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Cyclic carbonates synthesised from CO₂: Applications, challenges and recent research trends

Paolo P. Pescarmona

Cyclic carbonates are a class of versatile compounds that can be prepared using the greenhouse gas carbon dioxide as a building block and that can find applications as green solvents and as a sustainable alternative to toxic reactants currently used in the chemical industry. The current trends in research related to cyclic carbonates are reviewed in this contribution.

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Keywords

Cyclic carbonates, CO₂ conversion, Catalysis, Green solvents.

Introduction

Cyclic carbonates are a class of compounds that is receiving growing interest both at academic and industrial level because their preparation and applications present several attractive features in the context of green chemistry and sustainability (Fig. 1). Yet, there are important challenges that still need to be tackled in terms of catalytic synthesis, of renewability, and of scope and efficacy of the applications of cyclic carbonates. This leads to a teeming research area, which is reviewed here with special focus on current research trends.

Synthesis of cyclic carbonates

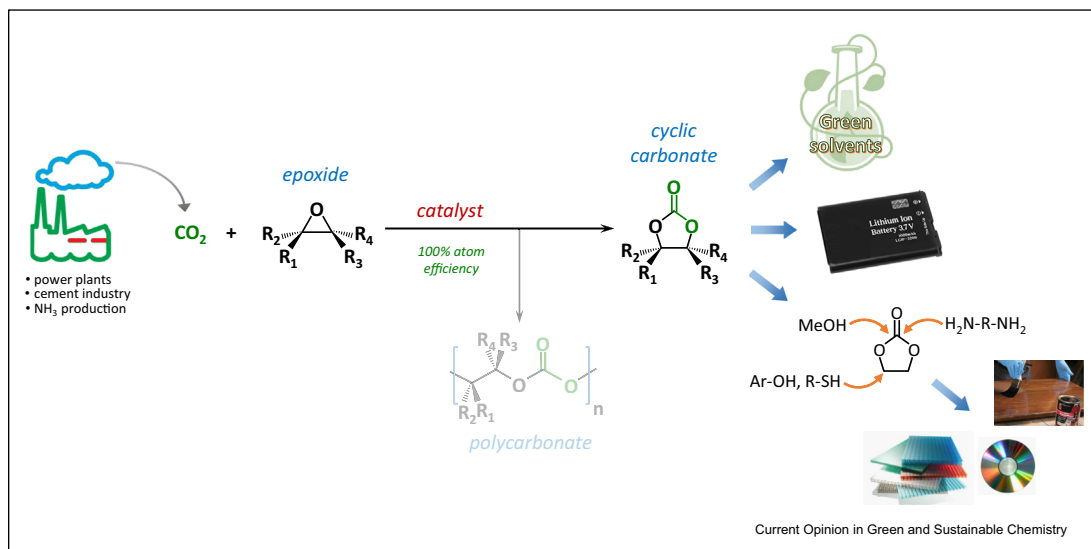
The most common and effective route to prepare cyclic carbonates, also at industrial level, is the cycloaddition of CO₂ to epoxides. This reaction has several assets in the context of green and sustainable chemistry, as it uses a renewable, nontoxic and widely available reactant as carbon dioxide; it displays 100% atom efficiency, as all reactants are incorporated in the product (Fig. 1); and can be carried out effectively without requiring a

solvent. The reaction is thermodynamically favourable as it exploits the high free energy of epoxides to counterbalance the high thermodynamic stability of carbon dioxide.

On the other hand, it should be noted that this route alone cannot have a major impact on decreasing the atmospheric CO₂ concentration caused by anthropogenic emissions, as the current yearly production of cyclic carbonates (estimated to be in the order of 100 kton/y) [1] is significantly lower than the worldwide carbon dioxide emissions (about 37 000 Mton/y, of which less than the half are emitted from large point sources, from which concentrated CO₂ could be captured and utilised directly, thus preventing it from entering the atmosphere) [2]. Tackling the global CO₂ challenge will most likely require a diversified approach including carbon capture and utilisation techniques, mitigation of CO₂ emissions by improving energy efficiency and minimising heat losses, switching to nonfossil fuels (*e.g.* hydrogen) and to renewable power (*e.g.* wind, solar); and climate engineering (*e.g.* reforestation) [1].

