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Review

Hybrid Catalysts for CO_2 Conversion into Cyclic Carbonates

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Abstract: The conversion of carbon dioxide into valuable chemicals such as cyclic carbonates is an appealing topic for the scientific community due to the possibility of valorizing waste into an inexpensive, available, nontoxic, and renewable carbon feedstock. In this regard, last-generation heterogeneous catalysts are of great interest owing to their high catalytic activity, robustness, and easy recovery and recycling. In the present review, recent advances on CO_2 cycloaddition to epoxide mediated by hybrid catalysts through organometallic or organo-catalytic species supported onto silica-, nanocarbon-, and metal–organic framework (MOF)-based heterogeneous materials, are highlighted and discussed.

Keywords: carbon dioxide; cyclic carbonate; heterogeneous catalysis; ionic liquids; carbon nanotubes; fullerene; graphene; MOF

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1. Introduction

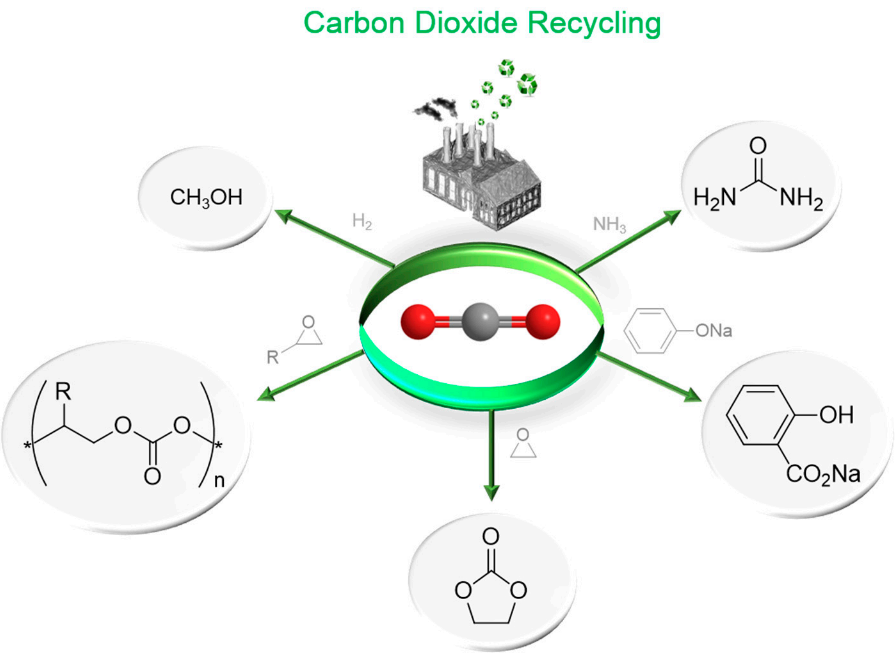
1.1. Carbon Dioxide: From Waste to Feedstock

The design of new technologies able to mitigate the environmental impact of CO_2 is an issue of growing interest from both academic and industrial standpoints. CO_2 is a common product of biological processes such as aerobic respiration or the alcoholic fermentation of sugars. However, carbon dioxide emission is also associated with the combustion of fossil fuels arising from anthropogenic activities for the production of energy, transportation, and industrial processes.

Since the Industrial Revolution, the concentration of carbon dioxide in the atmosphere steadily increased, becoming an environmental issue to be addressed. In this scenario, carbon dioxide capture, utilization, and storage emerged as tangible processes moving toward sustainable development [1]. Focusing on its utilization, carbon dioxide found application in separation processes, dry-cleaning, refrigerators, fire extinguishers, in the food or agrochemical industry, or as a solvent for several reactions under supercritical conditions [2].

The conversion of carbon dioxide into valuable chemicals is attracting the attention of the scientific community due to the possibility of valorizing industrial waste into an inexpensive, available, nontoxic, and renewable carbon feedstock [3–5]. Moreover, carbon dioxide was tested as a one-carbon (C1) building block in organic synthesis for the preparation of several chemicals including methanol, urea, lactones, various heterocycles, biodegradable polymers, and carboxylated structures, among others [6,7].

Scheme 1 summarizes some industrial organic syntheses using carbon dioxide as a C1 synthon.



Scheme 1. Industrialized organic syntheses using CO_2 as a one-carbon (C1) feedstock.

All these processes make CO_2 a key pillar for the sustainable and resource-efficient production of chemicals [8]. Independently of the specific application, the drawback of the conversion of carbon dioxide is mainly represented by its elevated thermodynamic stability. The carbon atom in CO_2 is present in its most oxidized state, resulting in a low molecular reactivity. To overcome this problem, highly energetic starting materials such as hydrogen, epoxides, and amine, among others, are usually employed together with a catalyst able to properly decrease the activation energy of the selected reaction (Figure 1). For doing so, in the last few decades, several catalytic systems able to work under both homogeneous and heterogeneous conditions were developed in the perspective of greener chemical processes.

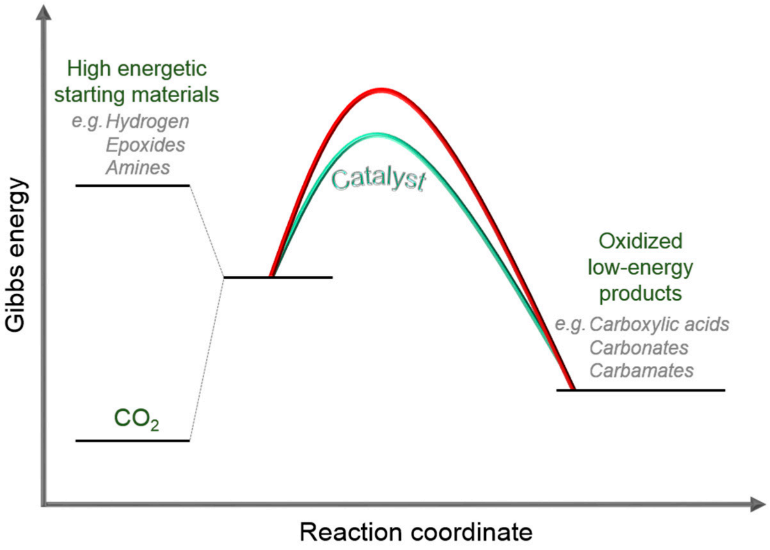


Figure 1. Organic synthesis using CO_2 as a building block.

