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CO_2 fixation: cycloaddition of CO_2 to epoxides using practical metal-free recyclable catalysts†

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The conversion of CO_2 into valuable chemicals is a crucial field of research. Cyclic organic carbonates have attracted great interest because they can be prepared under mild conditions and because of their structural versatility which enables a large variety of applications. Therefore, there is a need for potent and yet practical catalysts for the cycloaddition of CO_2 to cyclic carbonates that are able to combine availability, low cost and an adequate performance. We review here several recyclable catalytic systems that are readily available, easy to prepare, and inexpensive with an eye to the future development of more efficient practical catalysts through the provided guidelines.

Introduction

Fixation of CO_2 in the form of value-added chemicals able to provide long-term CO_2 storage is a main direction of research in current chemistry.[1–3] CO_2 conversion to chemicals, along with CO_2 capture and geological storage,[4] is regarded as a way to mitigate its unrestricted environmental release from human activities and to decrease the dependence of the industry on C1 carbon sources derived from fossil fuels.[3,5–8] The main traditional process employing CO_2 as a feedstock, which is the synthesis of urea from ammonia,[9] is actually a CO_2-producing process due to the high carbon footprint of ammonia production.[10] The need for more sustainable CO_2-conversion pathways has spurred an intense academic and industrial race to investigate the reaction of CO_2 with available reagents such as alcohols[11] and diols,[12] hydrogen,[13,14] olefins[15,16] and epoxides.[17–21] The production of chemicals and fuels such as methanol, dimethyl ether and methane from

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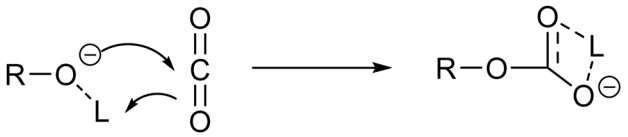

Scheme 1 Typical elementary step of CO_2 activation in the fixation of CO_2 into organic carbonates. L is a metal atom of a complex or base or represents a hydrogen bond donor.

CO_2 reduction with hydrogen is regarded as a way to establish a man-made carbon cycle,[6,22] thereby lowering the demand for fossil fuels.[23] However, besides technical and economic challenges,[24,25] a significant limitation of reductive processes is the need for cheap, ubiquitously available green hydrogen which, as a highly flammable gas, poses serious safety issues.[26] A different approach is the nonreductive CO_2 conversion into products where the C1 carbon centre retains its initial oxidation state. This is typically accomplished *via* formation of a carbonate moiety (–OC(=O)O–)[27] by the attack of a (partially) negatively charged oxygen atom on the CO_2 carbon (Scheme 1).

In this way, useful CO_2-based compounds are formed such as cyclic carbonates,[28–30] dialkyl and diaryl carbonate esters[31] and alternate CO_2-epoxide copolymers (Scheme 2(a)–(d)).[32,33] The catalytic synthesis of these carbonate-containing compounds from CO_2 is the subject of intense investigation.[34–36] Scheme 2 (based on a SciFinder search, see also the footnote for details) displays a comparison of the number of publications in academic journals and patents in the last five years for several reactions leading to carbonate compounds (Scheme 2(a)–(d)) and for reactions of CO_2 reduction with molecular hydrogen (Scheme 2(e)–(g)). Despite the search being restricted to works using propylene oxide as the substrate, the CO_2 cycloaddition reaction in Scheme 2(a) emerged as the most investigated CO_2-conversion reaction when considering academic journals. It was also the second most reported in patents just after the cognate alternate copolymerization of CO_2 with epoxides (Scheme 2(b), considering all possible epoxide substrates and the presence of additional monomers leading to terpolymers). These data strongly point at the cycloaddition of CO_2 to epoxides as a leading reaction in CO_2 fixation at the present time in terms of research focus. There are multiple reasons for the strong attention towards the latter process. On the one hand, the synthesis of cyclic carbonates from CO_2 and epoxides is a thermodynamically favourable transformation,[37] occurring in high yields under mild or even ambient conditions of temperature and pressure when using a suitable catalyst.[38–41] This is at variance with the reaction in Scheme 2(c), leading to cyclic carbonates from diols, and with the carboxylation of alcohols for the synthesis of industrially attractive linear organic carbonates (Scheme 2(d)). Both processes are thermodynamically limited[12,42] and provide very low yields under harsh conditions when carried out in the absence of dehydrating agents or other additives.[11,43] Indeed, linear carbonates are industrially produced from epoxide-generated cyclic carbonates[44] while the efficient carboxylation of polyols is often carried out using more reactive agents than CO_2 such as dimethyl carbonate (DMC).[45,46] Depending on the choice of catalyst, the cycloaddition of CO_2 to epoxides is resilient to moisture[47,48] and can even be carried out in aqueous media.[49,50] Moreover, the cycloaddition of CO_2 to epoxides is operatively simple to set at the laboratory scale using stainless steel autoclaves at low to moderate pressures (5–20 bar) or even standard glassware and CO_2-filled balloons for catalysts operating under atmospheric pressure.[51,52] Importantly, impure CO_2 feedstocks such as actual or laboratory-generated flue gas can be employed[53,54] indicating the potential of the CO_2-epoxide cycloaddition process to serve in the direct industrial CO_2 capture and conversion process. Importantly, in terms of applications, cyclic carbonates produced from CO_2 cycloaddition to variously substituted epoxides have multiform chemical structures and properties, leading to diverse industrial and academic applications.

Industrially relevant EC (ethylene carbonate) and PC (propylene carbonate) are reacted with alcohols for the synthesis of glycols and linear carbonates which are used as precursors of aromatic polycarbonates[55] and in various applications.[56,57] EC and PC also serve as components of electrolyte solutions in lithium ion batteries,[58,59] and as plasticizers for polymers.[60] Additionally, PC is also a solvent for multiple reactions.[61–66] Glycerol carbonate (GC) is an increasingly popular compound for industrial applications.[46,67,68] GC is indeed used as a solvent,[69,70] reagent[71] or precursor for the preparation of other functional cyclic carbonates.[72,73] Other cyclic carbonates are increasingly reported in the literature for applications with potential for implementation at a large scale. For instance, long-chain 1,2-hexadecene carbonate can serve as a non-ionic surfactant to stabilize water-in-oil emulsions.[74] ECHC (epichlorohydrin carbonate) has been recently used as a polar component of a demulsifier for actual crude oil.[75] Fluorinated cyclic carbonates are investigated in lithium batteries due to their high compatibility with anodic materials and ability to form an efficient solid electrolyte interface.[76–78] Cyclic carbonates functionalized with olefin groups have been used as monomers for the synthesis of functional polyolefins with

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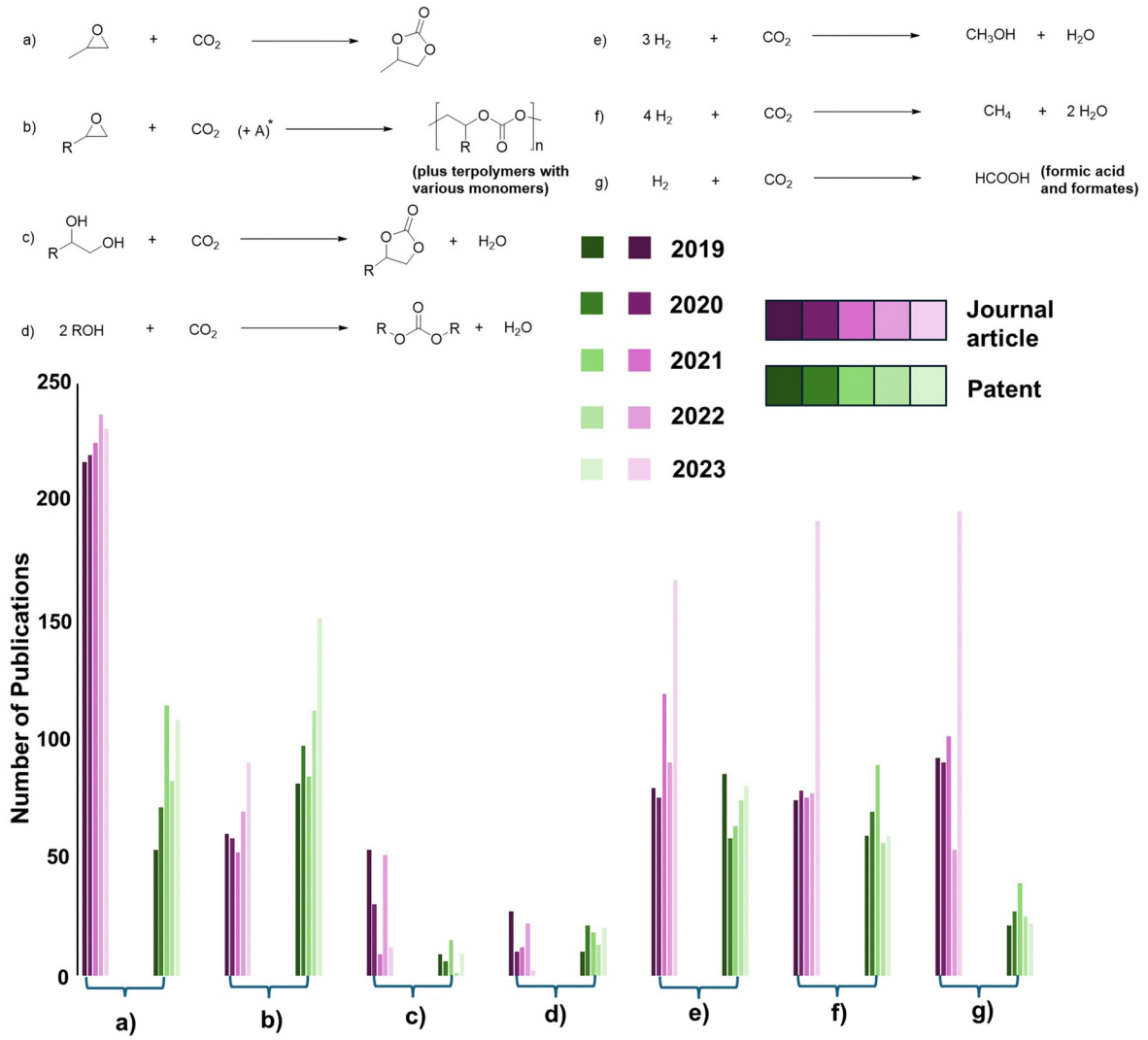


Scheme 2 Overview of the number of publications in academic journals and patents for selected, highly-investigated CO_2 conversion reactions (see reaction schemes a–g on top and the corresponding hit counts in the provided histogram) in the 2019–2023 period based on a SciFinder search performed in July 2024. To avoid duplicate results originating from publications using multiple epoxide substrates, only studies using propylene oxide as the substrate (leading to propylene carbonate as the product) are considered for the cycloaddition of CO_2 to epoxide. The copolymerization of CO_2 and epoxides includes multiple epoxide substrates and additional monomers leading to terpolymers (*A indicates the possible use of additional comonomer(s) leading to the formation of terpolymers, tetrapolymers, *etc.*). For (d) R = $-CH_3$, $-CH_2CH_3$. Further information on data collection, searched reaction schemes and the number of results is given in the ESI.†

pendant carbonate groups[79–81] and for the synthesis of polymeric materials for lithium batteries.[82] Specifically, GCMA (glycerol carbonate methacrylate) has emerged as a promising sustainable CO_2-based monomer[83] for the synthesis of polymers with applications as crosslinking agents for coatings[84] and in catalysis.[85] Finally, compounds containing multiple cyclic carbonate moieties (multi-5CCs) are used as monomers for the synthesis of isocyanate-free polyhydroxyurethanes (PHUs) by polyaddition with polyamines.[86–91] In this context, compounds bearing multiple olefin moieties such as polyunsaturated fatty acids and terpenes, that exist abundantly in nature, can be converted into biobased multi-5CCs by cycloaddition of CO_2 to the corresponding epoxides.[92–94] Through the synthesis of PHUs[95,96] these biobased multi-5CCs offer a chance to bridge the upcycling of natural resources and CO_2 utilization offering a pathway to low carbon footprint polymers.[72]

According to the rich display of applications reported above, cyclic carbonates emerge as multiform chemicals able to mediate recycling of CO_2 into a variety of products, many of which have the potential for large scale industrial implementation. Therefore, it is important to emphasize convenient catalysts that could be used in the production of cyclic carbonates on large scales. Such catalysts should be recoverable, to avoid tedious operations associated with purification of the final product, and recyclable to lower the catalyst impact on the cost and carbon footprint of the cyclic carbonates. On this basis, we highlight in this work some crucial literature dealing with the cycloaddition of CO_2 to epoxides by catalytic systems that are

based on highly available, inexpensive materials while avoiding highly toxic compounds (GHS06, GHS08, and GHS09). Moreover, the discussed catalysts are structurally simple to avoid tedious multistep synthetic procedures, and the use of overstoichiometric coupling agents and noble metals (in the final structure and in the catalyst synthesis). In particular, this article will focus on two classes of metal-free catalysts for the cycloaddition of CO_2 to epoxides: recyclable molecular organocatalysts and polymer-based materials.