Another important aspect that should be considered when evaluating the green character of the synthesis of cyclic carbonates is the use of epoxides as reactants in the cycloaddition with CO₂. The industrial synthesis of cyclic carbonates is concentrated on propylene carbonate and ethylene carbonate (Table 1), which are prepared from propylene oxide and ethylene oxide, respectively. These two epoxides are in turn produced from the petroleum-based propylene and ethylene. Besides the nonrenewable origin of the starting materials, another concern in terms of sustainability is the high toxicity and volatility of propylene oxide and, particularly, of ethylene oxide (which is a gas at room temperature). Several approaches are currently investigated to tackle these issues, with the target of achieving the safe production of fully renewable cyclic carbonates. For what concerns the nonrenewable origin of the starting compounds, alternative routes for the industrial production of ethylene from bio-based ethanol are being established worldwide, whereas different routes have been proposed for the production of propylene from bio-based resources, but these are not yet at the stage of industrial implementation [1]. In addition, the chemical industry will most likely adopt these more sustainable routes only if they become cost-competitive with the current petroleum-based manufacture, unless driven by specific governmental regulations or incentives. Several

Figure 1

Synthesis of cyclic carbonates from CO₂ and epoxides and selected applications.

other epoxides are commonly investigated for the synthesis of cyclic carbonates, although the main motivation is currently the academic interest for achieving the conversion of a wide scope of epoxides including more challenging ones as styrene oxide or cyclohexene oxide. Among these epoxides, growing attention has been devoted to those derived from renewable, bio-based compounds, such as (R)-(+)-limonene, which is a naturally occurring terpene that can be extracted from abundant citrus peels waste from juice production [3]; and unsaturated fatty acids and esters containing one or more double bonds, which can be prepared from triglycerides present in vegetable oils. The double bonds in these compounds can be converted catalytically into epoxide groups, preferably by using a sustainable oxidant as hydrogen peroxide, which generates water as the only side product [4]. The successive cycloaddition of CO₂ to the epoxide groups in these compounds is rather challenging due to steric hindrance [3,5–7]. It is worth noting that bicyclic carbonates can be obtained from (R)-(+)-limonene and both bicyclic and tricyclic carbonates can be prepared from unsaturated fatty acids [6–8]. The obtained fully renewable compounds with multiple cyclic carbonate groups can find application as precursors in the synthesis of nonisocyanate polyhydroxyurethanes (*vide infra*) [6]. Another widely studied epoxide, epichlorohydrin, can be prepared from a renewable resource as glycerol, which is available on a large scale as the main side product of the manufacture of biodiesel. However, the sustainability of the synthesis of epichlorohydrin is decreased by the use of HCl as chloride source. It should be noted that epichlorohydrin is often selected as a substrate in academic studies

mainly because the electron withdrawing nature of the chlorine renders the conversion to the cyclic carbonate easier than with other epoxides [9]. Glycerol carbonate is a more relevant cyclic carbonate that can be obtained from renewable glycerol [10,48]. This versatile compound can be prepared through a transcarbonation reaction between dimethyl carbonate or propylene carbonate and bio-based glycerol. This synthesis route is more viable than the direct reaction between glycerol and CO₂, which is thermodynamically unfavourable and, therefore, results in low yields unless the formed water is removed using sacrificial dehydrating agents. An attractive, alternative synthesis approach to produce glycerol carbonate consists in the one-pot reaction of propylene oxide, CO₂, and glycerol [11].

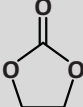
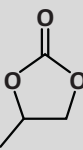
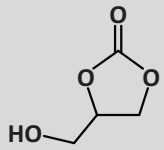
Strategies have been also investigated to overcome the toxicity of epoxides, particularly in the case of the most volatile ones, that is, ethylene oxide and propylene oxide. This can be achieved through the one-pot, direct synthesis of cyclic carbonates from alkenes, involving two steps: the epoxidation of the alkene and the subsequent cycloaddition of CO₂ to the formed epoxide [1,12]. This approach would allow avoiding the purification and handling of the toxic epoxides, thus increasing significantly the sustainability of the process while at the same time reducing its costs. However, different challenges still need to be tackled to make this approach viable, particularly in the development of catalytic systems that are able to promote both steps of the one-pot process at mild conditions, using a green oxidant such as H₂O₂ or O₂ (rather than organic peroxides) and while minimising the formation of side

Table 1

Selected physicochemical properties of the main cyclic carbonates employed as green solvents [10,13].