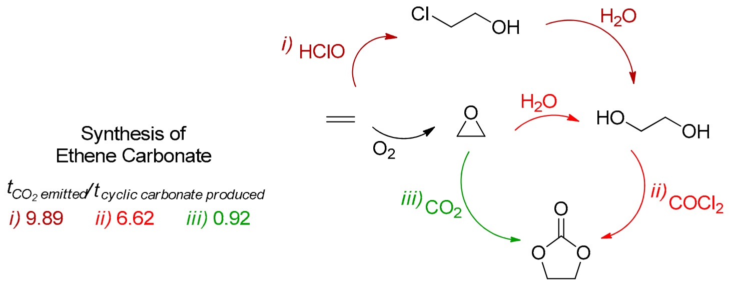
The activation of carbon dioxide is pivotal for its effective transformation. The basic features of CO_2 reactivity must be considered to reach a good conversion of this molecule into useful chemicals. Carbon dioxide is a linear molecule, in which the carbon–oxygen bonds are polar, with a net partial charge on carbon and oxygen atoms. Therefore, the carbon atom, bearing a partial positive charge, can behave as an electrophile. On the other hand, the oxygen atoms, with a partial negative charge, can act as nucleophiles. Owing to the linear geometry of the molecule, with the two dipole moments opposite each other, the overall molecule is apolar. From the above, the amphoteric CO_2 behavior leads to two possible activation pathways: the oxygen atoms can exhibit a Lewis base characteristic, while the carbon atom can play the role of a Lewis acid center. As the electrophilic characteristic of carbon is higher than the nucleophilicity of the oxygen atoms, carbon dioxide is a better acceptor than donor of electron density.

Herein, the conversion of carbon dioxide into cyclic carbonates via reactions with epoxides is discussed, focusing on heterogeneous hybrid materials based on catalytic active species supported onto silica, metal–organic frameworks (MOFs), and carbon nanostructures. Several reviews on the production of cyclic carbonates are proposed for a detailed overview covering a broad scope of catalytic systems working under both homogeneous and heterogeneous conditions [9–16].

1.2. Carbon Dioxide Conversion into Cyclic Carbonates

One of the most interesting pathways to valorize CO_2 is represented by its fixation into epoxides for the production of cyclic carbonates [9].

Cyclic carbonates are organic compounds with interesting properties, such as low vapor pressure, high boiling point, low toxicity, and biodegradability. Based on these features, cyclic carbonates find widespread applications as aprotic high-boiling polar solvents, electrolytes for batteries, precursors for polymeric materials, fuel additives, plastic materials, and intermediates for the synthesis of fine chemicals such as dialkyl carbonates, glycols, carbamates, and pyrimidines, among others [17–19]. In industry, cyclic carbonates are traditionally prepared via synthetic methodologies involving the use of phosgene. However, such procedures allow the production of equimolar amounts of carbonate and chlorinated salts and large volumes of chlorinated solvents. Moreover, even if phosgene is a versatile building block widely used in the production of plastics and pesticides, it is also hazardous, toxic, corrosive, and difficult to handle. Exposure to phosgene may cause collateral health effects. Therefore, its application as feedstock in industrial large-scale synthesis should be replaced with sustainable alternative routes having a lower environmental impact. Among them, the synthesis of cyclic carbonates from carbon dioxide and epoxide emerged as a low-toxicity alternative. For instance, Scheme 2 shows three possible synthetic routes for the conversion of ethene into the corresponding cyclic carbonate: (i) hydrochlorination of ethylene, followed by hydrolysis, and conversion with $COCl_2$; (ii) formation of ethylene oxide, subsequent hydrolysis, and reaction with $COCl_2$; (iii) formation of ethylene oxide and CO_2 fixation. Life-cycle assessment (LCA) methodology was applied to evaluate the ratio between the amount of CO_2 emitted and ethene carbonate produced [3]. The obtained results clearly identified the reaction between ethylene oxide and CO_2 as the most sustainable route for the production of ethylene carbonate.



Scheme 2. Synthetic routes for the production of ethene carbonate [3].

According to green chemistry principles [20], carbon dioxide fixation into epoxides for the synthesis of five-membered cyclic carbonates is a productive catalytic process displaying an atom economy of 100%. In order to face the challenging thermodynamic stability of carbon dioxide, epoxides have to be used combined with a catalyst to reduce the activation energy of the process.

1.3. Catalytic Systems for the Synthesis of Cyclic Carbonates

In this context, a growing interest toward the synthesis of cyclic carbonates via reaction of CO_2 with epoxides led to the design of catalytic systems bearing Lewis acid sites for the electrophilic activation of epoxide and/or carbon dioxide and Lewis base sites as nucleophilic species. Both sites can be included into two different systems (e.g., the metal of a complex as a Lewis acid and the anion of a salt as a Lewis base) or can belong to a sole bifunctional catalyst (e.g., a complex with a cationic metal center and a labile anionic ligand). Several catalysts, working under both homogeneous and heterogeneous conditions, were developed for the conversion of CO_2 into cyclic carbonates via reaction with epoxides. In particular, metal oxides [21], metal–organic frameworks (MOFs) [22–24], metal salts [25], metal complexes [12,26–28], Lewis base systems [29], ionic liquids (ILs) [30–35], and organic polymers [32,36,37] were proposed as catalysts for this reaction. Based on the environmental impact and the cost efficiency, the overall sustainability of this process has to be evaluated and improved according to some key criteria such as (i) the presence of solvents, (ii) the use of metal species, (iii) the achieved yields and selectivity, and (iv) the required reaction conditions (temperature, pressure, reaction time). The choice between metal-based or organo-catalysts for CO_2 fixation brings strengths and weaknesses. Metal-based systems lead to milder reaction conditions (e.g., lower temperature, reduced catalytic loading) owing to their ability to activate and/or stabilize substrates or intermediates via coordination interactions. On the other hand, organo-catalysts can be considered as suitable and safer alternative for the design of sustainable processes because of their low cost, non-toxic nature, and good stability and inertness toward moisture and air. With the aim to increase the catalyst lifetime, several heterogeneous organo-catalysts were developed, providing simplified work-up procedures combined with the possibility to use them under continuous flow conditions. It is well known that the design of heterogeneous catalysts is particularly envisaged from industrial parties because of their simple recovery from the reaction medium and the possibility of using them in fixed-bed reactors.