Because most articles focusing on the development of inexpensive and readily-available recyclable catalysts for the cycloaddition of CO_2 have appeared in more recent years, we mainly discuss literature covering a period from 2021 to the present. Besides, some earlier reviews covering the period antecedent 2021 may contain some systems compatible with our selection criteria.[37,97–100]

Design and structures of readily-available catalysts

The main challenge in producing efficient catalytic systems for the cycloaddition of CO_2 to epoxides under mild conditions is to generate multifunctional systems. The catalyst should display, at the same time, active sites able to activate the epoxide, and nucleophilic moieties able to ring-open the activated epoxide[38,101,102] or to attack CO_2,[103,104] thus initiating the catalytic cycle (see Scheme 3). The moieties able to activate the epoxide are generally Lewis acidic metals[105–107] or metalloids,[52,108] while N- or O-nucleophiles or halide anions are typically used as nucleophilic moieties.[109–111] Amino groups have also been proposed to interact with CO_2 or to coordinate it as a carbamate anion as the initial step (Scheme 3).[112,113] Catalysts operating without strong epoxide activation, for instance the anion exchange material containing quaternary ammonium halide groups used to synthesize EC in the industrial Asahi–Kasei process, typically require very harsh conditions (100 °C, with liquid CO_2 as the starting material in this specific case).[44]

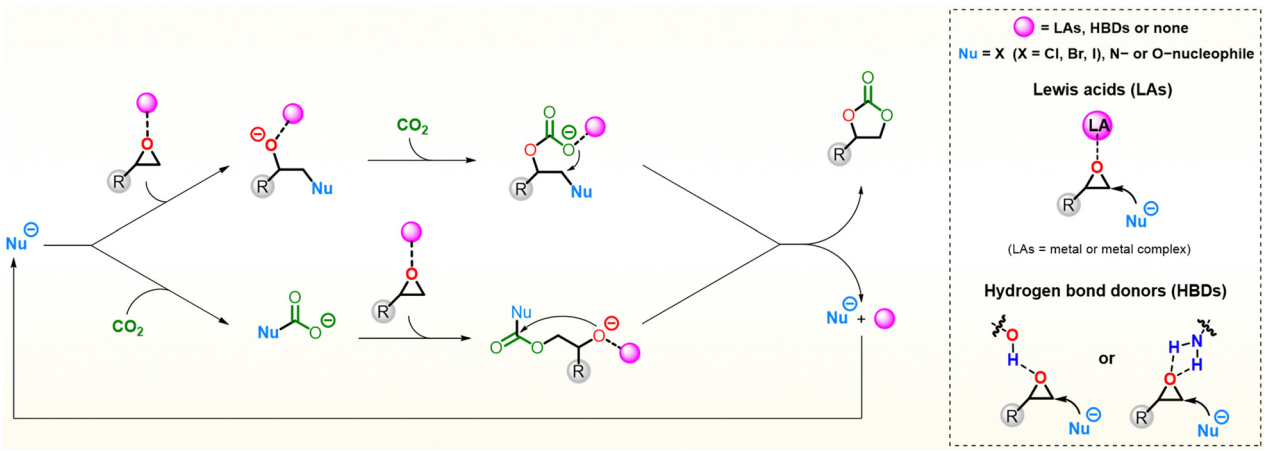
In heterogeneous systems, where the active sites are not free to diffuse in the reaction medium, it is challenging to create suitable catalytic pockets where different types of active moieties can act in a cooperative fashion.[114]

While very active multifunctional heterogeneous catalysts for the cycloaddition of CO_2 to epoxides exist, they are often produced *via* tedious multistep/multiday synthetic procedures,[115–120] or from expensive and/or highly toxic building blocks[116,118,119,121,122] and through the use of noble metal catalysis or overstoichiometric coupling agents such as Grignard reagents or metal halides.[115,117,118,122] However, in recent times, several classes of highly available materials (Scheme 4), have been investigated for preparing active catalysts for the cycloaddition of CO_2 to epoxides. To note, in this work, only the metal-free recyclable catalysts in Scheme 4(d) and (e) are discussed in detail while a condensed overview of the catalysts in Scheme 4(a)–(c) is provided in the next section.

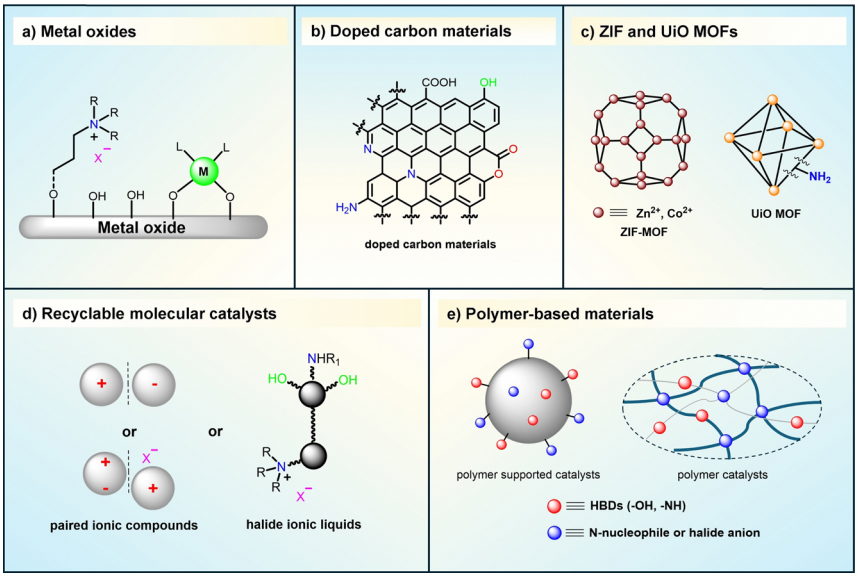
Metal oxides, doped carbons and ZIF-based catalysts

Structurally simple heterogeneous catalytic systems based on traditional, highly available materials and supports (metal oxide, doped carbon materials) are shown in Scheme 4(a) and (b) (given the variety of diverse functionalities present in doped carbon materials, the structure in Scheme 4(b) is only representative).

Oxides and metal oxides are workhorse catalysts for the chemical industry[123] due to their inexpensive and ubiquitous nature. They are optimal candidates for the cycloaddition of CO_2 to epoxides due to the presence of Lewis acidic metal centres in the lattice and of surface –OH groups that may act as HBDs.[124] Moreover, the surface of oxides and metal oxides can be functionalized with highly Lewis acidic metals to enhance their activity in the cycloaddition of CO_2 to epoxides.[125–127] However, metal oxides lack nucleophilic moieties for ring-opening of the epoxide under mild conditions. Indeed, the basic sites of oxides such as CeO_2–ZrO_2[128] or Mg–Al mixed oxides[129] promoted the cycloaddition process only at high temperatures (100–150 °C) and in the presence of DMF as a non-innocent solvent.[130] A possible solution to this drawback is



Scheme 3 General mechanistic pathways of the cycloaddition of CO_2 to epoxides initiated by the attack of a nucleophile (Nu) on the activated epoxide or on CO_2 followed by ring-opening of the activated epoxide.



Scheme 4 Overview of classes of readily-available, recyclable catalysts for the cycloaddition of CO_2 to epoxides. (a) Metal oxides functionalized with ionic liquids and surface-supported metal species; (b) carbon materials bearing heteroatoms, basic and acid sites (representative structure); (c) Inexpensive MOF-based catalysts such as ZIF- and UiO-type frameworks; (d) recyclable molecular catalysts such as paired ionic compounds or halide ionic liquids; (e) Polymer-based heterogeneous materials such as polymer-supported molecular catalysts or crosslinked polymeric networks.

the anchoring of functional molecules containing quaternary ammonium halide groups to the oxide surface resulting into single-component hybrid catalysts.[100,131,132] In particular, Sodpiban *et al.*[133] demonstrated that an Aerosil silica surface decorated with Lewis acidic metal halide complexes and pendant quaternary ammonium groups catalyzed the cycloaddition of CO_2 to epoxides under ambient conditions including when using impure sources as the CO_2 feed. Mitra *et al.* have reported that guanidine-grafted γ-Al_2O_3 is a readily-available catalyst for the cycloaddition of CO_2 to various epoxides at 80 °C, 1 bar.[51] More recently, the same group reported another aluminum-based metal oxide, diaspore (α-AlO(OH)), as a halide-free catalyst for the coupling of CO_2 and epoxides under atmospheric conditions, which, however, required the addition of DMF, possibly, for the step of epoxide ring-opening.[134] An alternative and less expensive approach than surface grafting is the use of metal oxide-based catalysts such as ZrO_2-doped with single cobalt atoms,[135] nitridated fibrous silica nanoparticles,[136] SnO_2 nanoparticles,[137] in the presence of very low loadings ($\leq$0.5 mol%) of soluble homogeneous nucleophilic additives such as KI or TBAX (tetrabutylammonium halide, X = Br, or I). Such compounds have recently shown the ability to catalyze the synthesis of terminal cyclic carbonates from CO_2 and epoxides under mild conditions (80–90 °C, 1–2 bar CO_2). However, this approach leads to the presence of trace amounts of organic halide salts in the final product.

Doped carbons are potent and versatile materials[138] that are typically derived from biobased sources. Useful functional groups for the cycloaddition of CO_2 to epoxides such as basic nitrogen atoms and –OH, –COOH, and –NH_2 moieties as HBDs can be easily introduced into carbon materials depending on precursors used at the pyrolysis stage. Doped recyclable carbon materials for the cycloaddition of CO_2 to epoxides have been recently produced from inexpensive and/or waste organic materials such as waste distiller grains,[139] sodium phytate,[140] shrimp shells,[141] chitosan,[142] and arginine–glucose.[143] While these materials generally contain basic pyridinic nitrogen atoms and –NH_2 groups that may provide interaction and activation of CO_2, doped carbons, as in the case of metal oxide-based materials, generally lack strongly nucleophilic groups for epoxide ring-opening under mild conditions. Indeed, the conversion of highly reactive substrate epichlorohydrin to the corresponding cyclic carbonate by single-component N-doped carbons rich in pyridinic nitrogen atoms obtained by the pyrolysis of waste shrimp shells, did not take place below 120 °C at a CO_2 pressure of 30 bar. The latter halide-free catalyst generally required 150 °C for full substrate conversion.[141] Moreover, the presence of basic pyridine moieties and traces of moisture led to the formation of diols as minor byproducts for all epoxide substrates as observed by others.[112] Similarly, a microporous N- and O-rich mesoporous carbon was prepared by CO_2-assisted pyrolysis of chitosan.[142] Due to the presence of basic nitrogen (pyridinic, pyrrolic, and graphitic) and H-bonding moieties (–OH, –COOH) the obtained material was an active catalyst for the conversion of activated terminal epoxides to cyclic carbonates. Analogous N-free carbon materials derived from the pyrolysis of cellulose did not show any activity due to the lack of nitrogen atoms despite the presence of HBD moieties. However, for most epoxides, only moderate conversion was observed under relatively harsh conditions (120 °C, 20 bar) in 12 h. Alternatively, some bioderived doped carbon materials have been used in the presence of very small amounts ($\sim$0.5 mol%) of halide-based additives such as TBAB[139] or KI.[143] These materials still required high temperatures for the conversion of a variety of epoxides (120 °C, 10–20 bar) but led to

quantitative conversions in short reaction times (5–8 h) due to the assistance of the homogeneous nucleophiles. Recent progress by Wang *et al.*[140] has shown that nucleophilic halides can be directly incorporated into a doped carbon structure. The authors prepared carbon dots from the hydrothermal treatment of biobased phytic acid with poly(ethylene imine) and KI, hence obtaining a material rich in HBDs (–OH, NH_2, phosphates) and incorporating nucleophilic halide ions. Importantly, the produced carbon dots catalyzed the cycloaddition of CO_2 to numerous epoxides at relatively mild temperatures (typically 80 °C) under atmospheric pressure as an effect of the small particle size and the presence of abundant active functionalities. However, the complete substrate conversion required 34 h. The catalytic performance of the recycled carbon dots progressively decreased due to leakage of KI arising from the lack of a covalent interaction with the carbon host.

