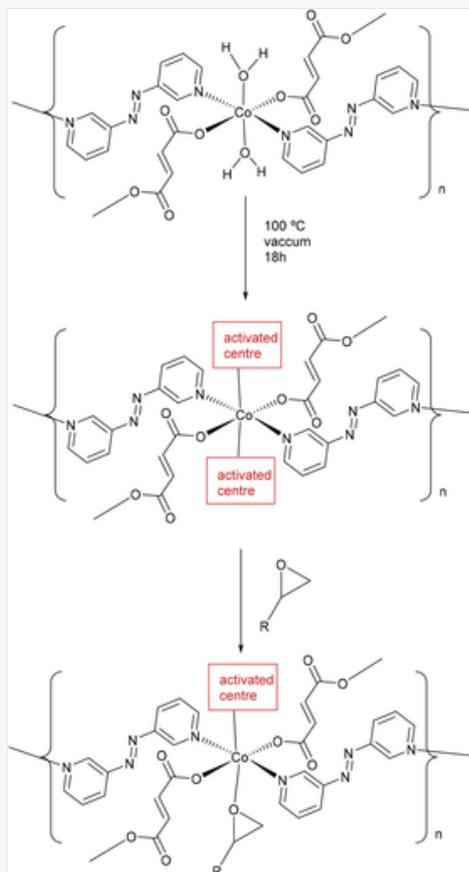
Under the same conditions, the ascorbic acid/TBAC catalytic system transformed polyunsaturated EFAEs such as methyl linoleate and linolenate (EFAE4a and 5a, Table 8) into the corresponding cyclic carbonates (CCFAE4b and 5b, Table 8) with 85% and 75% yield, respectively, under optimised conditions (entries 6 and 7, Table 8). Allylic alcohols AAFAE4c–5c were the main by-products produced (76–87%).¹⁸⁸

EVOs such as FAME (fatty acids methyl esters), olive oil, soybean and canola oil were carbonated with high yields of polycarbonate products (85–99%, Scheme 34).¹⁸⁸

The recyclability of the ascorbic acid/TBAC catalytic system was examined by separating the catalytic system by extraction with water, but conversion in the cycloaddition of methyl oleate with the recovered product was poor.¹⁸⁸

Fumaric acid (FMA) was used for the construction of a 3D-metal-organic framework Co(II)-FMA-MOF (Fig. 21, $\{Co(FMA)(L)(H_2O)_2S\}_n$ (L = 3,3'-azobis pyridine, S = disordered solvent) in which the aqua ligands were bound to the metal centres. Activating the Co(II)-MOF at 100 °C under vacuum for 18 h the coordinated and the structure solvent molecules could be removed, maintaining the framework structure and generating open metal active sites (Scheme 35).¹⁸⁷ Although this material showed no affinity to absorb carbon dioxide, the activated MOF was an active catalyst for the cycloaddition of CO₂ to styrene oxide, producing 50% cyclic carbonates at 80 °C, under 0.1 MPa CO₂ pressure at 0.5 mol% loading (based on Co(II)) in 12 h. The conversion increased to 86% in the presence of TBAB. The authors proposed that the reaction took place at the surface of the MOF, initiated by coordination of epoxide to the activated Co(II) centres (Scheme 35). Further evidence for this was seen in that other epoxides such as butylene oxide, epichlorohydrin and allyl glycidyl ether were transformed at high conversion rates (78–90%), while the conversion of larger substrates with long alkyl chains dropped (61–30%). The approximate diameter of the 1D channels was 3.6 Å which is smaller than the size of the larger substrates.

Scheme 35



Cobalt(II) coordination centre in Co(II)-FMA-MOF, $\{Co(FMA)(L)(H_2O)_2S\}_n$ ($L = 3,3'$ -azobis pyridine and $S =$ disordered solvent). Proposed activation mechanism and initiation step in the cycloaddition of CO_2 to epoxides.¹⁸⁷