2. Hybrid Catalysts for the Synthesis of Cyclic Carbonates

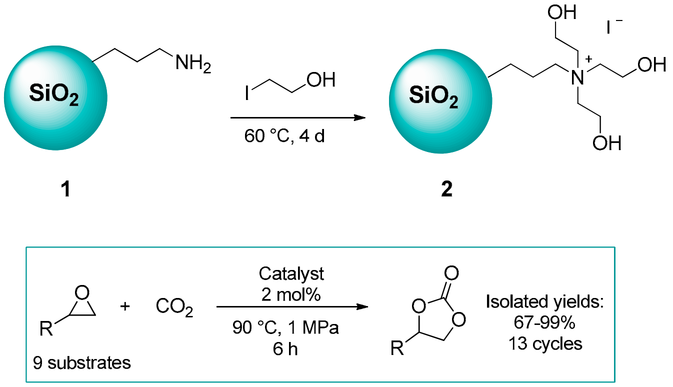
2.1. Silica-Based Hybrid Catalysts

Silica gel and ordered mesoporous silicas display useful features, e.g., high surface area, narrow range of pore sizes (microporous to mesoporous), good thermal and mechanical stability, widespread availability, and easy covalent functionalization strategies covering a broad range of organic or organo-metallic moieties. The huge variety of chemical modifications onto the silica surface is linked to the presence of silanol groups. The covalent functionalization of the silica surface is usually performed via condensation reactions between the silanol groups and a selected organo-silane [38,39]. Therefore, silylating coupling agents such as chlorosilanes, alkoxy-silanes, and silyl-amines found widespread application. Their reaction with surface silanol functionalities usually occurs on free and geminal silanol groups, whereas hydrogen-bonded silanol moieties are less reactive owing to the local hydrophilic networks. Silicas are employed as supports for the covalent grafting of organic salts in order to improve their applicability and reusability the conversion of carbon dioxide into cyclic carbonates. In this scenario, several heterogeneous catalytic systems based on alkylammonium, imidazolium, pyridinium, and phosphonium salts were developed.

2.1.1. Ammonium-Functionalized Silica

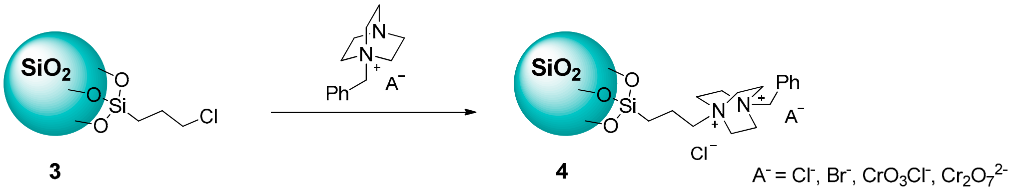
In recent years, ammonium salts were grafted onto silica-based supports in order to be tested as organo-catalysts, as well as bifunctional catalytic systems endowed with Lewis acids sites, for the synthesis of cyclic carbonates via reaction of carbon dioxide with epoxides.

In 2015, Werner and Kort [40] reported silica-supported ammonium iodide salts as a recyclable heterogeneous organo-catalyst able to work even at reaction temperatures lower than 100 °C. As reported in Scheme 3, the synthesis of the above material was carried out by reacting aminopropyl-functionalized silica gel **1** with 2-iodoethanol under argon at 60 °C. The catalytic tests were run under solvent-free reaction conditions at 90 °C with a CO_2 pressure of 1 MPa. The solid **2** showed much higher activity if compared with tetrabutylammonium iodide as a homogeneous catalyst. The co-catalytic role of the hydroxyl functionalities in the epoxide activation was highlighted by comparing the performance of tetrabutylammonium iodide with that of tri-*n*-butyl-(2-hydroxyethyl)ammonium iodide in the conversion of butylene oxide into the corresponding carbonate (19% vs. 96%). Catalyst **2** was tested at 2 mol.% for 13 cycles affording full conversion and excellent isolated yields of butylene carbonate ($\geq$93%). Under the same reaction conditions, a broad range of epoxides were converted with selectivity toward the corresponding carbonates of $\geq$98% and isolated yields in the range 67–99%.



Scheme 3. Silica-supported ammonium iodide salts as a recyclable heterogeneous organo-catalyst.

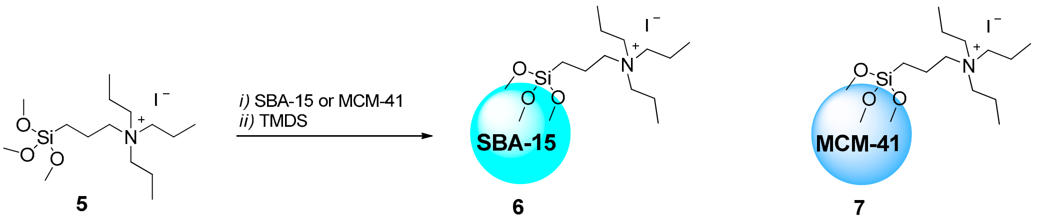
In the same year, Hajipour and co-workers [41] grafted onto a pre-functionalized silica **3** 1,4-diazabicyclo[2.2.2]octane (DABCO)-based ammonium salts (**4**, Scheme 4). The reaction of styrene oxide with CO_2 was chosen to investigate the influence of the anionic species leading to the order of activity of $Br^- > Cl^- > CrO_3Cl^- > Cr_2O_7^{2-}$.



Scheme 4. Preparation of SiO_2-supported ammonium salts based on 1,4-diazabicyclo[2.2.2]octane (DABCO).