Some representative MOF-based catalytic systems for the cycloaddition of CO_2 to epoxides are shown in Scheme 4(c). In general, the application of MOFs as heterogeneous Lewis acids for the synthesis of cyclic carbonates has long been known but has various limitations. Early examples often used high loadings of homogeneous nucleophiles.[144,145] Additionally, many efficient MOF-based catalytic systems for the target cycloaddition reaction are based on highly expensive building blocks and rare-earth metals.[146,147] The synthesis of the organic linkers may require multiple steps,[148] while the synthesis of the MOF itself may require several days.[147] Nevertheless some archetypal MOFs such as MOF-5, ZIF-8, and UiO-66 are readily prepared from highly available materials.[149,150] In particular, zeolitic imidazolate network frameworks (ZIF) are attractive materials for the cycloaddition of CO_2 to epoxides because they are readily produced from inexpensive imidazole linkers and metal salts. Therefore, they possess Lewis acidity from the metal nodes and basic nitrogen atoms from the imidazole ligands for interaction with CO_2 and its nucleophilic activation, thus serving as halide-free catalysts for the cycloaddition of CO_2 to epoxides.[151] The catalytic performance of ZIF-type MOFs in the synthesis of cyclic carbonate can be enhanced by introducing additional Lewis acidic metal sites as framework-coordinated dopants,[152] or by replacing the 2-methyl imidazole linker with different heterocycles such as 1,2,4-triazoles. Through the latter strategy,[151] a remarkable acceleration of the kinetics of the reaction of CO_2 cycloaddition to epoxides was observed compared to standard ZIF-8, attributed to the experimentally observed increase in acidic and basic sites in the hybrid MOF (due to the formation of multiple defective sites). As an effect, the triazole-modified ZIF-8 catalyzed the cycloaddition of CO_2 to epoxides under very mild conditions for a halide-free system (80 °C, 1 bar, 24–48 h) showing, in addition, good recyclability. Similar results were obtained by the same group by introducing 3-amino-1,2,4-triazole in a Co/Zn ZIF as a framework linker with pendant amino groups.[153] Further details on the cycloaddition of CO_2 to epoxides by ZIF-type catalysts can be found in a recent review.[154]

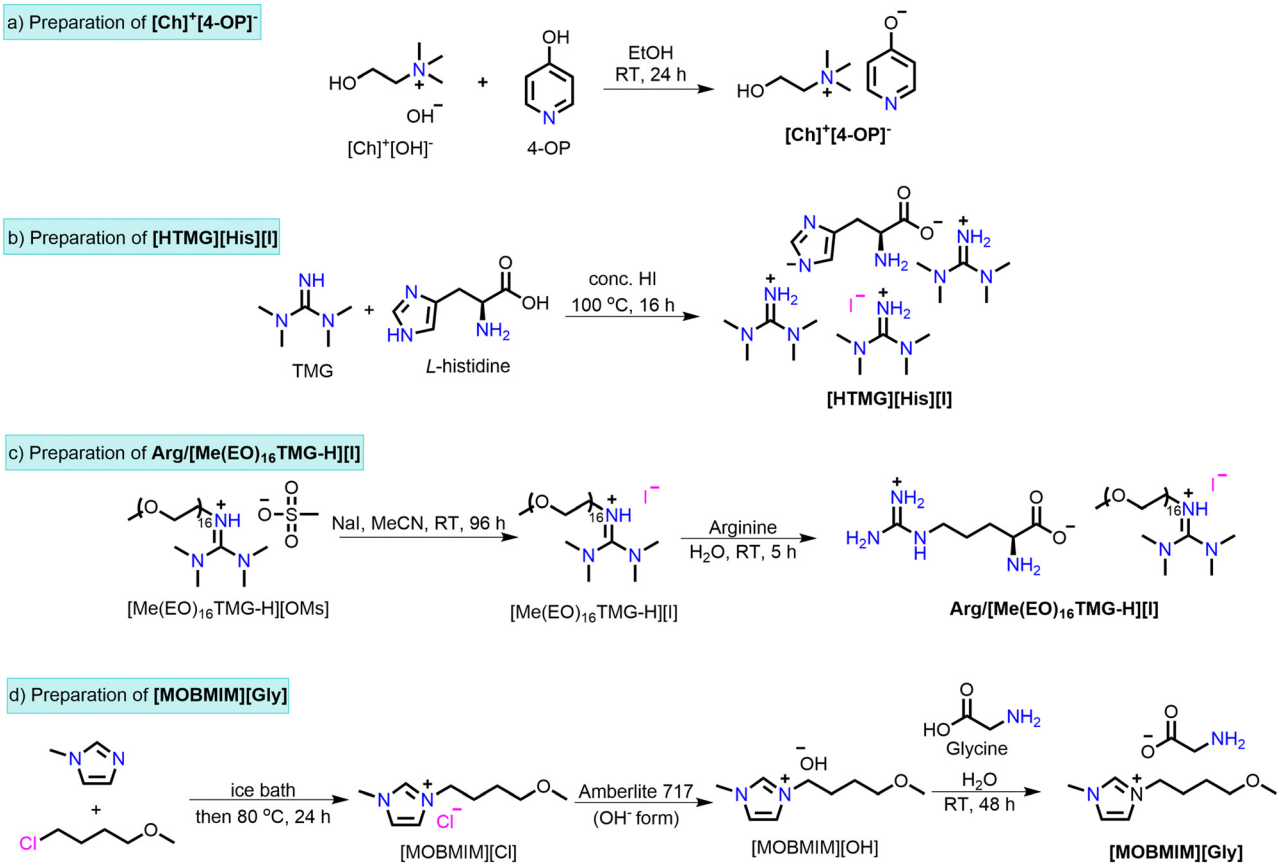
Other readily-available MOFs such as UiO-66 have been used as catalysts for the cycloaddition of CO_2 to epoxides. However, due to the lack of nucleophilic moieties in the structure of the standard UiO-66, a UiO-66-NH_2 (Zr-based with 5% Ce to induce a more efficient defective structure) derivative was prepared using 2-aminoterephthalic acid as the linker to provide nucleophilic activation of CO_2 through the pendant amino group.[155] However, the efficient cycloaddition of CO_2 to selected epoxides at 100 °C, 10 bar in 4 h, required the addition of small quantities of homogeneous TBAB (0.5 mol%) and the recyclability of the material was generally lower than that observed for the previously discussed ZIF-based systems.

Other classes of structurally simple recyclable catalysts such as polymer-supported nucleophilic moieties[156] or biobased alginates[157] can be used to synthesize GC by the cycloaddition of CO_2 to glycidol[158,159] through a proton-shuttling mechanism occurring with epoxy alcohols.[160] Such catalytic protocols, that are specific to GC synthesis, will not be discussed in detail in this manuscript which focuses on catalytic systems able to convert a variety of epoxide substrates.

Recyclable molecular catalysts

The concepts of recyclability and recoverability are typically associated with heterogeneous catalysts that are in a different phase than the reagents during reaction. However, molecular homogeneous catalysts, that are dissolved in a homogeneous phase with (part of) the reagents during the reaction, may be recovered by strategies such as precipitation, extraction or evaporation of the final reaction mixture at the end of the reaction.[161,162] The latter option is, however, unsustainable in the case of cyclic carbonates synthesis due to their high boiling temperature and low vapour pressure, and therefore will not be discussed further.

Recyclable molecular catalysts for the cycloaddition of CO_2 to epoxides are generally ionic compounds such as organic halide salts, often occurring in the form of halide ionic liquids, or as pairs or combinations of ionic compounds each carrying a separate catalytically active component (Scheme 4(d)). Due to their polarity, they can be precipitated or extracted at the end of the reaction, thus facilitating their recovery. Schemes 5 and 6 display a selection of readily-available ionic compounds recently used for the cycloaddition of CO_2 to a variety of epoxides divided into two classes (paired ionic species, Scheme 5, and organic halide salts, Scheme 6). The performance of the compounds shown in Schemes 5 and 6 in the cycloaddition of CO_2 to epoxides (using generally moderately reactive epoxides[105] such as 1-hexene oxide (HO) and styrene oxide (SO) as reference compounds) is shown in Table 1 with an emphasis on the recyclability and recovery strategy of the catalysts. Given the strong interest toward the development of halide-free systems for the cycloaddition of CO_2 to epoxides,[103,163,164] cholinium pyridinolate $\mathbf{[Ch]^+[4\text{-}OP]^-}$ was produced by mixing equimolar amounts of choline hydroxide and 4-hydroxypyridine (Scheme 5(a)).[165] While the pyridinolate ring contains a nucleophilic pyridinic nitrogen[166,167] that can serve in the ring-opening of epoxides,[109,112,168] the negatively charged oxygen atom of the pyridinolate was expected to rapidly attack CO_2, generating a carbonate intermediate for the subsequent ring-



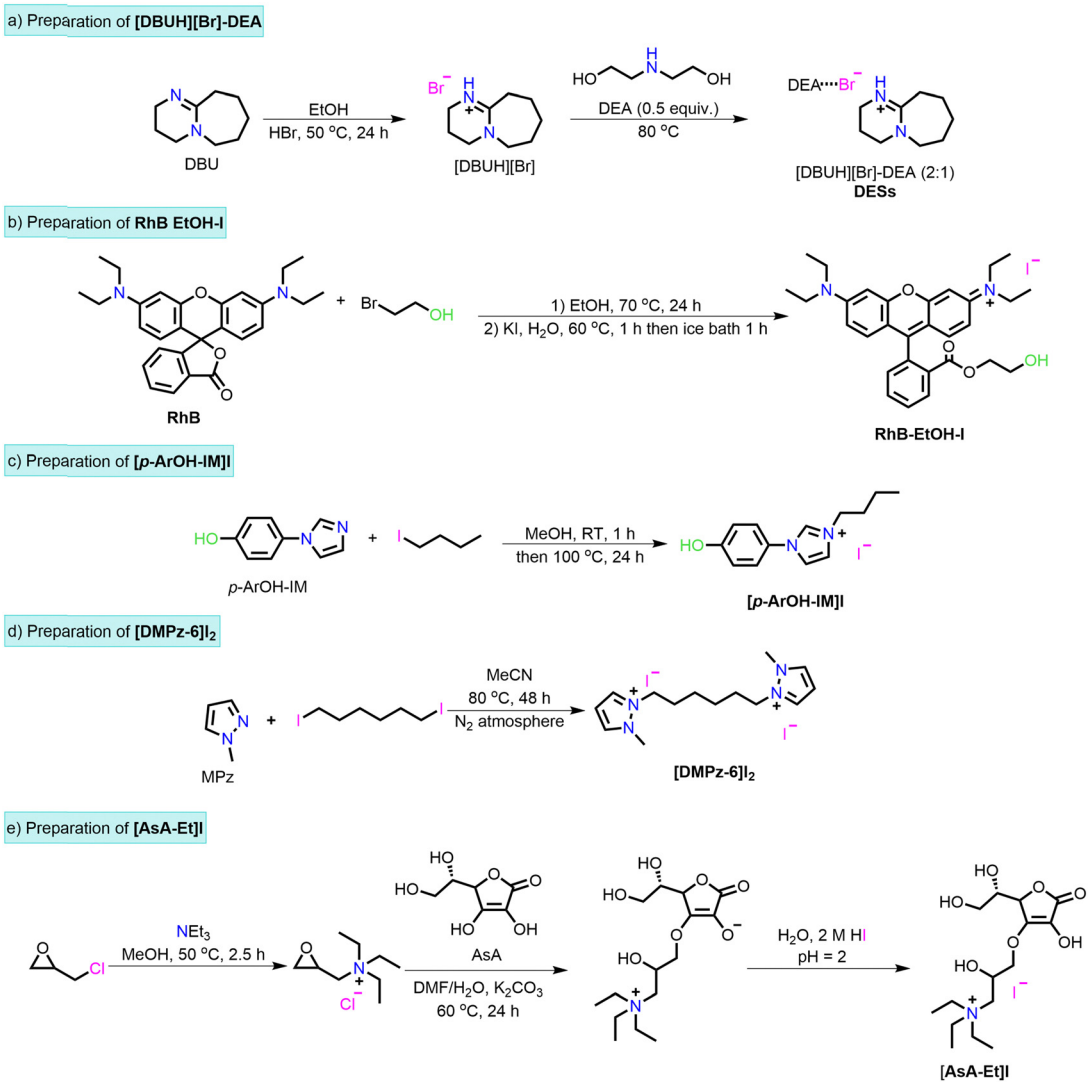
Scheme 5 Preparation of paired ionic compounds for the CO_2-epoxide cycloaddition reaction; cholinium 4-pyridinolate (**[Ch]$^+$[4-OP]$^-$**) from choline hydroxide ([Ch]$^+$[OH]$^-$) and 4-hydroxypyridine (4-OP) (a); 1,1,3,3-tetramethylguanidinium-histidine iodide (**[HTMG][His][I]**) from 1,1,3,3-tetramethylguanidine (TMG) and histidine (His) (b); arginine-polyether guanidinium iodide (**Arg/[Me(EO)$_{16}$TMG-H][I]**) from polyether guanidinium iodide ([Me(EO)$_{16}$TMG-H][I]) and arginine (Arg) (c) and 1-methoxybutyl-3-methylimidazolium glycine (**[MOBMIM][Gly]**) from 1-methoxybutyl-3-methylimidazolium hydroxide ([MOBMIM][OH]) and glycine (Gly) (d).