Besides the specific physicochemical properties (*e.g.* polarity, protic/aprotic nature, viscosity) that are desirable for being a good solvent in a chosen application, green solvents should ideally be:

- > nontoxic and nonhazardous (*e.g.* nonflammable and noncorrosive)
- > unreactive under operating conditions and yet biodegradable
- > easy to separate and to recycle
- > sustainably produced (from renewable resources, through a manufacturing process with low energy demand, involving few steps, and in which no harmful compounds are used or produced)

| | Ethylene carbonate | Propylene carbonate | Glycerol carbonate |
|----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| |  |  |  |
| Formula | C ₃ H ₄ O ₃ | C ₄ H ₆ O ₃ | C ₄ H ₆ O ₄ |
| Molecular mass [g/mol] | 88.063 | 102.090 | 118.088 |
| Melting point, T _m [°C] | 36 | -49 | -69 |
| Boiling point, T _b [°C] | 248 | 242 | 100-115 (at 0.1 mmHg) |
| Density, d [g/mL] | 1.3214 (39 °C) | 1.2047 (20 °C) | 1.4 |
| Viscosity, η [mPa·s] | 1.93 (40 °C) | 2.53 (25 °C) | 85.4 (25 °C) |
| Dielectric constant, ε | 89.78 (40 °C) | 66.14 (20 °C) | 111.5 |
| Dipole moment, μ [D] | 4.9 | 4.9 | n.a. |
| Refractive index, n _D | 1.4148 (50 °C) | 1.4189 (20 °C) | n.a. |
| Vapour pressure [kPa] | 0.003 (25 °C) | 0.131 (50 °C) | n.a. |
| Flash point [°C] | 143 | 135 | 190 |
| Δ _f H ⁰ [kJ/mol] | -581.6 (25 °C, solid) | -613.2 (25 °C, liquid) | n.a. |
| C _p [J/(mol·K)] | 133.9 (50 °C, liquid) | 218.6 (25 °C, liquid) | n.a. |
| Solubility (at 20 °C) | Miscible in H ₂ O, ethanol, ethyl acetate, acetic acid, ethyl ether, chloroform, benzene | Very soluble in H ₂ O (240 g/L), ethanol, acetone, benzene | Very soluble in H ₂ O (>1000 g/L) |
| Hazards | Harmful if swallowed, causes serious eye irritation, may cause damage to organs (kidney) through prolonged or repeated exposure if swallowed | Causes serious eye irritation | No hazard currently mentioned in the Safety Data Sheet (SDS) |

products to achieve high selectivity towards the cyclic carbonate product [1].

Catalysts for the cycloaddition of CO₂ to epoxides

Different epoxides have different reactivity towards the cycloaddition of CO₂, but in all cases a catalyst is required for the reaction to proceed with acceptable rates. The nature of the catalyst, in combination with the nature of the epoxide and the reaction conditions, plays a crucial role also in determining the selectivity between the two possible products of the reaction of CO₂ with epoxides, that is, cyclic carbonates and polycarbonates (Fig. 1). Based on these premises, it is not surprising that the design and development of active and selective catalytic systems is a central topic of research in the domain of the conversion of CO₂ into cyclic carbonates. The most common and active catalytic systems for this reaction comprise sites with Lewis acid character that are able to coordinate the O atom of