Carbon dioxide conversion was carried out at 100 °C, under solvent-free conditions for 24 h, using 0.6 g of catalyst for 10 mmol of epoxide with 0.4 MPa CO_2. Styrene carbonate was obtained with yields from 19% to 91% and selectivity in the range 25–99%. The most active catalyst was tested for four consecutive cycles showing a decreased efficiency from 94% styrene carbonate yield to approximately 72% upon the fourth use due to the leaching of the catalyst under the heating regimes.

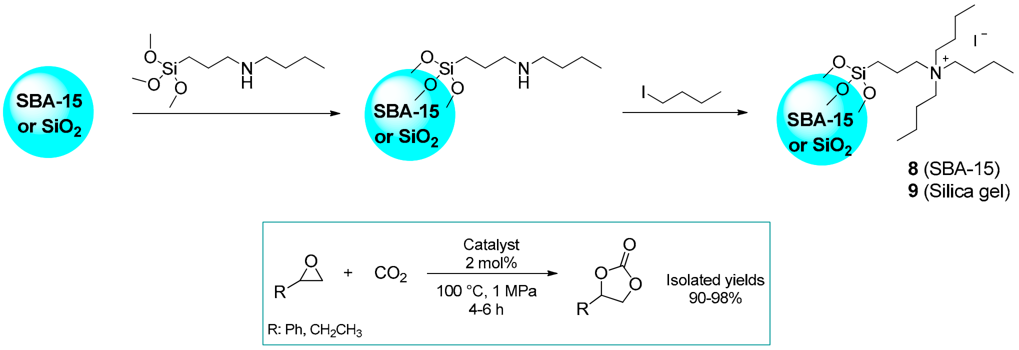
A couple of years later, SBA-15 and MCM-41 were used by Fontaine et al. as supports for the grafting of an active ammonium salt **5** modified with a trimethoxysilane as the linker [42]. The surface of the obtained hybrids was passivated with 1,1,3,3-tetramethyldisiloxane (TMDS) leading to the solids **6** and **7** (Scheme 5).



Scheme 5. Grafting of ammonium iodide salts **5** onto silica supports.

Both materials were employed for the conversion of styrene oxide and hexene oxide, whereby the MCM-41-supported catalyst was more active than the analogous ammonium salt supported onto SBA-15. In particular, the conversion of carbon dioxide was performed using a catalyst loading of 10 mol.%, at room temperature for 24 h and with a CO_2 pressure in the range 0.1–0.3 MPa. Furthermore, the reusability of **6** and **7** was investigated over three catalytic cycles of styrene oxide. The catalyst **7** displayed higher recyclability over four cycles with preservation of high styrene carbonate yield (99–92%) whereas the efficiency of the ammonium salt grafted onto SBA-15 decreased after three cycles providing from 86% to 20% yield of the final product owing to some leaching of the catalyst from the support.

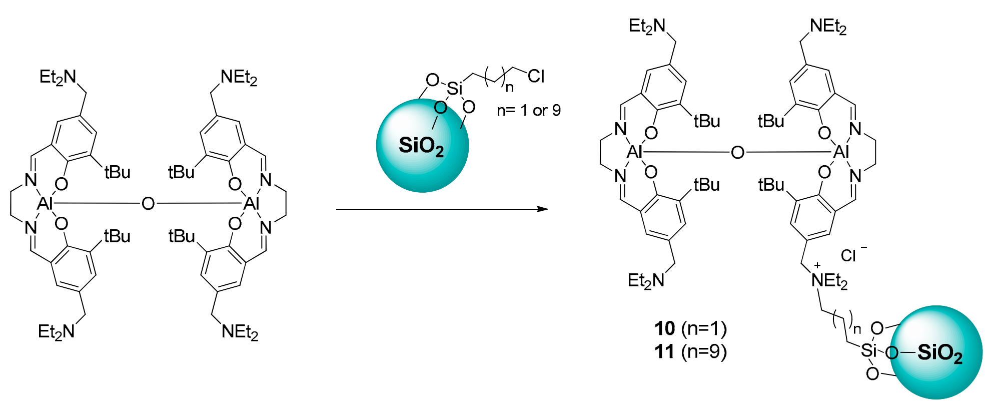
More recently *N*,*N*,*N*-tributyl-*N*-propylammonium iodide-functionalized mesoporous silicas were proposed as catalysts for the solvent-free synthesis of cyclic carbonates from epoxides and CO_2 [43]. SBA-15 and a silica gel were used as support for the synthesis of the solids **8** and **9**, respectively (Scheme 6). Styrene oxide and 1,2-butylene oxide were selected as target substrates to evaluate the performance of the solids, using a catalytic loading of 2 mol.% under mild conditions (1 MPa CO_2, 100 °C and 4–6 h).



Scheme 6. Preparation of *N*,*N*,*N*-tributyl-*N*-propylammonium iodide-functionalized mesoporous silicas and their catalytic performances.

The reusability of the catalysts was found to be dependent on the nature of the support and the substrate. In the presence of 1,2-epoxybutane as substrate, the SBA-15-based catalyst (**8**) exhibited a constant catalytic activity for five reaction cycles (yield > 96%). Conversely, in the presence of styrene oxide, a gradual decrease in yield was observed. Based on textural properties and ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR measurements, such decline was ascribed to the adsorption of solid reaction product (styrene carbonate) onto the catalyst surface. Using a silica gel as support and an improved catalyst recovery step gave rise to a more efficient and reusable catalyst. Furthermore, by comparison with the homogeneous tetrabutylammonium iodide salt, both **8** and **9** showed improved catalytic activity owing to the synergistic effect of the silanol groups of the solid supports.

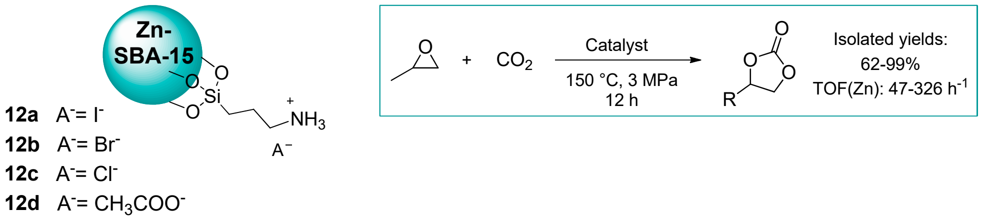
Turning to bifunctional catalytic systems based on the presence of Lewis acid sites, in 2012, silica-supported bimetallic aluminum(salen) complexes bearing pendant quaternary ammonium groups were used by North [44] in the synthesis of cyclic carbonates from epoxides and carbon dioxide in both batch and gas-phase flow reactors (Scheme 7).