opening of the epoxide substrate activated by the choline moiety –OH as a hydrogen bond donor. A comparable nucleophilic mechanism, but without hydrogen-bond activation, was reported earlier by Zhou *et al.*[104] using CO_2 adducts of phosphorus ylides as catalytically active species. To note, **[Ch]$^+$[4-OP]$^-$** was slightly more effective than 4-hydroxypyridine alone, showing that a catalytic mechanism using the pyridinic nitrogen as a nucleophile could also function efficiently.

[Ch]$^+$[4-OP]$^-$ required relatively harsh reaction conditions for the efficient cycloaddition of CO_2 to a variety of epoxides (Table 1). **[Ch]$^+$[4-OP]$^-$** was recycled by extraction from the reaction mixture showing high recyclability for six cycles.

The catalytic systems shown in Scheme 5(b)–(d) are derivatives of amino acids. Amino acids are suitable inexpensive catalysts for the cycloaddition of CO_2 to epoxides due to their biobased nature and high availability.[177] However, despite the availability of various –NH_2, –OH, guanidine (for arginine), and imidazole (for histidine) hydrogen bonding moieties in natural amino acids, their catalytic activity for the target reaction is generally low due to the absence of strong nucleophilic moieties. Therefore, natural amino acids require very harsh reaction conditions for efficient epoxide conversion.[178] Combinations of amino acids and organic halide salts led to more active catalytic systems although at the cost of involving oil-based compounds such as imidazolium salts.[179,180] Recent reports have been focused on amino acid-based catalytic systems operating under mild conditions. **[HTMG][His][I]** (Scheme 5(b)) was prepared by simple neutralization of mixtures of histidine and tetramethylguanidine (TMG) with HI.[169] In this catalytic system, the protonated TMG (HTMG) serves as an HBD. Moreover, the authors proposed the formation of an imidazolate anion serving as a CO_2 capture unit. **[HTMG][His][I]** carried out the cycloaddition of CO_2 to epoxides at mild temperatures (Table 1) and even just at 30 °C when extending the reaction time to 20 h, however, incomplete substrate conversion was observed. **[HTMG][His][I]** showed very good recyclability after extraction from the reaction product.

A more elaborate amino acid-based system than **[HTMG]-[His][I]** was reported by Wang *et al.*[170] (Scheme 5(c)). In arginine-based **Arg/[Me(EO)$_{16}$TMG-H][I]** a polyether functionalized analogue of TMG, (Me(EO)$_{16}$TMG), was used. The latter moiety provided a slightly higher catalytic performance than unfunctionalized TMG under identical conditions due to the presence of the long polyether chain. The role of the polyether was to envelope the TMG moiety through H-bond interaction



Scheme 6 Synthesis of halide ionic liquid catalysts: **[DBUH][Br]-DEA** (DES) from DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), HBr and diethanolamine (DEA) (a), rhodamine B hydroxyethoxy iodide (**RhB-EtOH-I**) from rhodamine B (RhB) and bromoethanol (b), 4-(imidazole-1-yl)phenol-1-butyl-imidazolium iodide (**[*p*-ArOH-IM]I**) from 4-(imidazol-1-yl)phenol (*p*-ArOH-IM) and 1-iodobutane (c), 2,2′-(hexane-1,6-diyl)-bis(1-methylpyrazolium) diiodide (**[DMPz-6]I_2**) from 1-methyl pyrazole (MPz) and 1,6-diiodohexane (d), and a functionalized alkyl ammonium halide of ascorbic acid (**[AsA-Et]I**) from glycidyl ammonium halide and ascorbic acid (AsA) (e).

thus reducing the contact between the halide anion and the TMG-based cation. In this case, the protonated guanidium moiety of arginine acted as the hydrogen bond donor. **Arg/[Me(EO)$_{16}$TMG-H][I]** was applied under harsher reaction conditions than **[HTMG][His][I]** (Table 1) but with significantly lower catalytic loading and with a nearly complete substrate conversion. As in the case of **[HTMG][His][I]** it showed excellent recyclability upon extraction from the product.

Qu *et al.* (Scheme 5(d)) reported a halide-free **[MOBMIM][Gly]** system through simple synthetic steps such as imidazole alkylation, ion exchange and neutralization with glycine.[171] **[MOBMIM][Gly]** and analogous compounds based on different amino acids showed the ability to capture over-stoichiometric amounts of CO_2 (*ca.* 2 equiv. CO_2 per mol of **[MOBMIM][Gly]**). This observation was attributed to the interaction of CO_2 with the amino group of the amino acid moiety and with the imidazolium ring. **[MOBMIM][Gly]** catalysed the CO_2 cycloaddition reaction to epoxides under conditions similar to **Arg/[Me(EO)$_{16}$TMG-H][I]** (Table 1) but in a longer reaction time. The catalytic process was proposed to proceed through H-bond activation (imidazolium ring) and nucleophilic ring opening of the epoxide by the glycinate anion. Overall, it allowed the mildest reaction conditions for the amino acid-based compounds in Scheme 5(b)–(d) but the conversion of SO was generally moderate. Moreover, **[HTMG][His][I]** required the highest catalytic loading compared to **Arg/[Me(EO)$_{16}$TMG-H][I]** and **[MOBMIM][Gly]**. All amino acid-based catalysts discussed in this section showed very good recyclability due to their ability to undergo quantitative extraction or precipitation with solvents.

DESs (deep eutectic solvents) are increasingly used in catalysis as solvents and catalysts.[181,182] DESs are easy-to-prepare

Table 1 Overview of the performance and recyclability of molecular catalysts for the cycloaddition of CO_2 to epoxides

Catalyst	Loading (mol%)	Conditions			Conversion[a] (%)	Selectivity (%)	Substrate: recyclability[b] (%)	Catalyst recovery
		T (°C)	P (bar)	Time (h)				
[Ch]$^+$[4-OP]$^-$[165]	5	120	10	12	96 (HO) >99 (SO)	98 90	SO: constant for 6 runs	Extraction with ethyl acetate from the reaction mixture
[HTMG][His][I][169]	5	80 30	20 10	3 20	61 (SO) 43 (SO)	90 90	PO: run 1 (94) Run 6 (>90)	Extraction with ethyl acetate from the reaction mixture and drying
Arg/[Me(EO)$_{16}$TMG-H][I][170]	0.5	110	15	5	87 (HO) 96 (SO)	97 > 99	SO: constant for 8 runs	Extraction with methyl *tert*-butyl ether from the crude product
[MOBMIM][Gly][171]	1.2	110	20	12	65 (SO) 90 (BO)	80 99	PO: constant for 5 runs	Precipitation by the addition of ethyl acetate
[DBUH][Br]-DEA[172]	20	25	1	48	94 (HO) 97 (SO)	>99	SO: run 1 (97) Run 5 (93)	Dilution of the product with ethyl acetate and water, evaporation of the aqueous layer
RhB EtOH-I[173]	1	60	10	24	52 (HO) 54 (SO)	>99	PO: run 1 (59) Run 2 (59)	Precipitation by the addition of diethyl ether and centrifugation (note: only 64% of the catalyst was recovered)
[*p*-ArOH-IM][I][174]	20	25	1	10	95 (HO) 98 (SO)	>99	ECH: run 1 (>95), Run 5 (~90)	Extraction with ethyl acetate from the reaction mixture and centrifugation
[DMPz-6]I$_2$[175]	2	100	10	10	94 (SO)	>99	PO: run 1 (98) Run 7 (>95)	Separation by centrifugation
[AsA-Et][I][176]	4	80	10	24	99 (HO) 99 (SO)	99 99	HO: run 1 (99) Run 5 (93)	Phase separation between the organic and aqueous phase

[a] Conversion of 1-hexene oxide (HO) and styrene oxide (SO) as reference compounds; BO: 1-butene oxide (1,2 epoxybutane) was used as a reference when HO was not available. [b] Refers to the substrate conversion in the first and in the last catalytic experiment.

ionic systems that generally involve a halide salt and a hydrogen bond donor.[183] Their structure makes them viable candidates as catalysts for the cycloaddition of CO_2 to epoxides.[184–186] Readily available DESs were prepared through the combination of two equivalents of protic halide salts of commercially available strong organic bases such as DBU (1,8-diazabicyclo(5.4.0)undec-7-ene), DMAP (4-dimethylaminopyridine) and TMG (tetramethylguanidine) with one equivalent of amines or amino alcohols (see Scheme 6(a) for **[DBUH][Br]-DEA** as a representative example).[172] Amines are known to efficiently capture CO_2 and could have a role in enriching the reaction medium with CO_2.[187] Protonated organic bases are known to serve as HBDs for the activation of the epoxide through the N^+–H group and as carriers of the nucleophilic halide.[188] Importantly, **[DBUH][Br]-DEA** performed more efficiently, under identical conditions, than the amine free catalyst [DBUH][Br] in the cycloaddition of CO_2 to styrene oxide under ambient conditions. This observation was attributed to the role of DEA as an additional HBD. There was no strong effect of the structure of the strong base on catalytic performance. Indeed, TMGH, DMAPH, and DBUH bromide salts performed similarly in the presence of DEA. **[DBUH][Br]-DEA** served as a catalyst for the complete conversion of a variety of terminal epoxides into cyclic carbonates under ambient conditions of temperature and pressure. However, the reaction time was 48 h and the catalyst loading was as high as 20 mol% (Table 1). **[DBUH][Br]-DEA**, recovered through an extraction procedure, showed excellent recyclability through five cycles with styrene oxide as the substrate.