6. Conclusions and future perspectives

Bio-based products and their derivatives have been widely explored as catalytic systems for the coupling of carbon dioxide to epoxides to form cyclic carbonates. They are highly functionalised molecules that can activate carbon dioxide and/or epoxide by catalysing their reactivity. The best results are obtained when they are combined with nucleophiles or bases in binary catalytic systems, or when they are modified to form bifunctional materials. For example, amino acids are active catalysts under harsh reaction conditions, but their catalytic activity increases when combined with halide-based nucleophiles or hydrogen-bond donors leading to active systems under milder conditions. For instance, the combination of KI with His (1 : 1),⁶⁹ cellulose (2 : 1),¹¹⁴ chitin (1 : 1)¹²⁸ or β -CD,¹²⁹ provides high yields of cyclic carbonates in 2–4 hours. Interestingly, raw materials that undergo a simple modification of their natural form, such as wool powder/KI or /TBAB,¹¹¹ sugar cane bagasse/KI¹⁵¹⁺³⁰ or /TBAB,⁵¹ or Luffa sponge/TBAB,¹⁵²⁺³¹ can also be used as catalysts in binary systems.

The industrial process to produce cyclic carbonates from epoxides and CO_2 is typically catalysed by halide-containing salts such as KI or TBAB.¹⁸⁹ The addition of bio-based components not only increases the catalytic activity but also may decrease the content of potentially toxic halogenated species by 20–50% while providing a cheaper and more sustainable catalyst. These systems also have some limitations. One of them is that the reported optimised reaction conditions are like those used in industrial processes and require a temperature of over 100 °C. However, the cycloaddition of CO_2 to epoxides is an exothermic reaction, and temperatures below 100 °C are difficult to control.¹⁸⁹

Modifying natural products to obtain bifunctional catalytic systems by adding groups such as nucleophiles or bases is relatively straightforward thanks to the high functionalisation of these materials. Quaternization of the amino groups present in amino acids or chitosan,¹²⁰ for example, or introducing new groups by modifying cellulose,¹¹⁶ makes it possible to include the nucleophile in the molecule itself.

A common focus among researchers is the separation of catalytic materials and their possible reuse. A range of different strategies have been reported to achieve these goals such as supporting a catalyst on silica, polystyrene or polyethyleneglycol. The resulting materials can be reused several times, some of them with only a slight loss in activity,

such as quaternised tyrosine supported on polystyrene. With these modifications, very high yields can be obtained in 3–6 h at $T > 100$ °C and carbon dioxide pressures of 0.1–1 MPa. When natural products are combined with metallic compounds such as ZnX_2 or phthalocyanines of $Cu(II)$, mild reaction conditions are required ($T < 100$ °C). Some of the best TOFs reported are obtained using metal-containing systems such as $ZnCl_2$ –CS/bmimBr (TOF, 2717 h^{-1})¹²⁶ or the chromium–salen based system Cr–TBD–X (TOF, 2120 h^{-1}).¹⁵⁴ However, although these values are higher than those obtained with systems without metal, they are still far from the best TOFs reported in the literature, for example, the aluminium(III) aminotris(phenolate) systems developed by Kleij's group (TOF of up to $36\,000\text{ h}^{-1}$)¹⁹⁰ or they require harsher conditions than the aluminium–salen based complexes reported by North's group.⁵⁸ Very efficient catalytic systems under mild conditions ($T < 100$ °C) can also be obtained with ionic liquids or deep eutectic solvents with some bio-based components. Efficient deep eutectic solvent systems include the combinations of choline and amino acids $[ChCl][AA]$ ¹⁸¹ and choline iodide with *N*-hydroxysuccinimide or poly(ethyleneglycol).¹⁸⁰ The latter catalytic system is remarkable in that it provides a relatively high yield (72%) of cyclohexene carbonate,¹⁸⁰ although the activity obtained with disubstituted epoxides is generally moderate. High yields (>90%) in short times (1–3 h) were also obtained with ionic liquids based on guanidinium salt HBGX.^{162,164–166}

Regarding the mechanism of reaction, most experimental and computational studies agree on a three-step mechanism for this reaction, regardless of the type of catalyst used. The first step is the ring-opening of an epoxide, which is, in principle, ~~is~~ the highest energy process. For this reason, efficient catalysts decrease this energy barrier by activating the epoxide (Lewis acids or HBD) and providing a nucleophile (Lewis bases or anions) to attack one of the C atoms of the epoxide. Nevertheless, in general, this first process continues to be the rate-determining step of the cycloaddition reaction. The next step is CO_2 insertion. Catalysts containing mainly amines, but also other functional groups like sulphonates, can activate CO_2 to form carbamates or similar structures. Some studies suggest that these species may be responsible for activating the epoxide and contributing to ring-opening, while also initiating the insertion of CO_2 . The last step is the carbonate ring closure, which is the rate-determining step only in the few particular cases where the transition state of the ring-opening step was noticeably stabilised by the action of a catalyst.