Scheme 7. Synthesis of silica-supported bimetallic aluminum(salen) complexes.

The influence of particle and pore size of the silica support on catalyst activity was investigated with smaller particle sizes (<80 mm) being advantageous to catalyst activity, whereas the silica pore size had little effect on the catalytic performance. The nature of the silica support also affected catalyst stability, and the Fluorochem LC301 silica gave a catalyst with both the highest intrinsic activity and the lowest rate of deactivation. The catalysts were attached to the silica through a linker containing three or eleven carbon atoms (**10**, **11**). The longer linker allowed obtaining a catalyst loading three times higher than the shorter linker, but this was offset by a threefold lower activity for the catalyst with the longer linker. After a reaction time of 24 h, the ethylene carbonate production in a flow reactor at 100 °C gave rise to turnover frequency values up to 1.38 h^{-1}. In a batch reactor at 26 °C, the most active catalyst (2.35 mol.%) led to a 60% conversion of styrene oxide after 24 h, corresponding to a turnover number of 25.5.

Jianmin Sun et al. [45] developed a series of bifunctional Zn/SBA-15-supported ammonium salts as single-component heterogeneous catalysts for the coupling of CO$_2$ with epoxides. The catalytic activities of bifunctional solids **12a–d** were tested on the reaction of propylene oxide and carbon dioxide at 150 °C and 3 MPa CO$_2$ for 12 h (Scheme 8). Based on the nature of the nucleophilic species, the catalytic activity increased in the order $I^- > Br^- > Cl^- > CH_3COO^-$. In particular, the most performing catalyst **12a** led to almost quantitative conversion and 99% propylene carbonate yield with a turnover frequency (TOF) of 326 h^{-1}. It is worth mentioning that TOF values were calculated as moles of propylene carbonate produced per mole of zinc ion per hour, whereas zinc content was based on X-ray photoelectron spectroscopy (XPS) elemental analysis. The overall versatility of **12a** was verified with five substrates bearing both electron-withdrawing and electron-donating substituents. The recyclability of **12a** was studied for five runs showing a loss in the catalytic conversion of about 20% probably due to a partial leaching of alkyl ammonium moieties, as well as a structural collapse.

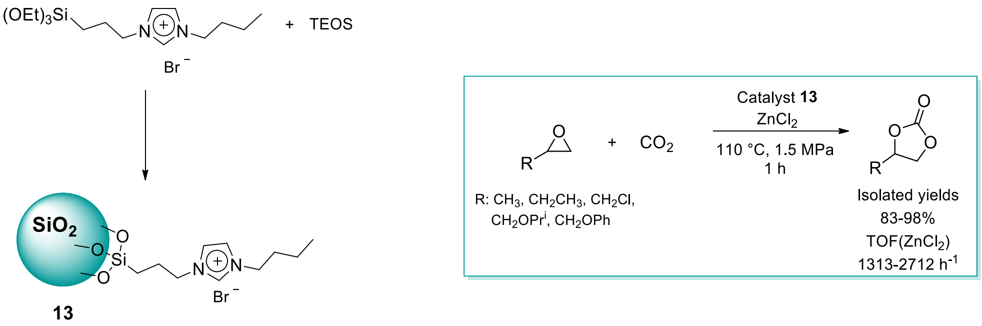


Scheme 8. Bifunctional NH$_3$I-Zn/SBA-15 catalyst for CO$_2$ conversion into cyclic carbonates.

2.1.2. Imidazolium-Functionalized Silica

Imidazolium salts represent one of the most investigated active species for the design of heterogeneous catalysts based on silica supports for the synthesis of cyclic carbonates from CO$_2$ and epoxides. In this context, several catalysts able to work under solvent-free reaction conditions were prepared as both metal-free systems and bifunctional hybrids endowed with co-catalytic species.

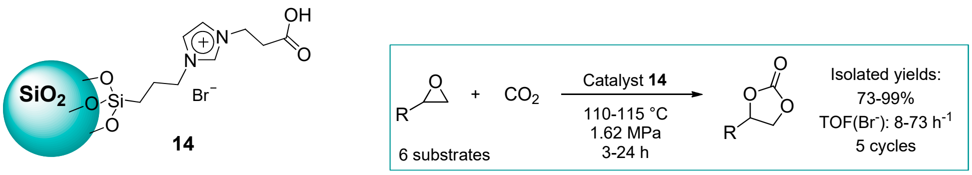
In 2006, Xia et al. reported the first example of carbon dioxide conversion into cyclic carbonates using a novel heterogeneous catalyst based on silica-supported imidazolium bromide ionic liquid and different metal salts as co-catalytic species [46]. Material **13** was prepared via the sol–gel method by reacting 1-(triethoxysilylpropyl)-3-*n*-butylimidazolium bromide in the presence of tetraethyl orthosilicate (TEOS) under acidic conditions. Once characterized, the hybrid was tested using propylene oxide as the target reagent (Scheme 9). The catalytic performance was evaluated using several Lewis acids. Among them, zinc-based salts proved to be the most active, whereas no reaction occurred when $ZnCl_2$ was used as the sole catalytic species. Then, such a catalytic system composed of an imidazolium-based solid and $ZnCl_2$ was investigated with different epoxides and used for three consecutive runs, showing a modest decrease in catalytic activity, probably due to the loss of zinc chloride.



Scheme 9. Preparation of a silica-supported imidazolium salt via the sol–gel method and its catalytic performances.

Imidazolium-based ionic liquids were easily synthesized and immobilized onto commercial silica by Park and co-workers [47]. Typically, several imidazolium salts were grafted as organo-silanes onto a silica surface under inert reaction conditions. The catalytic performance of the obtained materials was deeply studied considering both the influence of the alkyl chain length, the nature of the nucleophile (Cl^-, Br^-, and I^-) as active species, and the co-catalytic effect in the epoxide activation promoted by zinc chloride. In particular, the activity of these catalytic systems was examined by considering the coupling reaction of CO_2 with allyl glycidyl ether. Collected data proved that longer alkyl chains and higher nucleophilicity of the anions led to improved allyl glycidyl ether conversion. Moreover, these catalysts were stable for up to five consecutive runs without any considerable loss of their initial activities.