An expedient way to generate a readily-available organic halide salt for the synthesis of cyclic carbonates was reported by Chen *et al.*[173] starting from industrially available dyes. Dyes such as rhodamine B (RhB) and rhodamine 6G (Rh6G) exist in the form of chloride salts and contain H-bonding moieties (–COOH, $-NH^+$) that may promote the cycloaddition reaction.[189] Furthermore, rhodamine B displays a tertiary amine group, which can efficiently fix CO_2.[190,191] To improve the catalytic efficiency of these dyes compared to their native forms, the authors carried out some simple modifications such as the exchange of chloride anion with more nucleophilic iodide which also improved the dye's solubility. Under relatively mild reaction conditions (80 °C, 10 bar) the iodide-exchanged rhodamine-based dyes were more efficient than methylene blue in the cycloaddition of CO_2 to styrene oxide due to the presence of HBDs in their scaffolds. The catalytic activity of all dyes was further increased by the addition of small amounts of water to the reaction mixture as an additional H-bond donor, leading to quantitative styrene oxide conversions.[47] To improve the catalytic performance under mild conditions, the authors installed a more flexible H-bond donor than the –COOH moiety of RhB. This was achieved by the reaction with bromoethanol (Scheme 6(b)), leading to **RhB-EtOH-I** upon ring-opening. The latter catalyst converted a range of terminal epoxides to the corresponding cyclic carbonates in moderate to high yields at 60 °C (Table 1) with a low catalytic loading (1 mol%). **RhB-EtOH-I** could be recovered by precipitation with diethyl ether and was recycled for a single additional run, but a significant portion of the catalyst was left in the product (~35%). Its successful removal from the product was carried out by membrane nanofiltration due to the

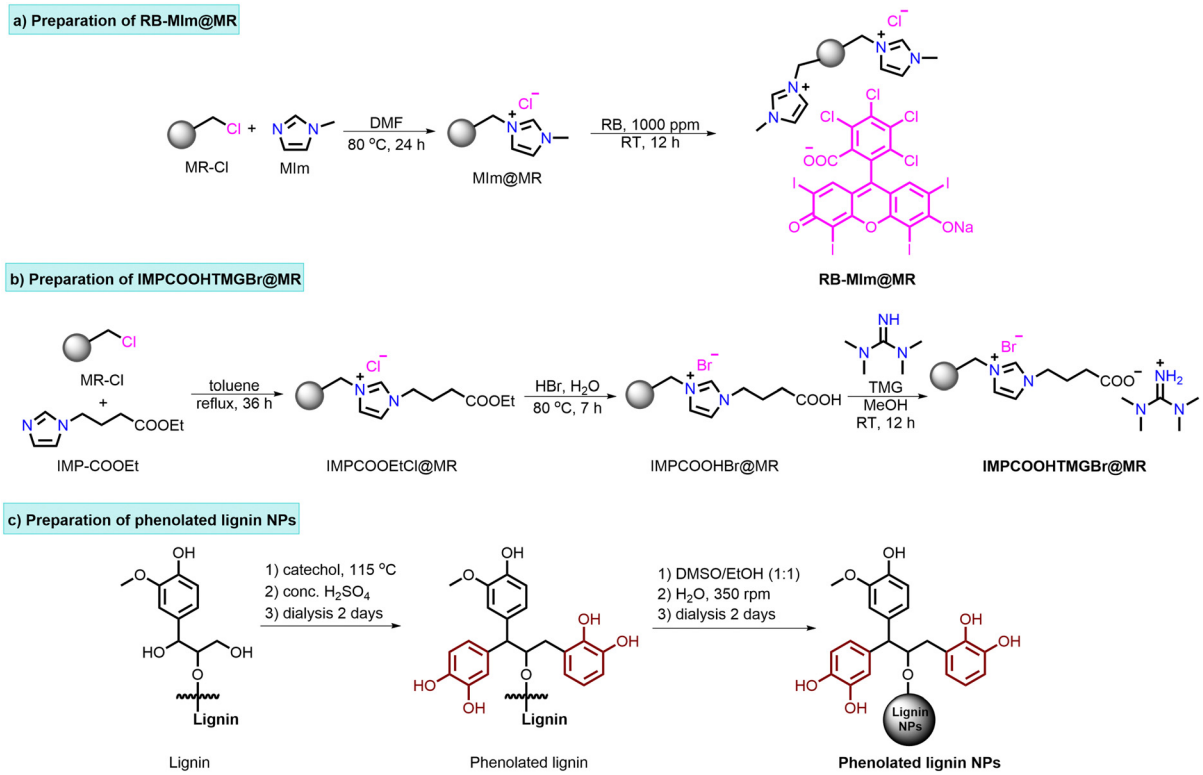
high molecular weight of the catalyst compared to the substrate. Two recent examples of highly recyclable organic halide salts for the cycloaddition of CO_2 to epoxides have been reported by Guo *et al.* (**[p-ArOH-IM]I**)[174] and Damascene *et al.* (**[DMPz-6]I_2**)[175] (Scheme 6(c) and (d)). Phenolic compounds are highly active HBDs for the cycloaddition of CO_2 to epoxides due to their suitable pK_a ($\sim$9–10) which is high enough to allow the efficient activation of the epoxide, but not so acidic to fully neutralize the alkoxide intermediate formed upon ring-opening.[40] At the same time, imidazolium salts are active halide-bearing organocatalysts for the cycloaddition of CO_2 to epoxides due to the H-bonding ability of the aromatic ring protons.[192] Moreover, bulky substituents at the imidazole ring are known to weaken the electrostatic interaction between the halide and imidazolium cation, resulting into more nucleophilic halides.[193] In 2018, Castro-Osma *et al.* reported a catalytic system combining the phenolic scaffold with an imidazolium halide functionality to yield active single-component organocatalysts for the target cycloaddition reaction.[194]

More recently, Guo *et al.* carried out a systematic optimization of phenol-functionalized imidazolium compounds (**[p-ArOH-IM]I** and analogous compounds and positional isomers).[174] **[p-ArOH-IM]I** emerged as the most efficient catalyst for the cycloaddition of CO_2 to epichlorohydrin in virtue of a moderate repulsion between the imidazolium cation and the nucleophilic halide arising from the side chain at the imidazolium nitrogen and from the optimal position of the phenolic –OH relative to the imidazole ring. Therefore, the iodide anion served as an efficient nucleophile for the epoxide ring-opening step, and as an efficient leaving group in the final cyclization step that reformed the catalyst. The optimized **[p-ArOH-IM]I** showed the ability to catalyze the cycloaddition of CO_2 to various epoxides under atmospheric pressure in the presence of a very high catalytic loading (20 mol%, Table 1). Nevertheless, **[p-ArOH-IM]I** could be used at very low loadings (0.0011 mol%) under harsh reaction conditions (120 °C, 30 bar) resulting in TON values $>80\,000$ at high substrate conversion which were unusually high for organocatalysts. Dual pyrazolium compounds such as **[DMPz-6]I_2** and analogous compounds with shorter aliphatic linkers were obtained by the straightforward combination of pyrazole and terminal diiodoalkanes.[175] An initial screening for the cycloaddition of CO_2 to PO (propylene oxide) revealed an increase in activity with the length of the linker between the pyrazolium units attributed to the increased flexibility of the catalyst. Moderate loadings of **[DMPz-6]I_2** could catalyze the cycloaddition of CO_2 to epoxides at 100 °C, 10 bar in high yields (Table 1) and could be used in the presence of diluted CO_2 feedstocks as a simulated flue gas. Through DFT calculations, the epoxide activation was attributed to the acidic C3/C5 protons of the pyrazolium scaffold while the dual pyrazolium units were found to act independently without specific cooperation.

The overview of catalyst recovery and recyclability provided in Table 1 shows that, in general, the molecular homogeneous catalysts need to be isolated by extraction or by precipitation with solvents that eventually require evaporation to recover the catalyst and stripping from the unavoidably polluted final product. In general, much larger volumes of solvents than the volume of carbonate synthesized need to be used for extraction, precipitation and catalyst washing resulting into a solvent-intensive process. Even when the solvent is recycled, its use and energy-intensive evaporation seriously affect the atom economy, footprint and solventless nature of the cycloaddition process.[195] In general, from the standpoint of sustainability, solvent-intensive processes should be avoided,[196] while solvent-free processes are recommended.[197] In order to avoid the use of solvents in the cycloaddition reaction by recyclable molecular catalysts, Theerathanagorn *et al.*[176] prepared **[AsA-Et]I** (Scheme 6(e)) from environmentally benign ascorbic acid and quaternary ammonium functionalized epoxides derived from glycerol-based epichlorohydrin.[198] The (nearly) complete insolubility of the catalyst in the epoxide substrates and in the final carbonate products allowed the use of **[AsA-Et]I** in a biphasic catalytic setting involving a lower volume of water phase containing the catalyst compared to the organic epoxide phase. In this kind of water-in-oil catalytic process, the catalyst acts at the interface between the aqueous and organic phases.[199] This allowed reuse of the catalyst through a simple decantation of the aqueous layer that was recycled as such for the next catalytic run with only a minor drop in performance after five reaction cycles (Table 1). **[AsA-Et]I** was applied for the quantitative conversion of various terminal epoxides into the corresponding cyclic carbonates at 80 °C, 10 bar. The addition of simple inorganic salts such as NaCl to the aqueous phase (or the direct use of seawater as the aqueous layer) allowed, for some substrates, a more efficient separation between the organic and aqueous layer and an acceleration of the catalytic process. This result may derive from the formation of smaller water droplets and/or salting out[200] of the catalyst towards the interface, increasing its contact with the substrates. An analogous compound, **[AsA-Bu]I**, was used for the biphasic cycloaddition of CO_2 to epoxidized fatty acids as challenging internal epoxides resulting into a rare recyclable catalyst for the synthesis of challenging biobased cyclic carbonates.[201]

Polymer-based organocatalysts

Polymer-based organocatalysts are a well-established class of heterogeneous materials for the cycloaddition of CO_2 to epoxides.[101,202–204] They can be divided into two groups according to the location of the active sites in the polymer structures (Scheme 4(e)). In polymer-supported molecular catalysts, active sites are typically generated or immobilized on catalytically inert polymeric beads or polymers.[167,205] On the other hand, in catalytic polymers, the catalytic active sites are included in the polymeric backbone or side-chains. This can be achieved by the copolymerization of suitable monomers bearing active sites,[206–209] or by post-polymerization modification of the polymeric materials at specific locations to create active sites.[85,101] Moreover, the generation of crosslinked geometries with different degrees of porosity typically facilitates the access of substrates to active sites.[204,210] In this context, recent progress has led to the preparation of affordable and easy-to-synthesize polymer-supported (Scheme 7) and polymeric



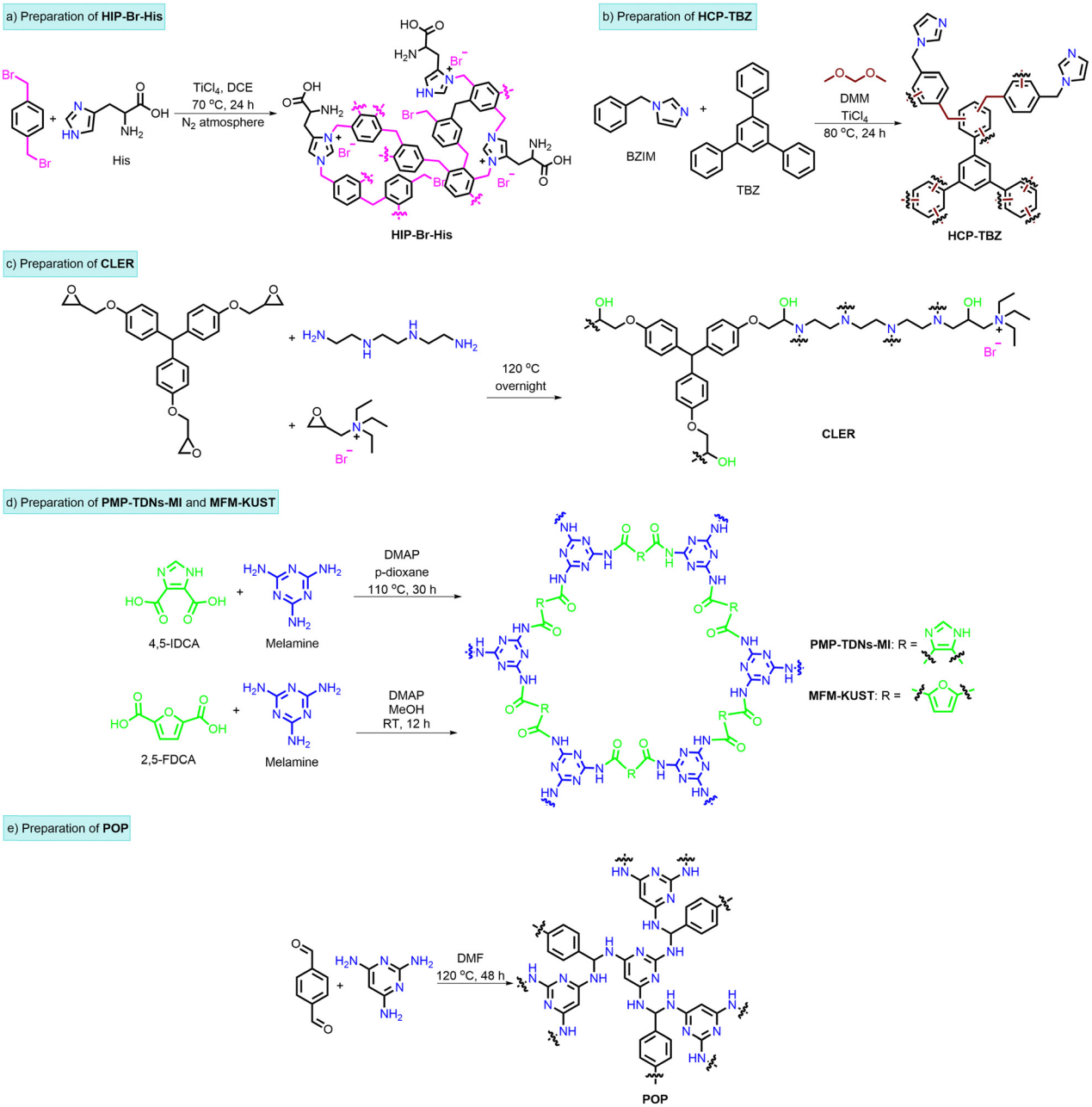
Scheme 7 Preparation of polymer supported catalysts: Rose Bengal and methylimidazolium chloride supported on Merrifield resin (**RB-MIm@MR**) from Rose Bengal (RB), methylimidazole (MIm) and Merrifield resin (MR) (a), propyl imidazole carboxylate bromide-1,1,3,3-tetramethylguanidinium on MR (**IMPCOOHTMGBr@MR**) from ethyl 1-ethoxycarbonyl propyl imidazole (IMP-COOEt), 1,1,3,3-tetramethylguanidinium (TMG) and MR (b), **and phenolated lignin NPs** from lignin and catechol (c).