the epoxide, thus activating the molecule towards the nucleophilic attack by a Lewis base, which leads to ring opening of the epoxide. Next, the insertion of CO₂ takes place leading to a carbonate intermediate, which undergoes intramolecular ring closure to yield the cyclic carbonate product (Fig. 2). The sites with Lewis acid character can be provided by one or more metal centres (*e.g.* in a metal complex) or by metal-free hydrogen bond donor species (*e.g.* organic molecules with -OH groups) [14], whereas the Lewis base species are typically provided by halides (Cl⁻, Br⁻, I⁻). The two types of active species can be present within a bifunctional single-component catalyst or in a binary system consisting of two separate components. Complete selectivity towards the cyclic carbonate product is generally achieved with metal-free catalysts, whereas for metal-containing catalysts the selectivity between cyclic and polymeric carbonate typically depends on the nature of the nucleophilic species and of the metal, on the nucleophile-to-metal ratio and on the reaction

conditions, all of which can be tuned to maximise the formation of the desired product [1]. Other, less common catalytic systems have been proposed to operate through the initial activation of CO₂ via a nucleophilic attack by a non-ionic base (typically N- or P-containing organic bases) [15,16]. The formed CO₂ adduct can carry out a nucleophilic attack on the epoxide, with formation of a carbonate intermediate from which the cyclic carbonate is obtained by ring closure.

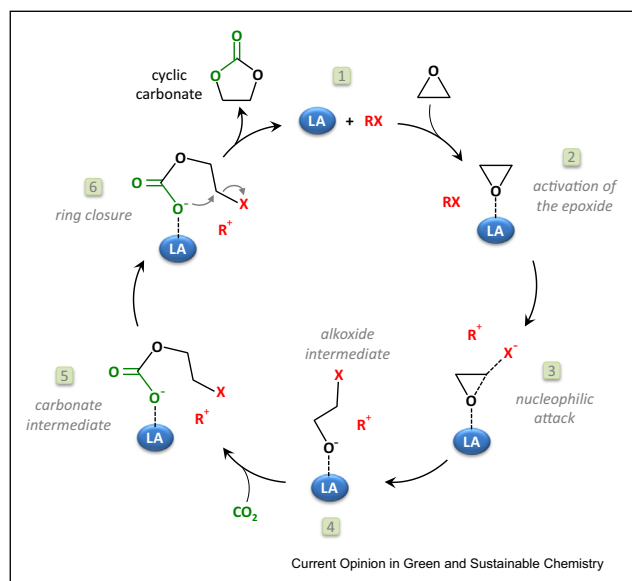
Several homogeneous and heterogeneous catalytic systems have been developed for the cycloaddition of CO₂ to epoxides, with the former having in general higher activity and the latter having the important asset of easier separation and reusability.

- Among homogeneous catalysts, the class that has been most widely studied consists of metal complexes, either as bifunctional or binary catalytic systems. Recent research trends are focussed on developing robust, air- and moisture-stable complexes based on earth-abundant, inexpensive and low-toxicity metals (*e.g.* Al and Fe) [17–21]. The most active among these catalysts are able to operate with very low catalyst loading (≤ 0.5 mol%, Table 2, entries 1–2), at very mild conditions, including room temperature reactions and $p_{\text{CO}_2} \leq 10$ bar, while achieving high cyclic carbonate yields with a broad scope of epoxide substrates [22]. Although metal complexes can reach excellent catalytic activity, their large-scale applicability is typically hampered by complicated and