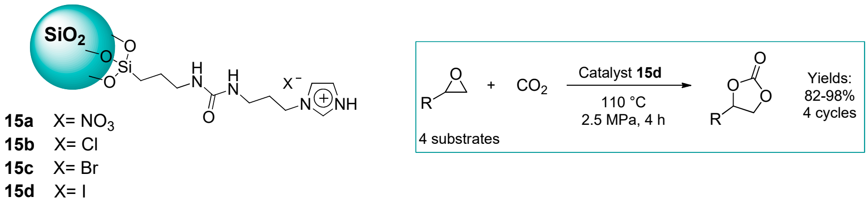
Then, a few years later, the same research group further explored the catalytic performance of those catalysts incorporating different metal chlorides ($CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, and $MnCl_2$) into silica-grafted 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride [48]. Furthermore, a series of imidazolium-based ionic liquids functionalized with carboxyl moieties was prepared and grafted onto a silica gel [49]. The catalytic activity of the obtained hybrids was studied by considering the effect on the imidazolium structures focusing on the nature of the anionic species (Cl^-, Br^-, I^-) and on the reaction parameters. The synergistic effect of the carboxylic group with the halide anions was evidenced by comparison with the analogous material based on imidazolium-salt-functionalized alkyl moieties. Then, in order to investigate the recyclability and the applicability of this type of catalyst, material **14**, based on imidazolium bromide salts modified with carboxyl units, was tested for deeper studies (Scheme 10). In particular, the solid was successfully used for five runs in the reaction between carbon dioxide and allyl glycidyl ether at 110 °C for 3 h with a CO_2 pressure of 0.83 MPa in the absence of solvents. Then, the applicability of the catalysts was verified with other epoxides (five substrates) affording high yields and selectivity corresponding to TOF values ranging from 8–73 h^{-1}.



Scheme 10. Silica-supported imidazolium bromide salts modified with carboxyl units for the synthesis of cyclic carbonates.

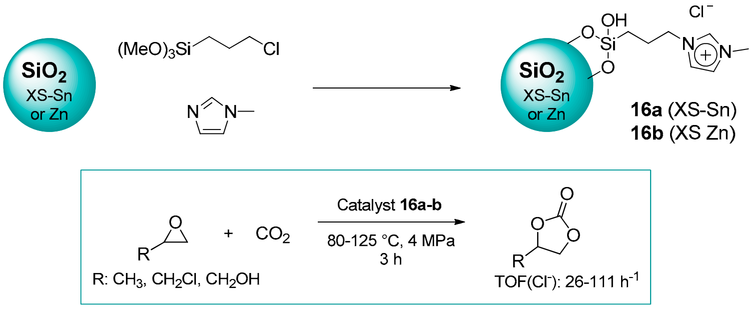
In 2015, a heteropolyacid-based ionic liquid immobilized onto fibrous nano-silica was proposed as an efficient catalyst for the synthesis of cyclic carbonate from carbon dioxide and epoxides [50]. In this study, the preparation of a novel nanocatalyst, based on core–shell ionic liquid-modified dandelion-like fibrous nano-silica (KCC-1/IL/HPW), was applied for the synthesis of cyclic carbonates and easily separated from the reaction mixture for reuse up to 10 cycles with an overall leaching of 3.6%.

More recently, several zwitterionic imidazolium-urea derivative framework bridged mesoporous hybrid silica materials were prepared by Arai and co-workers [51]. The materials displayed hydrogen-bond donor capability and nucleophilicity (Scheme 11). The solid **15d** bearing iodide as anionic species emerged as the most active catalysts showing a high structural stability. Compound **15d** was tested with different epoxides under solvent- and metal-free conditions. Moreover, the material was separated by simple filtration and used four times without significant loss of activity. This type of hybrid represents an alternative to Lewis acid activation and avoids the use of transition metal ions.



Scheme 11. Silica-supported zwitterionic imidazolium-urea derivative frameworks.

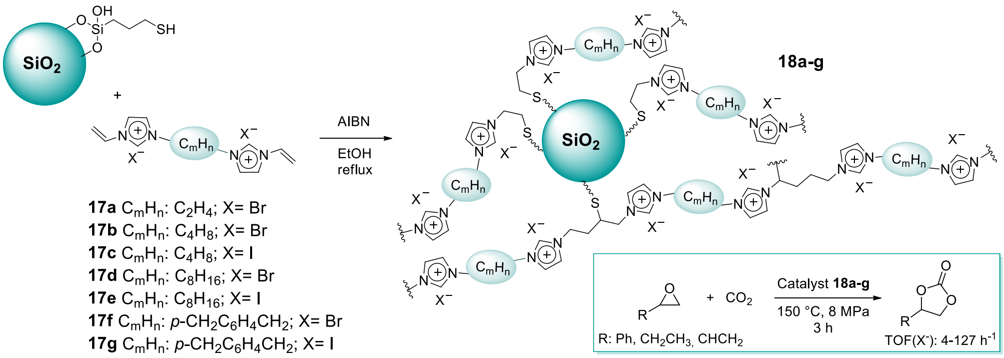
Recently, novel heterogeneous catalysts with a silica architecture were proposed by Aprile et al. as bifunctional systems endowed with imidazolium chloride salts and tin or zinc inserted within the solid support [52]. The synthetic route started from the preparation of the solid support bearing a metal element incorporated as a single site within the silica framework, followed by the grafting of an imidazolium chloride salt. Both Sn- and Zn-based solids (**16a**,**b**) displayed improved performance compared to the analogous metal-free material (Scheme 12). The solids showed promising features for catalytic applications including good surface area, reduced particle size, and acid properties estimated via microcalorimetry analysis. The chemical fixation of CO_2 into epoxides was carried out using Sn- and Zn-based catalysts with a reaction temperature below 150 °C and a pressure of 4 MPa.