catalysts (Scheme 8). The preparation of polymer-supported catalysts is generally straightforward with the main challenge being the design of the suitable linkage connecting the polymer bead and the catalytically active moiety.[211] On the other hand bifunctional polymeric catalysts such as ionic polymers are generally produced by the combination of comonomers bearing different active moieties (for instance a monomer bearing a halide anion and a monomer bearing a HBD moiety).[212] In the majority of the cases, this kind of approach required the use of sophisticated monomers,[213] multiday synthetic procedures,[214] environmentally noxious polyhalogenated aromatic compounds,[212] overstoichiometric coupling agents,[209] or hazardous organometallic reagents.[215] Nevertheless, some inexpensive and active polymer catalysts for the cycloaddition of CO_2 to epoxides using readily available starting materials were recently reported.[216–218] Among such catalysts, for the sake of brevity, the overview presented in this section will focus on active catalytic polymers prepared in a single synthetic step using commercially available monomers and using cycloaddition reaction times not higher than 30 h.

Polymer-supported catalysts

In order to allow recyclability and/or for application under a dynamic flow, efficient molecular catalysts can be anchored to inert supports.[156,219,220] The active site grafting takes place *via* well-established and efficient reactions. Thus, 1,3-dipolar cycloaddition (or "click reaction"),[102,211] or the nucleophilic attack on the $-CH_2Cl$ moiety of crosslinked polystyrene-based materials such as Merrifield resin are often used.[221] Polymer-supported catalysts were investigated in earlier attempts to produce inexpensive heterogeneous catalysts for the cycloaddition of CO_2 to epoxides.[222] In such reports, catalytically active moieties such as quaternary ammonium halide salts,[223] imidazolium salts,[224] phosphonium halide salts,[225] and pyridinium salts,[226] were generated on various polymeric supports. Due to the lack of strong H-bonding activation of the epoxide substrates, these catalysts were found to be active only under harsh conditions (120 °C, 25–80 bar CO_2) or to require the presence of polar solvents.

Recently, Valverde *et al.*[227] reevaluated the cycloaddition of CO_2 to epoxides by polystyrene-supported imidazolium catalysts in the presence of Rose Bengal (RB), a common anionic dye, that was introduced *via* ion exchange. The authors observed a remarkable improvement in the catalytic performance of **RB-MIm@MR** (Scheme 7, MR: Merrifield resin). Compared to the classical polystyrene supported imidazolium chloride (just 39% SO conversion), **RB-MIm@MR** led to a good SO conversion to SC under relatively mild conditions (Table 2). This observation was attributed to the deprotonation of the C2 carbon by RB and the formation of a N-heterocyclic carbene (NHC). The NHC could form an NHC–CO_2 adduct with CO_2, leading to an efficient nucleophilic catalyst for the coupling of CO_2 and epoxides (see Scheme 3). Additionally, water from moisture and the



Scheme 8 Preparation of polymer catalysts: histidine-based hypercrosslinked ionic polymer bromide (**HIP-Br-His**) from 1,4-bis(bromomethyl)benzene and histidine (His) (a), imidazole-based hyper-crosslinked polymers with triphenylbenzene (**HCP-TBZ**) from 1-benzylimidazole (BZIM) and 1,3,5-triphenylbenzene (TBZ) (b), crosslinked epoxy resin (**CLER**) from glycidyl triethyl ammonium bromide, crosslinked epoxide monomer and triethylenetetramine (c), periodic mesoporous polyamides with triazine-derived networks of melamine and 4,5-imidazoledicarboxylic acid (**PMP-TDNs-MI**) from melamine and 4,5-imidazoledicarboxylic acid (4,5-IDCA), and polyamide heterogeneous catalyst (**MFM-KUST**) from melamine and 2,5-furandicarboxylic acid (2,5-FDCA) (d), and porous organic polymer (**POP**) from terephthaldehyde and 2,4,6-triaminopyrimidine (e).

formed phenolic hydroxyl of RB upon protonation were proposed to serve as HBDs in the activation of the epoxide.

In place of testing the catalyst recyclability in batch reactions, a co-immobilized version of the **RB-MIm@MR** catalyst was applied under flow conditions for the conversion of SO and showed good stability on-stream, but very harsh conditions (150 °C, 140 bar) were required for a moderate SO conversion. An alternative way to enhance the activity of polymer-supported imidazolium catalysts for the cycloaddition of CO_2 to epoxides is to append suitable catalytically active functional groups to the *N*-alkyl chain of imidazole rings.[101,230] Liu *et al.*[228] prepared a supported ionic liquid **IMPCOOHTMGBr@MR** through simple reaction steps of imidazolium moiety anchoring to MR and ethyl ester deprotection with HBr, also leading to an anion exchange with the more nucleophilic bromide, and neutralization with guanidine (Scheme 7(b)). The catalyst design was

Table 2 Overview of the performance and recyclability of polymer-supported catalysts

Catalyst	Loading	Conditions			Conversion[a] (%)	Selectivity (%)	Substrate: recyclability[b] (%)
		T (°C)	P (bar)	Time (h)			
RB-MIm@MR[227]	36.7 mg	100	10	5	76 (SO)	>99	SO: flow reactor 5 h (80) After 50 h (50)
IMPCOOHTMGBr@MR[228]	3 mol%	100	1	4	89 (SO)	>99	ECH: run 1 (97)
		80	1	4	64 (SO)	>99	Run 9 (91)
Phenolated lignin NPs[229]	100 mg	60	1	24	76 (SO) 95 (BO)	>99 >99	SO: constant for 10 runs

[a] Conversion of styrene oxide (SO) as reference compounds and BO, when available. [b] Refers to the substrate conversion in the first and in the last catalytic experiment.

based on a previous publication by the same group on molecular guanidinium salts of imidazolium-tethered carboxylates.[231] The authors proposed that the guanidinium carboxylate could serve as a unit able to capture and activate CO_2. Additionally, the protonated guanidinium group serves as a HBD.[51] A **IMPCOOHTMGBr@MR** catalyst with a high loading of guanidinium carboxylate ionic liquid obtained a nearly quantitative ECH conversion at 80 °C, 1 bar matching the performance of the previously reported analogous molecular compound under identical conditions. This was possibly due to the flexibility of the tethered carboxylate group allowing better access to the reagents in the solution phase, as observed in the past for other MR-supported organocatalysts.[167] Under the same conditions, less reactive epoxides afforded moderate to good yields of cyclic carbonates in just 4 h. An increase in the temperature to 100 °C was required to obtain high conversion rates (Table 2). The catalyst showed good recyclability through nine reaction cycles despite a significant (~50%) loss of the supported ionic liquid as observed by elemental analysis.

As discussed for the case of metal oxide catalysts, an alternative to the use of multifunctional polymeric compounds bearing nucleophilic moieties and HBDs, is the use of polymer HBDs in the presence of very low loadings (≤0.5 mol%) of homogeneous halide salts. Despite leading to the presence of trace amounts of homogeneous additives in the final product, this approach allows for the upcycling of hydroxyl-rich biopolymers such as lignin and cellulose as HBDs for the cycloaddition of CO_2 to epoxides.[232,233] In particular, lignin is one of the most abundant natural polymers and is produced in large amounts as a waste product of the paper industry.[234] Moreover, lignin is an aromatic biopolymer and contains abundant phenolic hydroxy groups, which are the most active HBDs for the cycloaddition of CO_2 to epoxides under atmospheric conditions.[40] Bulk soda lignin was reported to catalyse the cycloaddition of CO_2 to epoxides under relatively mild conditions (80–120 °C, 10 bar) in the presence of low amounts of KI. Jaroonwatana *et al.*[229] postulated that the use of lignin in the form of nanoparticles could significantly boost its performance as a HBD. In a study focusing on the catalytic activity of nanoparticles and microparticles of phenol-rich biopolymers (melanin, lignin) for the cycloaddition of CO_2 to epoxides, lignin nanoparticles were the most efficient HBDs. Indeed, the results showed satisfactory conversion of SO to SC under very mild conditions (60 °C, 1 bar). Switching from pure lignin nanoparticles to **phenolated lignin NPs** produced after phenolation of lignin with catechol (Scheme 7(c)) led to a further enhancement in catalytic performance, as expected from the increase in H-bonding moieties on the particles' surface. As well as excellent recyclability over ten reaction cycles (Table 2), **the phenolated lignin NPs** could convert several epoxides to the corresponding cyclic carbonates in 24 h under atmospheric pressure at just 60 °C in the presence of TBAI. Importantly, the loading of TBAI could be reduced to 0.5 mol% without significant reduction in catalytic performance and even to just 0.25 mol%, although slightly harsher reaction conditions (80 °C, 5 bar) were required for efficient substrate conversion. Overall, aromatic biopolymers are attractive, readily available HBDs for the cycloaddition to epoxides, but further research is required to completely avoid the use of homogeneous additives even in very small amounts as further discussed in the outlook section.

Polymeric catalysts

A histidine-based hypercrosslinked polymer (**HIP-Br-His**, Scheme 8(a)) with a surface area of about 720 $m^2\ g^{-1}$, was prepared by the Friedel–Crafts alkylation reaction of 1,4-bis(bromomethyl)benzene catalysed by $TiCl_4$ in the presence of histidine. Histidine was included in the polymer *via* alkylation and quaternization of the imidazole nitrogen atoms.[235] In a catalytic screening for the cycloaddition of CO_2 to PO at 110 °C, 10 bar in 3 h, **HIP-Br-His** (97% PO conversion) performed more efficiently than the analogous **HIP-Cl-His** (SA: 967 $m^2\ g^{-1}$, 78% PO conversion) despite a lower surface area. This result indicated that the presence of a more nucleophilic anion (bromide) had a stronger effect than a larger surface area. **HIP-Br-His** was also slightly more efficient than its analogue prepared by replacing histidine with imidazole (**HIP-Br-Im**, SA: 123 $m^2\ g^{-1}$, 91% PO conversion). It is not clear whether the slightly better performance of **HIP-Br-His** compared to **HIP-Br-Im** was due to the presence of the carboxylic acid HBD from histidine in the latter or to its much larger surface area. However, based on the conversion values, the effect of both factors seems, at best, marginal. **HIP-Br-His** performed as a versatile catalyst for the quantitative conversion of a variety of epoxides to cyclic carbonates at high temperature (110 °C, 10 bar) but in just 3 h. Alternatively, high conversions at 70 °C in 24 h were obtained (Table 3). Importantly, **HIP-Br-His** also served as a catalyst for the conversion of PO to PC using diluted CO_2 (15% in N_2) as simulated flue gas. Finally, **HIP-Br-His** showed excellent recyclability through eight catalytic cycles with only a minor drop in conversion.

$TiCl_4$-catalyzed Friedel–Crafts alkylation was also used for the preparation of halide-free, imidazole-based **HCB-TBZ** (Scheme 8(b)) by reacting benzylimidazole and 1,3,5-triphenylbenzene (TBZ) in different proportions in the presence of dimethoxymethane (DMM).[236] The synthesized hypercrosslinked polymers had relatively high surface areas (up to about 1000 $m^2\ g^{-1}$ for a 4 : 1 imidazole to TBZ benzene molar ratio) which rapidly decreased by increasing the ratio of imidazole units in the polymer due to the lower content of polytopic TBZ units.