expensive synthesis procedures. This limitation stimulated the development of metal-free organocatalysts, which generally consist of an organic molecule that acts as hydrogen-bond donor to activate the epoxide towards the nucleophilic attack by a halide provided by an organic salt, such as a tetrabutylammonium halide (Bu₄NX, with X = Cl, Br, I) or bis(triphenylphosphine) iminium halide (PPNX) [1,5,16]. Although still less active than state-of-the-art metal complexes, the latest generation of organocatalysts is able to achieve high cyclic carbonate yields with a broad scope of epoxides under mild reaction conditions. This can be attained through the design and synthesis of tailored multifunctional organocatalysts in which all active sites are present in proximity to each other in the same compound [23]. The synthesis of chiral bifunctional organocatalysts has also been reported, allowing the kinetic resolution of epoxides to produce chiral cyclic carbonates [24], although with only moderate enantiomeric excess compared with what can be achieved with state-of-the-art chiral metal complexes [25]. A different trend in current research in metal-free catalysts for the synthesis of cyclic carbonates consists in identifying commercially available, nontoxic and renewable hydrogen-bond donors to be used in combination with inexpensive organic halides (*e.g.* Bu₄NX). An example in this context is the use of ascorbic acid as hydrogen bond donor, which is able to promote the cycloaddition reaction catalysed by Bu₄NI at room temperature and at 1–5 bar CO₂ (Table 2, entry 3) [26]. Recently, it was demonstrated that water, which can be considered as the most sustainable and cheapest hydrogen-bond donor, can effectively promote the activity of organic halide catalysts (Bu₄NX, PPNI), allowing to realise the cycloaddition of CO₂ to a variety of epoxides under very mild conditions (25–45 °C, 10 bar CO₂, Table 2, entry 4) [27]. Another notable development is the discovery of the ability of salophens, which are commonly used as ligands in metal complexes, to act as metal- and halide-free homogeneous catalysts for the cycloaddition of CO₂ to epoxides, although this requires relatively high reaction temperature (120 °C) [28]. In a different context, an important advance is the development of imidazolium hydrogen carbonate as metal-free bifunctional catalyst that is able to catalyse the one-pot synthesis of cyclic carbonates from CO₂ and styrene (or other aromatic compounds) with *tert*-butyl hydroperoxide (TBHP) as the oxidant [12].

- Among heterogeneous catalysts, a major trend in the current research is the design and development of tailored bifunctional catalysts, as in the case of metal organic frameworks (MOFs) [29,30] or porous organic polymers (POPs) [9]. For these classes of materials, the challenge has been to include both Lewis acid sites to activate the epoxide and Lewis bases acting as nucleophilic species in proximity to each other within

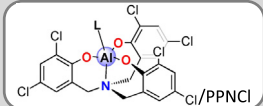
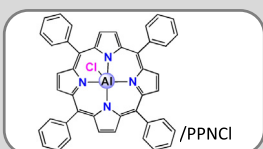
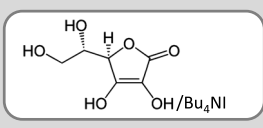
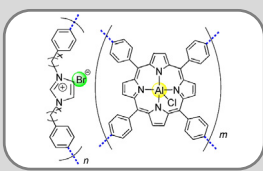
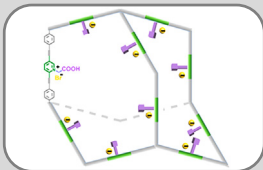
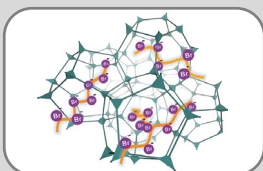
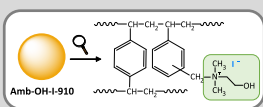
Figure 2



Most commonly proposed mechanism for the synthesis of cyclic carbonates through the catalytic cycloaddition of CO₂ to epoxides [LA = Lewis acid site; X = Cl, Br or I. LA and RX can be separate species (binary catalytic system) or be part of the same compound (bifunctional single-component catalyst)].

Table 2

Selected homogeneous (entries 1–4) and heterogeneous (entries 5–8) catalytic systems for the cycloaddition of CO₂ to epoxides. All the data in this table refer to the reaction of propylene oxide (PO) with CO₂, yielding propylene carbonate (PC).