Our review of the results published in this field has revealed that not much attention has been paid to scaling up the reaction, except with some catalysts (up to 29 g scale).¹⁵¹ Moreover, although many of the articles we reviewed describe the procedure and results for recycling the catalysts, only one study reports having worked under continuous flow conditions.¹¹⁷ In view of this, it seems clear that further advances in the development of these points are needed in order to find practical applications for bio-based catalytic systems in CO_2 /epoxide cycloaddition.

Regarding the scope of the reaction, although a few authors have reported using these kinds of catalytic systems to the synthesis of bio-derived carbonates, such as fatty acids esters, vegetable oils¹⁸⁸ and non-isocyanate poly(amide-hydroxyurethane),⁵¹ most of the works published have used only benchmark epoxides. This family of bio-based carbonates is often prepared using TBAX salts as catalysts, which have been proved to combine with bio-based products to improve their performance, pointing to the need for further study in this area.

Finally, despite the well-known ability of natural products to capture carbon dioxide^{32–35} very few studies combine the two processes, capture and transformation in carbonates.¹²⁷ The development of cheap and sustainable systems for the capture and utilization of carbon dioxide may be an important step to contribute to balance the emissions of this gas.

In summary, by optimally selecting bio-based products they can be used as catalysts on their own, supported, or combined with ~~co~~-catalysts to provide excellent results in the CO_2 /epoxide cycloaddition. The use of these systems can increase the sustainability and reduce the toxicity of catalysts by using non-toxic abundant products from natural sources. In addition, they can be used for a broad scope of different epoxides, and in some cases allow for the recovery of catalysts. Further research into bio-based catalysts will contribute to making these systems a real and meaningful alternative to be used of CO_2 .

Conflicts of interest

There are no conflicts of interest to declare.

Biography



Carmen Claver

Professor of Inorganic Chemistry at the Rovira i Virgili University of Tarragona (Spain) since 1991. Her research focuses on sustainable aspects of catalysis: selectivity through catalyst design; recycling of supported homogeneous catalysts and nanocatalysts; processes in continuous flow; development of efficient catalysis for CO₂ and biomass transformation. Research leader from 1985 in national and European competitive projects and industrial contracts, with 30 supervised PhD thesis. Vice-Rector of Research URV 1993–1997, Scientific Director of the “Technological Centre of Chemistry of Catalonia” and Director of the “Unit of Technology Chemistry” Eurecat from 2009 until 2020. She has been awarded several prizes for her research and is member of different Chemical Associations and Councils.



Md Bin Yeamin

Got a first degree in Chemistry with distinction from SUST, Sylhet. From 2010–2012 he worked on obtaining a M. Phil. degree at BUET, Dhaka focusing his research on efficient encapsulation of toxic dyes from wastewater using several biodegradable natural polymers and their composites along with a three-semester teaching assistantship. Thereafter, he started teaching general chemistry at IUBAT, Dhaka. During 2012–2014 he had European Master in Theoretical Chemistry and Computational Modelling (EMTCCM). He joined URV in 2018 as a doctoral student with Anna M. Masdeu Bultó and Mar Reguero. His doctoral thesis focuses on the catalytic conversion of carbon dioxide into cyclic carbonates.



Mar Reguero

PhD in Chemical Sciences (1989), she studied at the Universidad Complutense of Madrid. She worked as a postdoctoral researcher at King's College London, UK (1990), at the Spanish Research Council, Madrid (1991) and for Daresbury Laboratory, UK (1992). In 1993 she enrolled at the Department of Physical and Inorganic Chemistry of the Universitat Rovira i Virgili (URV at Tarragona, Spain), and has been Associate Professor since 1997. Her research in the Chemistry field, as a member of the Quantum Chemistry group of URV, is focused on the computational elucidation of mechanisms of photochemical and catalytic reactions.