However, the CO_2 uptake capacity under standard conditions remained similar for all polymers (between 2.23–2.30 mmol g^{-1}). Despite having the lowest surface area among the **HCB-TBZ** polymers, **HCB-TBZ** (16 : 1) exhibited the best catalytic performance for the cycloaddition of CO_2 to PO (120 °C, 10 bar) due to the highest content of active sites (imidazole). The use of **HCB-TBZ** (16 : 1) for various substrates led to epoxide conversions comparable to halide-based **HIP-Br-His** in a similarly short reaction time (5 h) under similar conditions (Table 3). However, the efficiency of **HCB-TBZ** (16 : 1) at mild temperatures (70 °C) was clearly lower than for **HIP-Br-His** due to the absence of halide nucleophiles in **HCB-TBZ** (16 : 1), with long reaction times (48 h) being required to obtain high epoxide conversion. Mechanistically, the only active site of the **HCB-TBZ** polymers is the imidazole ring, which has a dual role of attacking the CO_2 molecule with the free nitrogen atom and activating the epoxide with the acidic C2 hydrogen as the HBD. **HCB-TBZ** exhibited high levels of recyclability for at least 6 cycles.

Readily-available crosslinked epoxy resin organocatalysts (**CLER**) were synthesized by a one-pot reaction in water of multifunctional glycidyl ethers, triethylenetetramine and a monoepoxide bearing a quaternary ammonium halide moiety (Scheme 8(c)).[237] The ring-opening of the epoxide moieties during polymerization produced abundant aliphatic –OH functionalities as HBDs, while terminal quaternary ammonium halide groups were formed from the terminal monoepoxide. Additionally, the amino groups of triethylenetetramine interacted with CO_2 or reacted with traces of moisture to generate hydroxy anions as additional nucleophiles.[111] The authors initially synthesized various compounds by varying the structure of the multifunctional glycidyl ether and the halide anion at the functional monoepoxide. The introduction of rigid aromatic rings in the structure of the multifunctional glycidyl ether monomers led to an improved catalytic performance when compared to more flexible aliphatic diglycidyl ethers, while the halide anions followed the typical I > Br > Cl order of activity.[173,241] However, the bromide-based **CLER** catalyst in Scheme 8(c) was selected for further investigation due to the higher availability of epibromohydrin (precursor of the monoepoxide) compared to epiiodohydrin. The efficient conversion of several epoxides using the selected **CLER** catalyst generally took place at 100 °C, 20 bar in 24 h with high selectivity (Table 3). It is noteworthy that highly reactive ECH could be converted to ECHC under ambient conditions in high yields. **CLER** showed excellent recyclability for 7 reaction cycles when tested at intermediate (5 h) and complete SO conversion in 48 h.

Melamine is a highly available, nontoxic urea derivative that has attracted significant interest for the synthesis of halide-free porous polymers for the cycloaddition of CO_2 to epoxides.[242] Recently, a halide-free polymer, **PMP-TDNs-MI** (Scheme 8(d)), was prepared from highly available melamine and a dicarboxylic acid (4,5-imidazoledicarboxylic acid, 4,5-IDCA) in a single step through the formation of a network of amide bonds catalysed by DMAP.[238] The resulting triazinyl polyamide, **PMP-TDNs-MI**, displayed abundant HBD moieties (–NH groups, imidazole C2 proton) for epoxide activation and nitrogen atoms for interaction with CO_2. **PMP-TDNs-MI** had a negligible surface area (Table 3) which was one order of magnitude lower than an analogous polymer prepared by replacing melamine with the more expensive polytopic linker 1,3,5-tris-(4aminophenyl)triazine (TAPT).[243] Nevertheless, an initial screening using PO as the substrate (at 110 °C, 10 bar in 6 h) showed a slightly higher catalytic activity for melamine-based **PMP-TDNs-MI** compared to its TAPT-based analogue. A possible explanation for this result is that the type and acidity of the H-bonding

Table 3 Overview of the performance and recyclability of polymer catalysts

			Conditions					
Catalyst	Loading	Surface area ($m^2\ g^{-1}$)	T (°C)	P (bar)	Time (h)	Conversion[a] (%)	Selectivity (%)	Substrate: recyclability[b] (%)
HIP-Br-His[235]	100 mg	720	110	10	3	92 (SO)	97	PO: run 1 (97)
						96 (BO)	99	Run 8 (93)
			70	10	24	94 (SO)	99	
						93 (BO)	99	
HCP-TBZ (16 : 1)[236]	125 mg	683	120	10	5	92 (SO)	95	PO: run 1 (96)
						94 (BO)	96	Run 6 (>90)
			70	10	48	90 (PO)	99	
CLER[237]	1 mol%	n.a.	100	20	24	99 (SO)	99	SO: constant for 7 runs
PMP-TDNs-MI[238]	61.3 mg	8	110	10	30	95 (HO)	91	PO: run 1 (99)
			110	10	25	>99 (SO)	96	Run 5 (82)
MFM-KUST[239]	61.3 mg	17	110	10	20	51 (HO)	82	PO: run 1 (99)
			110	10	25	96 (SO)	99	Run 5 (90)
POP[240]	100 mg	219	130	1	24	83 (HO)	80	ECH: run 1 (67)
						50 (SO)	95	Run 5 (59)

[a] Conversion of 1-hexene oxide (HO) and styrene oxide (SO) as reference compounds; when not available, HO was replaced by BO. [b] Refers to the substrate conversion in the first and in the last catalytic experiment.

moieties played a more relevant role than surface area (at least in the low range of surface areas reported in this work, 5–50 $m^2 g^{-1}$, with the reaction likely occurring on the external surface of the catalysts). **PMP-TDNs-MI** was an efficient catalyst for the quantitative conversion of various epoxides to cyclic carbonates under the reaction conditions (Table 3), which were slightly harsher than for state-of-the-art halide-free systems operating under atmospheric pressure.[103,112] However, the preparation of the latter materials required several reaction steps or expensive monomers when compared to **PMP-TDNs-MI**. **PMP-TDNs-MI** displayed satisfactory recyclability (Table 3) with a slight drop in substrate conversion attributed to the adhesion of the polar products to the spent catalyst surface and active sites. The same group subsequently reported a more sustainable alternative to **PMP-TDNs-MI** by replacing 4,5-ICDA with biobased 2,5-FDCA (2,5-furandicarboxylic acid), leading to **MFM-KUST**[239] through a simple DMAP-catalysed polycondensation of readily-available monomers in methanol at room temperature (Scheme 8(d)). As for **PMP-TDNs-MI**, **MFM-KUST** had a very low surface area (Table 3) which was two orders of magnitude lower than that determined for the analogous **MFM-KUST** polymer prepared in DMSO. However, this difference in surface area did not reflect on the catalytic performance in an initial screening using ECH as the substrate, confirming the lack of any clear correlation between surface area and catalytic activity. As a drawback, when compared to **PMP-TDNs-MI**, **MFM-KUST** was a less efficient catalyst under similar reaction conditions, especially for the case of HO (Table 3) and aliphatic epoxides in general. This limitation may arise from the replacement of the imidazole ring used in **PMP-TDNs-MI**, which is known to serve as an efficient HBD,[192,227] with 2,5-FDCA in **MFM-KUST**.

Another example of the use of nitrogen-rich aromatic triamines for the one-step construction of halide-free catalysts for the cycloaddition of CO_2 to epoxides was recently reported by Mandal *et al.*[240] through the condensation of 2,4,6-triaminopyrimidine and terephthaldehyde (Scheme 8(e)). This approach resulted in a porous polymer (denoted as **POP** in the original manuscript) rich in –NH groups, that may serve as HBDs or for the interaction and activation of CO_2, and pyridinic nitrogen atoms that are known to open the epoxide ring by nucleophilic attack.[112] Different from the melamine-based catalysts discussed earlier, **POP** displayed a moderate surface area (about 220 $m^2 g^{-1}$, Table 3). It should be noted that optimization of the synthetic conditions could lead in principle to much higher porosity for such melamine-based materials.[244] **POP** was applied for the cycloaddition of CO_2 to a variety of epoxides under atmospheric pressure. For more reactive epoxides, temperatures in the 105–115 °C range were sufficient to obtain high conversions to cyclic carbonates in 24 h. More challenging epoxides such as SO and HO required a higher temperature (130 °C), leading to moderate or good conversion (Table 3). It is likely that milder reaction temperatures could be used with **POP** by increasing the CO_2 pressure to 10 bar as done for analogous **PMP-TDNs-MI** and **MFM-KUST** (Table 3). **POP** could be recycled for 5 runs with a marginal loss in catalytic efficiency attributed to pore blockage.

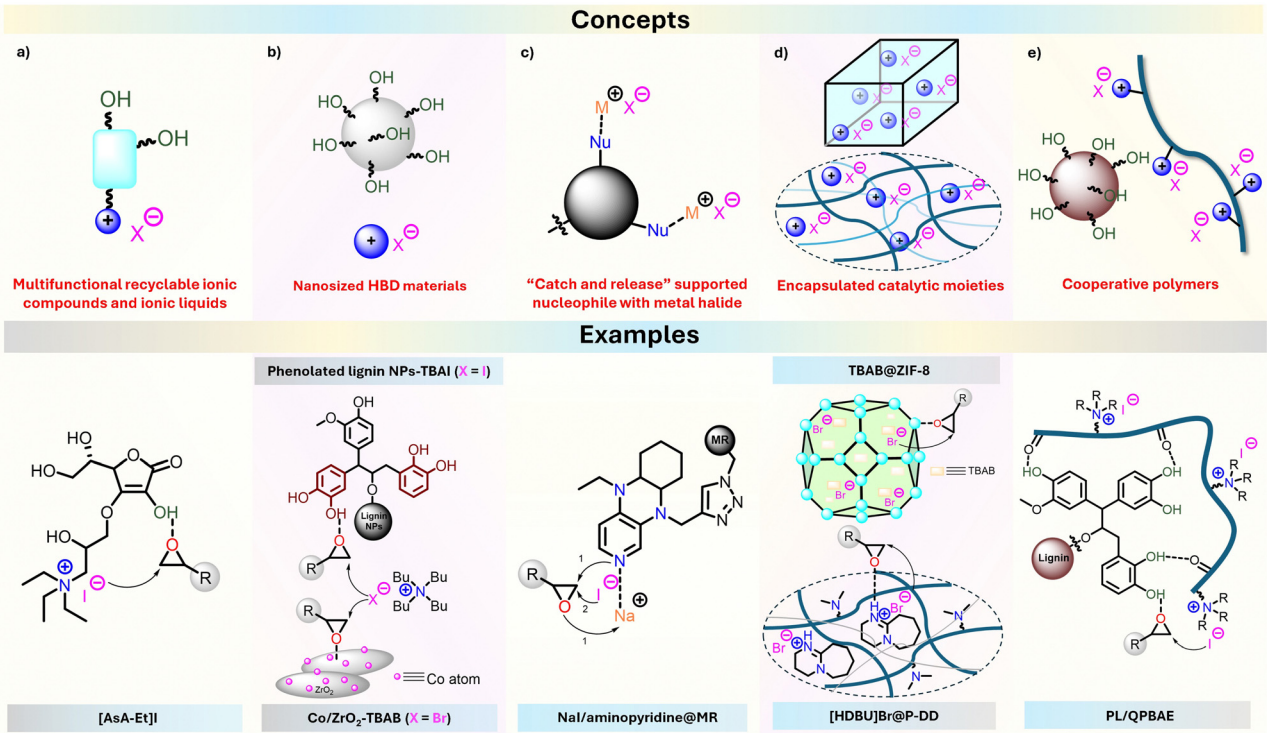
Future opportunities for catalyst design

With an eye to the preparation of more efficient catalysts, the results discussed in this work and previous literature,[207,245–247] clearly show that the systems operating efficiently under mild conditions are multifunctional compounds with multiple cooperative sites for the different mechanistic tasks of the cycloaddition process. In metal-free systems, this cooperativity is established through the simultaneous presence of HBDs with appropriate acidity (carboxylic or ascorbic acids, phenols)[40,103,248] and suitably placed nucleophiles (generally halides) with adequate mobility and flexibility.[174,192] However, it is often challenging to construct multifunctional recyclable systems using inexpensive and affordable building blocks without elaborate synthetic procedures, especially, when targeting coimmobilization of such moieties in close proximity. Therefore, we will provide in this section some guidelines and examples for preparing multifunctional catalysts for the cycloaddition of CO_2 to epoxides that do not involve the covalent coimmobilization of multiple active sites (Scheme 9).