| Entry | Catalyst | Cat. loading [mol%] ^a | T [°C] | p _{CO₂} [bar] | Time [h] | Conv _{PO} or Yield _{PC} [%] | Sel _{PC} [%] | TON _{LA} ^b | TON _{LB} ^b | Productivity [g _{PC} / (g _{cat} ·h)] | Ref |
|-------|-------------------------------------------------------------------------------------|----------------------------------|--------|-----------------------------------|----------|-----------------------------------------------|-----------------------|--------------------------------|--------------------------------|--------------------------------------------------------|-----|
| 1 |  | LA: 0.01 LB: 0.05 | 90 | 10 | 2 | 29 (Y) | >99 | 2900 | 580 | – | 22 |
| 2 |  | LA: 0.01 LB: 0.05 | 90 | 10 | 2 | 49 (Y) | >99 | 4900 | 980 | – | 22 |
| 3 |  | LA: 2 LB: 4 | RT | 5 | 23 | 82 (Y) | >99 | 41 | 21 | – | 26 |
| 4 | H ₂ O/Bu ₄ Ni | LA: 0.10 mL LB: 3 | 25 | 10 | 48 | 85 (Y) | ≥99 | 3 | 28 | – | 27 |
| 5 |  | LA: 0.1 LB: 0.175 | 40 | 10 | 3 | >99 (C) | ≥99 | 990 | 566 | 21.9 | 32 |
| 6 |  | LA: 0.3 LB: 0.3 | 60 | 10 | 8 | 97 (Y) | >99 | 334 | 334 | 7.4 | 33 |
| 7 |  | LA: 1.1 LB: 0.2 | 25 | 1.01 | 48 | 99 (Y) | >99 | 90 | 545 | 0.73 | 36 |
| 8 |  | LA: 1 LB: 1 | 80 | 10 | 18 | 95 (Y) | ≥99 | 81 | 81 | 1.0 | 37 |

^a Relative to the epoxide.

^b Turnover number expressed as mol_{converted epoxide}/mol_{active site} (when the conversion was reported) or mol_{cyclic carbonate}/mol_{active site} (when the yield was reported), where the active sites are either the Lewis acid sites (TON_{LA}) or the Lewis bases acting as nucleophiles (TON_{LB}).

RT = room temperature.

the material, without limiting the diffusion of reactants and products through the porous structure and while granting high stability and thus reusability under operating conditions. MOFs are crystalline materials with well-defined porous structure and often with very high specific surface area, whereas POPs are typically amorphous materials with disordered porosity. Although the lack of ordered pores with defined size might be considered as a drawback, POPs benefit from a larger degree of synthetic freedom, which allows tuning the type and number of active sites, the pore size and volume and the specific surface area. This is exemplified by the inclusion of metal complexes (*e.g.* Mg- or Al-porphyrins) [31,32] in the structure of the POP materials, which was reported to lead to reusable heterogeneous catalysts with remarkable activity in the cycloaddition of CO₂ to epoxides under mild reaction conditions and with low catalyst loading (Table 2, entry 5) [32]. A metal centre is not strictly necessary to achieve high catalytic activity: metal-free POPs containing halides as nucleophiles and hydrogen bond donors to activate the epoxide have been prepared through careful choice and tuning of the building blocks [33]. Although the catalytic performance of these materials is still generally inferior compared to metal-containing POPs, relatively high turnover numbers and good conversions under mild conditions can be achieved (Table 2, entry 6). Promising catalytic activity was also attained recently with hybrid organic–inorganic catalysts consisting of silsesquioxanes functionalised with imidazolium groups and covalently grafted on a silica support [34]. Another original approach in the design of heterogeneous catalysts for the cycloaddition reaction consists in preparing a composite material in which a polymeric ionic liquid is incorporated into the pores of a MOF (MIL-101) [35,36]. The halides provided by the ionic liquid moieties cooperate with the Lewis acid sites provided by the metal centres in the MOF, leading to promising catalytic activity (Table 2, entry 7). Although these developments in the materials design led to significant advances in the activity of heterogeneous catalysts, they typically require complex, multiple-step synthesis methods, making these systems too expensive for upscaling and industrial application. As a consequence, there is also interest for developing straightforward catalytic systems that are preferably metal-free and in any case consist of abundant elements, have an accessible and upscalable synthesis method or are commercially available and yet present catalytic sites that lead to high activity (*e.g.* I[−] as nucleophilic species and −OH groups as hydrogen-bond donors, Table 2, entry 8) and can be easily and efficiently recycled [37].