Scheme 12. Bifunctional catalysts endowed with imidazolium salts and tin or zinc inserted within silica supports and their performance in CO_2 conversion.

In the framework of our interest in carbon dioxide conversion, highly cross-linked imidazolium networks were immobilized onto silica supports for the design of heterogeneous metal-free hybrids bearing chloride and bromide as nucleophilic active species [53]. Such materials were prepared by grafting different bis-vinylimidazolium salts on thiol-functionalized silica. In particular, two bis-vinylimidazolium salts having the *p*-xylyl as organic linker were grafted on the silica support through a thiol-ene coupling reaction between the thiol groups of the modified silica and the double bond of the bis-vinylimidazolium salts, in the presence of 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator. This reaction offered all the envisaged features of a "click reaction", being highly efficient and simple to perform. The synthetic protocol allowed obtaining a series of materials showing good thermal stability combined with high catalytic loadings of around 3 mmol/g. These features are of paramount importance in terms of both catalyst recyclability and productivity (calculated as the ratio between the amount of cyclic carbonate produced and the amount of catalyst used). Such a study was performed under supercritical carbon dioxide at 150 °C, using a catalyst loading of 1 mol.% to compare the activity of each solid with three substrates, such as propylene oxide, styrene oxide, and cyclohexene oxide. The catalytic tests were run in a high-throughput unit that allowed reactions to be performed simultaneously in parallel batch reactors. The best catalyst identified in this work was prepared by supporting a bis-imidazolium bromide salt onto SBA-15 with *p*-xylyl as an organic linker between the imidazolium units.

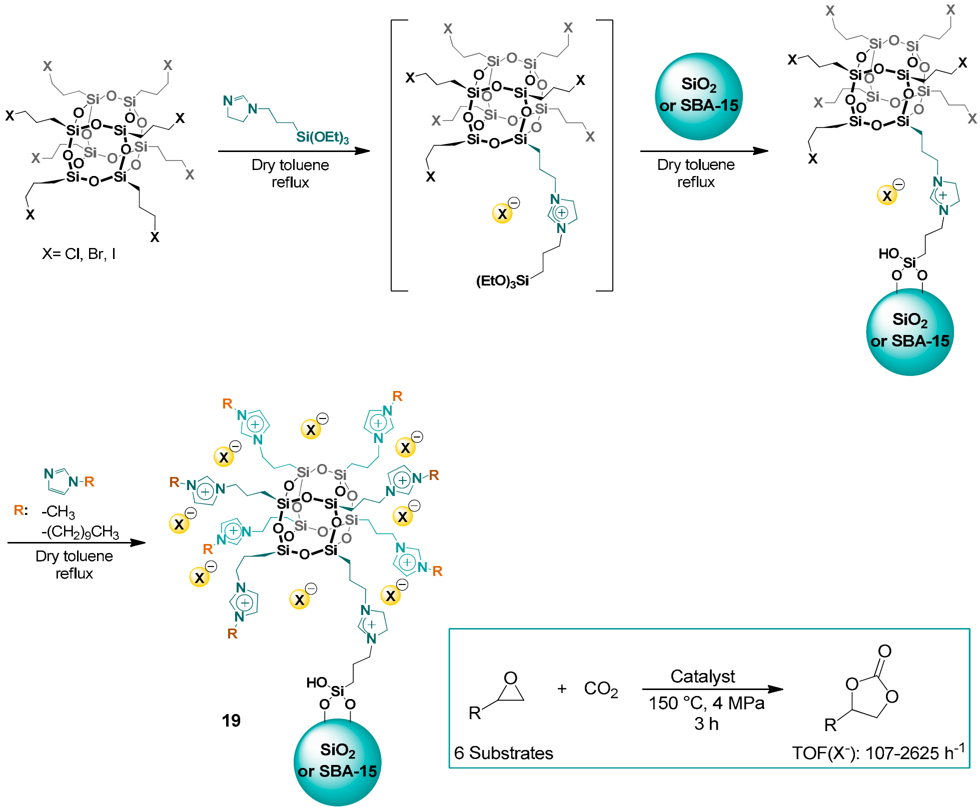
In order to further investigate the catalytic behavior of this type of material, an additional series of hybrids [54] was designed using bis-vinylimidazolium salts having different lengths and bulkiness of the organic linker connecting the two imidazolium units. Considering the previous results, the nature of the halide counterion was studied, focusing on bromide and iodide organic salts (Scheme 13).



Scheme 13. Multilayered supported imidazolium salts for the synthesis of cyclic carbonates.

The materials with iodide as the nucleophilic species displayed higher activity in terms of conversion, productivity, and turnover number compared to their counterparts with bromide as the counterion. A second catalytic trend was observed based on the specific organic linker; ranging from ethyl to octyl alkyl chains, the activity of the solids increased with the length of the linker. The material prepared by supporting a bis-vinylmidazolium iodide salt with the *p*-xylyl as the linker **17g** was identified as the most active catalyst in the reaction between CO$_2$ and styrene oxide with a turnover number of 237. The appealing features of this class of materials were also evaluated in terms of versatility with different substrates using catalytic loadings in the range 0.6–0.4 mol.%, whereas the reusability of a selected catalyst at 0.1 mol.% was verified for five consecutive runs.

More recently [55], we reported a series of hybrid materials based on silica-supported imidazolium-modified polyhedral oligomeric silsesquioxanes (POSS-Imi) as heterogeneous organo-catalysts for the conversion of epoxides and CO$_2$ into cyclic carbonates in solvent-free reaction conditions. All solids **19** were easily prepared following tailored procedures (Scheme 14) designed to study the influence of the solid support (SiO$_2$ vs. SBA-15) and the effect of both nucleophilic species (Cl$^-$, Br$^-$, I$^-$) and imidazolium alkyl side chain length. Such new hybrid materials were easily recyclable, as well as highly active toward the formation of cyclic carbonates, even with the less reactive oxetane, showing higher performance in terms of turnover number, productivity, and selectivity.