A noncovalent approach to prepare readily-available multifunctional catalysts discussed in this work is the use of molecular compounds where cations bearing HBDs are combined with anions bearing nucleophilic functionalities (Scheme 9(a)). This strategy includes various interconnected classes of compounds such as ionic liquids, organic halide salts, deep eutectic solvents and ion pairs. Given the abundance of charged organic species such as amino acid salts, carboxylates, phenolates, imidazolates, and ascorbates, a huge variety of structures can be explored in search for the most efficient combination. These compounds generally showed very good recyclability at the laboratory scale (Table 1). However, their recycling requires quite tedious and unsustainable precipitation and extraction procedures with solvents. Recent advances using water-soluble compounds such as **[AsA-Et]I** in biphasic reaction settings,[176] show that suitable ionic species can be used as interfacial catalysts and recycled with the whole aqueous layer for subsequent reaction cycles.

Further research in the field of recyclable ionic molecular catalysts should focus on extending the biphasic cycloaddition to ionic compounds of other abundant water-soluble, highly polar species available in nature such as amino acids and sugars. As a drawback, aqueous biphasic catalysis is not suitable for the production of anhydrous cyclic carbonates without carrying out additional drying steps.

Inexpensive and readily available heterogeneous materials such as metal oxides, doped carbons or biopolymers such as lignin carry highly active HBDs for the activation of epoxides in the presence of nucleophiles (Scheme 9(b)). The most practical way to bypass the coimmobilization of nucleophile-bearing functional groups on these materials is to use them in the presence of homogeneous nucleophilic additives such as TBAI or KI in low concentrations as discussed in this work for **phenolated lignin NPs** or ZrO_2-doped with single cobalt atoms (**Co/ZrO_2**).[135] While this strategy is not as elegant as the construction of coimmobilized systems, the purity of the final cyclic carbonate compound is only marginally affected when the loading of homogeneous components is kept very low.



Scheme 9 Overview of concepts and related examples for the design of recyclable multifunctional catalysts for the cycloaddition of CO_2 to epoxides without covalent coimmobilization of the active sites: molecular ion pairs (a); combination of readily available HBDs and homogeneous nucleophiles (b); combination of strong nucleophiles with metal halides (c); encapsulation of active species in polymeric or crystalline structures (d); cooperative heterogeneous components bearing different functionalities (e). "1" and "2" indexes in (c) refer to a proposed nucleophile switch during the reaction mechanism.[109]

For instance, the purities of PC batches produced from PO using 0.5 mol% TBAI or KI can be calculated as, respectively, 98 wt% and >99 wt% (assuming quantitative PO conversion) which are comparable to those of the commercially available products. The purity of the carbonate product would further increase if the homogeneous component were pre-adsorbed on the solid support.[140] This approach may be suitable for the production of cyclic carbonates that are used as chemical intermediates such as in the production of diols or PHUs as these processes should not be significantly affected by the presence of small amounts of halide impurities. As a drawback, the use of homogeneous halide additives is often considered inconvenient due to potential reactor corrosion and toxicity concerns.[249,250] Therefore, the discovery of powerful, highly available HBDs able to perform the cycloaddition of CO_2 to epoxides with even lower halide loadings (0.1–0.25 mol%) under mild conditions would be highly attractive. Recent developments discussed in this work, such as doped carbon dots[140] or **phenolated lignin NPs**[229] show that using the HBDs in the form of small nanoparticles can boost catalytic activity to a level comparable to their homogeneous counterparts.

A way to use catalysts comprising homogeneous halide salts without polluting the final product is to combine them with strong heterogeneous nucleophiles that can release the halides during reaction and capture them at the end of the process (Scheme 9(c)). A recent advance in this direction was reported by Natongchai *et al.*[109] The authors investigated the cycloaddition of CO_2 to epoxides by highly nucleophilic aminopyridines[166,167] in the presence of metal halides of groups I and II. They found that this "dual nucleophile" (pyridine, halide) system could carry out the synthesis of cyclic carbonates under very mild conditions (60 °C, atmospheric CO_2) due to a cooperative mechanism in which both nucleophiles participated to different mechanistic stages. To produce a recyclable heterogeneous system, the aminopyridine was supported on MR (**NaI/aminopyridine@MR**, Scheme 9(c)), while the metal halide (NaI, MgI_2) was used as a homogeneous component. The interaction between the immobilized nucleophilic species and the alkali metals allowed the catalytic system to be easily recovered by precipitation and recycled. Given the inexpensive nature of alkali metal halides and the recent development of new readily-available highly nucleophilic *N*-nucleophlies,[251] further catalytic discoveries in this area are expected.

Other attractive ways to create multifunctional catalytic systems without a covalent coimmobilization of the different functional groups are emerging. One possible approach is the encapsulation of both or of one of the catalytic components in a readily available polymeric or inorganic matrix (Scheme 9(d)). To note, a pioneering example of this kind of catalyst was earlier reported by Sun *et al.* by incorporating a flexible polymer (polymerized phosphonium salt) in a metal-based covalent organic framework.[252] However, the encapsulation of active,

inexpensive molecular species has only recently appeared in the literature for CO_2-epoxide cycloaddition. In a recent advance, [DBUH]Br was formed from DBU and bromopropionic acid during the polymerization of DMAEMA (2-(dimethylamino)ethyl methacrylate) and divinylbenzene (**[HDBU]Br@P-DD**).[253] While the authors did not directly demonstrate the encapsulation of [DBUH]Br, the obtained material performed as a recyclable catalyst for the cycloaddition of CO_2 to numerous epoxides under atmospheric conditions (80–100 °C, 24 h). A very recent example of efficient encapsulation of TBAB was reported by Luo *et al.* by preparing ZIF-8 in the presence of different amounts of TBAB.[254] The inclusion of TBAB did not strongly affect the crystallinity of ZIF-8 in **TBAB@ZIF-8** catalysts and led to a slight increase in surface area while the pore volume and CO_2 adsorption capacity of the encapsulated materials expectedly decreased. As an effect, the most efficient material for the cycloaddition of CO_2 to PO was a **TBAB@ZIF-8** compound with moderate TBAB loading. **TBAB@ZIF-8** acted as a recyclable catalyst for the conversion of PO to PC for at least 8 cycles before a limited decline in performance due to the loss of TBAB. However, the reaction conditions were quite harsh (120 °C, 25 bar) and the performance strongly decreased by increasing the steric hinderance at the epoxide side chain. Mechanistically, the epoxide is activated by the Lewis acidic Zn centres in ZIF-8 for ring-opening by the halide anion of the encapsulated TBAB. Further developments in this area could include encapsulated polymeric catalysts, ion pairs and HBDs in various porous materials. The key aspect for this class of promising encapsulated catalysts is the accessibility of the active site to the reagents which depends on porosity, swelling ability, CO_2 capacity and flexibility of the outer shell. The outer shell should be designed in a way to contain abundant HBDs and amino or ammonium groups in the inner walls for cooperation with the encapsulated active species.

Finally, a promising option for the synthesis of recyclable noncovalent multifunctional systems for the cycloaddition of CO_2 to epoxides is the design of cooperative heterogeneous systems. Such heterogeneous components bearing different active sites should be recovered together at the end of the catalytic process and recycled (Scheme 9(e)). In a recent example, phenolated lignin (PL) particles were used as heterogeneous HBDs in the presence of ionic polymers bearing quaternary ammonium groups for the cycloaddition of CO_2 to epoxides under mild conditions (60 °C, 1 bar). Compared to the use of previously discussed **phenolated lignin NPs**/TBAI,[229] this approach allowed upcycling of lignin within a fully recyclable catalytic system.[255] With both catalytic components being insoluble in the reaction medium, the choice of a suitable ionic polymer partnering with lignin represented the most crucial factor in determining the catalytic performance. Indeed, while rigid ionic polymers with high glass transition temperatures such as quaternized polyvinylpyridines failed to provide any significant catalytic activity, PL and a highly flexible quaternized polyaminoester (**QPBAE**) formed an efficient catalyst (**PL/QPBAE**). Importantly, the direct anchoring of quaternary ammonium groups on the surface of PL failed to produce any efficient catalyst due to the unavoidable capping of the phenolic hydroxyl HBDs of PL. The **PL/QPBAE** system could be recovered by precipitation from the reaction mixture and was used for 5 consecutive catalytic runs with a minor drop of catalytic performance possibly arising from the dissolution of traces of QPBAE in the product. These findings pave the way to the potential design of a plethora of dual component cooperative systems including rigid HBD particles (polymers, metal oxide, carbon dots) and ionic polymers bearing quaternary ammonium halide or amino groups. Due to the general difficulty to establish cooperative interactions between heterogeneous reaction components, the challenge is to induce proximity between the HBD and nucleophile during the catalytic process. This potential limitation favours the choice of flexible polymers over rigid polymers in order to optimise the cooperative activation and ring-opening of the substrate. Moreover, the existence of intermolecular interactions between the polymer chains will also influence the degree of contact between the catalytic components.

Conclusions

Previous studies on the catalytic cycloaddition of CO_2 to epoxides mainly focused on achieving systems able to achieve high catalytic turnovers,[18,256] gaining mechanistic insights[105,257,258] and in carrying out the target reactions under very mild or ambient conditions.[39,259–263] Very often, catalysts for the cycloaddition of CO_2 to epoxides are judged only on the basis of parameters such as TON (turnover number) and TOF (turnover frequency).[18,256] However, such parameters have very little use, especially in batch processes, when they are not benchmarked under identical reaction conditions[264,265] due to the strong dependency of the cycloaddition reaction kinetics on several factors such as temperature, pressure and substrate reactivity. More importantly, they do not provide information on the catalyst cost, availability, sustainability and recyclability. From a practical standpoint, with the cycloaddition of CO_2 to various epoxides reaching maturity for the implementation at a larger scale,[266] there is an increasing emphasis towards readily-available, inexpensive and easy-to-prepare catalysts.[267–270] Indeed, catalysts applied for other well-established crucial industrial transformations, for instance, oil cracking and olefin metathesis, ethylene polymerization or propane dehydrogenation, are based on relatively inexpensive zeolites,[271] or supported metal oxides,[272–274] respectively, despite the existence of far more active but more elaborate materials for the same processes in the academic literature.[275,276] The catalysts applied in the commercial Asahi–Kasei process for the synthesis of ethylene carbonate from CO_2 is a simple anion exchange material containing quaternary methylammonium groups.[44] However, the latter catalyst typically requires very harsh conditions (100 °C, with liquid CO_2 as the feed). Therefore, it is important to identify new, similarly affordable recyclable catalytic systems but with the ability to operate under mild reaction conditions. In this context, in this work we have identified several classes of catalysts such as metal oxides, doped carbons, ZIF-type frameworks, recyclable molecular organocatalysts and polymer-

based organocatalysts that serve as inexpensive and readily available compounds for the cycloaddition of CO_2 to epoxides. The latter two classes of catalysts have been discussed in detail and contain several examples of materials able to operate in a mild range of temperature and pressure (60–80 °C, 1–10 bar). Such reaction conditions using moderate temperature and low pressures are regarded as suitable for the already existing plants working in the field of epoxide conversion.[277] However, the results in Tables 1–3 also show that the catalysts operating in the abovementioned temperature and pressure ranges still require long reaction times (24–48 h) for quantitative epoxide conversion. Therefore, further research should focus on the preparation of more efficient catalytic systems for the cycloaddition of CO_2 to epoxide with enhanced kinetics under operable reaction conditions. In this context, we have proposed various guidelines for the future design of more active but unsophisticated catalysts for the synthesis of cyclic carbonates from CO_2 to epoxides through emerging strategies aimed at avoiding complex coimmobilization procedures to create multifunctional systems. These guidelines show that there is a cornucopia of available options for the future design of more efficient and inexpensive systems for the cycloaddition of CO_2 to epoxides. It is desirable that the development of enhanced catalysts based on abundantly available building blocks will propel the expansion of cyclic carbonate production as sustainable CO_2 derivatives with multiple applications.

Author contributions

Wuttichai Natongchai: writing – original draft, visualization. Daniel Crespy: writing – original draft, conceptualization. Valerio D' Elia: writing – original draft, supervision, conceptualization, data curation.

Data availability

The data collected for generating Scheme 2 is given in the ESI.†

Conflicts of interest

There are no conflicts of interest to declare.

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