Applications of cyclic carbonates

Among cyclic carbonates, propylene carbonate is the one most commonly used as green solvent [38–41]. Propylene carbonate displays suitable properties as polar aprotic solvent (Table 1), having high dielectric constant and dipolar moment, a large temperature range in which it is liquid at atmospheric pressure (*i.e.* between −49 and 242 °C), relatively low viscosity, and being colourless and odourless [10,40–42]. From the health and safety point of view, propylene carbonate is an excellent solvent, as it displays low vapour pressure, low toxicity, low flammability (high flash point) and is noncorrosive [10,40]. In addition, it is biodegradable in air and in water, where it slowly hydrolyses to low toxicity products as propylene glycol and carbon dioxide [10]. For these properties, propylene carbonate was graded with the highest score in all categories related to environment, human health and safety in the GSK Solvent Sustainability Guide [39], was listed as a safe chemical by both EU and USA Agencies [43,44] and is thus generally regarded as a highly green solvent. However, the definition and quantification of suitable metrics for determining whether a solvent can be considered green is a complex and challenging task, which requires making assumptions that contain a certain degree of arbitrariness [39,45]. This can explain the apparent discrepancies that are found in the evaluation of propylene carbonate, which is identified as problematic by the CHEM21 Selection Guide [45]. This ranking is most likely caused by the high boiling point of propylene carbonate, which implies that removal and recycling of the solvent would require energy-intensive distillation under reduced pressure. However, this limitation is not of general validity and is only relevant for specific applications in which removal of the solvent is required. Even in such case, there exist alternative separation approaches, such as crystallisation, extraction (followed by the less energy-intensive distillation of the extracting solvent) or advanced membrane technology (*e.g.* nanofiltration) [38]. Based on these considerations, it is reasonable to consider propylene carbonate as a green solvent, while being aware of the challenges related to its separation as a consequence of the high boiling point (which is a common feature of polar aprotic solvents) [38,41], and of the downsides related to the fossil origin and toxicity of the propylene oxide used in its preparation (*vide supra*).

The suitable properties of propylene carbonate as polar aprotic solvent and its green features make it an attractive, sustainable alternative to conventional, more harmful polar aprotic solvents such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide, dimethyl sulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP), hexamethylphosphoramide (HMPA) and acetonitrile [39,41].

Ethylene carbonate has similar properties to propylene carbonate (Table 1), but is a solid at room temperature ($T_m = 36\text{ }^\circ\text{C}$), which renders it less suitable for application as a solvent. To overcome this limitation, ethylene carbonate is generally used as solvent in combination with other compounds (e.g. dimethyl carbonate). A similar restraint is encountered for a number of other cyclic carbonates, which have melting points above room temperature (e.g. styrene carbonate and 1,2-limonene carbonate).

Ethylene carbonate and propylene carbonate are produced industrially by several companies worldwide and are the two cyclic carbonates with the largest scale and widest range of applications [46,47]. High-purity ethylene carbonate and, to a lesser extent, propylene carbonate find an important application as solvent components in the formulation of electrolytes for lithium-based batteries that can be used in electronics and electric vehicles. The cyclic carbonate provides the high dielectric constant component that is necessary to dissolve the lithium salts, thereby generating a conductive electrolyte [1]. Other relevant applications of propylene carbonate and ethylene carbonate as solvents include their use for cleaning, paint stripping and degreasing [1] and their utilisation in end-use products as paints and coatings, lubricants, dyes, cosmetic and personal care products [46,47].

Another cyclic carbonate that is receiving increasing interest is glycerol carbonate, owing to its renewable character (*vide supra*), low toxicity, low flammability, wide range of temperature at which it is a liquid, water solubility and biodegradability (Table 1) [10,48]. Although less established, the types of potential applications of glycerol carbonate are similar to those of ethylene carbonate and propylene carbonate [10,48]. However, the rather high viscosity of glycerol carbonate (Table 1) might be a limitation for its application as solvent.

Besides these industrial applications, cyclic carbonates, and particularly propylene carbonate, are increasingly investigated as green solvents for a wide range of (catalytic) chemical syntheses, alone or in mixtures with other solvents, often providing a suitable and more sustainable alternative to conventional solvents (e.g. DMF or dichloromethane) [10,40–42,49–51].