Anna M. Masdeu-Bultó

Dr Masdeu-Bultó is Associate Professor at the Department of Physical and Inorganic Chemistry (the University of Rovira i Virgili, Tarragona, Spain) since 1996. She obtained the PhD in Chemical Sciences (1992) at the University of Barcelona (Faculty of Chemistry of Tarragona) working on rhodium catalysed hydroformylation under Professor Carmen Claver and Aurora Ruiz guidance and pursued postdoctoral research at Ottawa University in Prof. Howard Alper's group (1992). Her research interest has been focused on different aspects of catalysis such as the use of green solvents and carbon dioxide transformation.

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Footnotes

[†] Ionic liquids are generally organic salts with melting points below 100 °C.

[‡] Deep eutectic solvents are mixtures of different components which in a given composition become liquids at room temperature.

Queries and Answers

Q1

Query: Funder details have been incorporated in the funder table using information provided in the article text. Please check that the funder information in the table is correct.

Answer: The funder details have been corrected

Q2

Query: For your information: You can cite this article before you receive notification of the page numbers by using the following format: (authors), Green Chem., (year), DOI: 10.1039/d0gc01870h.

Answer: Thank you

Q3

Query: Please confirm that the spelling and format of all author names is correct. Names will be indexed and cited as shown on the proof, so these must be correct. No late corrections can be made.

Answer: Could you please, add to author Mar Reguero the ORCID number 0000-0001-9668-8265.

Thank you

Q4

Query: Please check that the inserted Graphical Abstract image and text are suitable. If you provide replacement text, please ensure that it is no longer than 250 characters (including spaces).

Answer: The graphical abstract and text have been introduced.

Q5

Query: The citation to Scheme 10 in the sentence beginning “The authors proposed a...” has been changed to Scheme 11 as the text appears to discuss Scheme 11. Please check that this is correct.

Answer: Not correct. The appropriate citation to Scheme 11 has been added and the previous citation to Scheme 11 has been corrected.

Q6

Query: Text has been provided for footnote e in Table 5, but there does not appear to be a corresponding citation in the table. Please indicate a suitable location for the footnote citation.

Answer: Footnote citation "e" is placed in entry 23, column "yield" instead of "d", as indicated.

Q7

Query: The author's name is spelled “Borjian Boroujeni” in ref. 125, but in the text it is spelled “Botjian”. Please check and correct as necessary.

Answer: The name of the author in Scheme 18 and ref. 125 has been checked out and corrected

Q8

Query: “Prasetyanto” is not cited as an author of ref. 144. Please indicate any changes required.

Answer: Correct reference has been introduced

Q9

Query: In the term “([TMG-C₂H₄NH₂]-Y ILs)”, a closing bracket has been inserted. Please check that this is correct.

Answer: It has been checked and corrected.

Q10

Query: The citation to Scheme 27 in the sentence beginning “CO₂ was activated mainly with...” has been changed to Scheme 28 as the text appears to discuss Scheme 28. Please check that this is correct.

Answer: Checked and it is correct the change.

Q11

Query: The brackets appear to be unpaired in the sentence beginning “In the cycloaddition of CO₂…”. Please check this and indicate any changes required.

Answer: Revised

Q12

Query: Ref. 31: Please check that the initials for the 1st author are displayed correctly.

Answer: Checked and confirmed

Q13

Query: Ref. 33: Please check that the initials for the 1st author are displayed correctly.

Answer: Checked and confirmed

Q14

Query: Ref. 124: Please check that the initials for the 2nd and 5th authors are displayed correctly.

Answer: The initials of 5th author are correct.

The initials of the 2nd author have been corrected

Q15

Query: Ref. 127: Please check that the initials for the 4th author are displayed correctly.

Answer: The initials are correct

Q16

Query: Ref. 138: Please provide the name of the patentee(s).

Answer: Names of patentees provided

Q17

Query: Ref. 142: Please provide the name of the patentee(s) and year.

Answer: Names of patentees provided

Q18

Query: Ref. 145: Please check that the initials for the 6th author are displayed correctly.

Answer: The initials are correct

Q19

Query: Ref. 146: Please check that the initials for the 5th author are displayed correctly.

Answer: The initials are correct