Although cyclic carbonates have a broad range of applicability as solvents, they can undergo base-catalysed ring-opening reactions with alcohols and amines. While this represents a limitation for their scope of applicability as solvents, it offers opportunities as reactants for chemical syntheses, providing a sustainable alternative to toxic compounds as phosgene, isocyanates and epoxides [1]. The reaction of cyclic carbonates with aliphatic alcohols leads to a transcarbonation, as for example in the reaction of ethylene carbonate with methanol to produce dimethyl carbonate. This reaction is employed in the Asahi Kasei industrial process, which provides a

greener alternative for the synthesis of bisphenol-A-based polycarbonates (an important class of engineering plastics) compared with the conventional route that uses the extremely toxic phosgene as reactant [1]. The reaction of cyclic carbonates with aliphatic primary and secondary amines generates urethane groups. When carried out with a diamine, this reaction offers a greener alternative to the conventional synthesis of polyurethanes (an important class of polymers with application as coatings and foams), which is based on the reaction of toxic isocyanates with polyols [1,52]. Recent research in the field of nonisocyanate poly(hydroxy)urethanes is focussed on the development of soft and rigid foams [53,54]. The family of reactions between amines and cyclic carbonates is also exploited for modifying and tuning the properties of epoxy resins [1]. Cyclic carbonates can also be used in the base-catalysed alkylation of aromatic compounds with protic groups and of aliphatic thiols [1,10,54]. Notably, with these compounds the nucleophilic attack on the cyclic carbonate occurs on the methylene carbons, whereas it takes place on the carbon atom of the carbonyl group in the reaction with aliphatic alcohols and amines (Fig. 1). The products of these alkylation reactions find diverse applications in polymer chemistry [1].

Conclusions

Cyclic carbonates prepared from CO₂ find growing applications as green solvents in several industrial applications and as sustainable alternatives to toxic compounds used in the synthesis of polymers (e.g. polycarbonates, polyurethanes). Current research trends in the field of cyclic carbonates focus on expanding the scope of their applicability and on developing novel catalytic systems to maximise the efficiency and the greenness of their production.

A few notes on good practice in the testing of catalysts for the cycloaddition of CO₂ to epoxides

- To provide a balanced and complete evaluation of the activity of a catalyst, it is advised to express TON and/or TOF based on both the Lewis acid sites (e.g. the metal centres or the hydrogen-bond donors) and the Lewis base sites (e.g. the halides), as in Table 2
- For heterogeneous catalysts, it is recommended to calculate and report the productivity as an additional metric to evaluate the catalytic activity, as done in Table 2.
- It is advised to test new catalysts with a broad scope of epoxides (e.g. the industrially relevant propylene oxide, and more challenging substrates as styrene oxide, cyclohexene oxide and 1,2-limonene oxide).
- When performing catalytic tests, it is advised to use a nonvolatile internal standard (e.g. mesitylene) during the reaction. This would allow checking the mass balance and determining if any

evaporation of the epoxide occurred. This is particularly important for tests with propylene oxide as substrate, as this epoxide is highly volatile and can be lost during the depressurisation of the reactor. This would lead to an overestimation of the epoxide conversion and cyclic carbonate yield, and thus provide an incorrect evaluation of the catalytic activity. This issue can be avoided by using an internal standard during the reaction.

- Typically, the cycloaddition of CO₂ to epoxides is carried out under solvent-free conditions. In this context, catalytic tests with very small amounts of epoxide (i.e. < 10 mmol, which in the case of propylene oxide would mean < 700 μL) are not recommended, as it is unlikely that stirring would be efficient under these conditions.
- Care should be taken when performing catalytic tests at low CO₂ pressure (e.g. p_{CO₂} = 1 bar) as under these conditions chances are that the reaction becomes limited by the available amount of CO₂ (to give a measure of this: assuming an ideal gas behaviour, a 50 mL reactor filled with 1 bar CO₂ contains 2 mmol of carbon dioxide). In this context, it is crucial to report the volume of the reactor used in the catalytic tests, particularly for those at low CO₂ pressure.
- With the purpose of developing catalysts that could operate with CO₂ captured from industrial sources (Fig. 1), it would be useful to test the performance of the most promising catalysts not only with pure CO₂ but also with CO₂ containing the contaminants commonly found in flue gases (e.g. H₂S, CO, SO_x, NO_x, H₂O). [1, 15]

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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