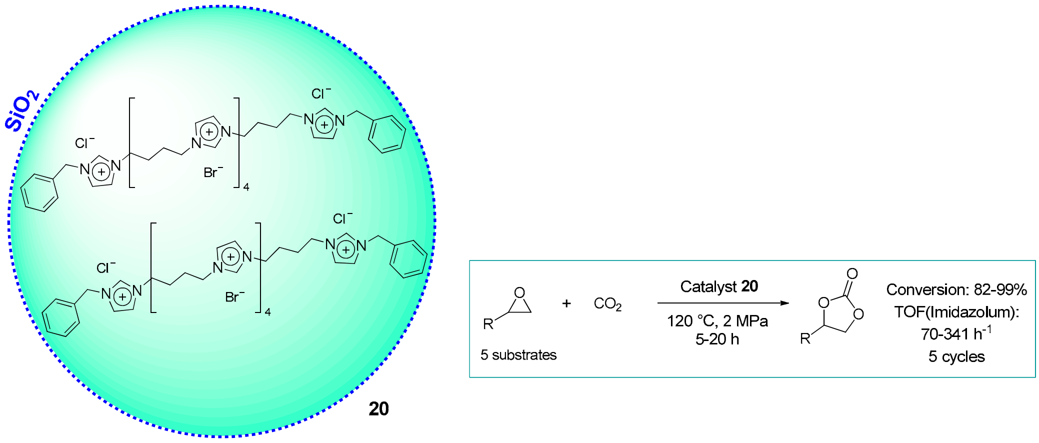


Scheme 14. Silica-supported imidazolium-modified polyhedral oligomeric silsesquioxanes for CO_2 conversion.

High turnover numbers (TON) and productivity values up to 7875 and 740, respectively, were reached for the conversion of CO_2 into cyclic carbonates using hybrid materials based on imidazolium-modified polyhedral oligomeric silsesquioxanes (POSS-Imi) grafted on amorphous silica (SiO_2) and mesostructured SBA-15. The heterogeneous organo-catalysts were easily prepared via a straightforward synthetic procedure allowing the generation of high local concentration spots of imidazolium active sites surrounding the POSS core.

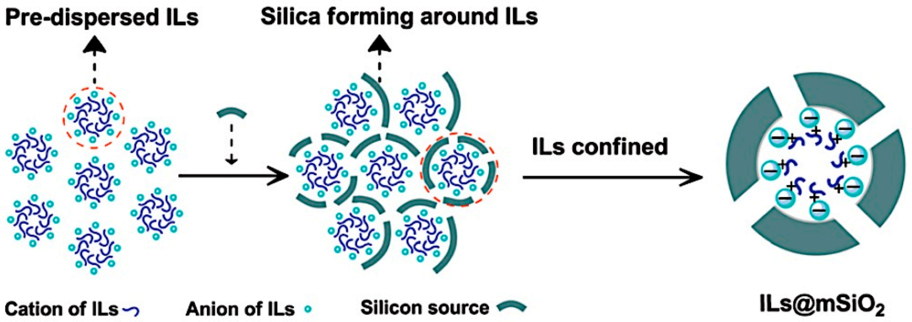
POSS nanocages were also employed for the design of imidazolium-based catalytic systems by Koo and co-workers [56]. They introduced a new methodology for the preparation of inorganic–organic hybrid ionogels and scaffolds through the cross-linking and solution extraction of POSS nanostructures modified with vinyl-imidazolium or alkyl ammonium salts. The hybrid scaffolds with well-defined, interconnected mesopores were used as heterogeneous catalysts for the CO_2 conversion into several cyclic carbonates at 110 °C, 0.76 MPa for 10 h using an epoxide concentration of 400 mM in MeCN. The obtained TOF values were calculated from the moles of ionic groups to be in the range of 16–21 h^{-1}. The material recyclability exhibited good performance with minimal to no depreciation in the catalytic conversion of ethylene oxide to ethylene carbonate, as the total catalytic conversion degree of decrease was only about 5%.

In 2017, a novel strategy for immobilizing a water-soluble oligomeric ionic liquid by coating the ionic liquid with mesoporous silica was presented by Ghiaci and Akbari [57]. The selected imidazolium halide oligomer trapped into mesoporous silica showed increased catalytic activity compared to the reaction carried out with the unsupported ionic liquid (Scheme 15). This behavior was ascribed to a synergistic effect between the ionic liquid and the silica support due to the hydrogen bonding between the oxygen of the epoxide and the silanol groups of the solid support. The catalyst **20** was tested with five epoxides with TOF values in the range 70–341 h^{-1}. The reusability of the material was studied in the coupling of CO_2 with styrene oxide for five consecutive runs at 120 °C for 5 h without losing its activity and selectivity.



Scheme 15. Imidazolium halide oligomer trapped into mesoporous silica.

Then, one year later, Zhang et al. proposed another example of confined imidazolium-based ionic liquids [58]. Different amounts of 1-ethyl-3-methyl imidazolium bromides (EmimBr) were tailored and confined via one-step assembly of mesoporous silica using a fixed amount of silicon source (Scheme 16). The confined ionic liquid retained the advantages of both homo- and heterogeneous catalysts, showing improved performance compared to bulk EmimBr under the same reaction conditions, owing to the cooperative effect of the silanol groups. The catalytic suitability of this type of hybrid was investigated with four different epoxides at 120 °C and with a pressure of 2.0 MPa, exhibiting TOF values (based on the amount of imidazolium units) from 115 to 127 h^{-1}. The recyclability of the most active material was examined in the reaction of CO_2 with propylene oxide for five cycles, showing a slight decrease in catalytic activity resulting in a reduction from 99% to 83% propylene carbonate yield. This trend was attributed to the leaching of the confined ionic liquids from the first to the fourth cycle.



Scheme 16. Reproduced from Reference [58]. Copyright (2018) Royal Chemical Society.

In Table 1, we summarize the adopted reaction conditions for the coupling between CO_2 and styrene oxide for selected catalytic systems based on alkyl-ammonium and/or imidazolium salts supported onto silica. It is worth mentioning that the catalytic performance of these systems was found to be not comparable owing to the different reaction parameters employed, including the nature of the nucleophilic species, the use of co-catalysts, the temperature, the CO_2 pressure, the reaction time, etc.

Table 1. Literature comparison for the synthesis of styrene carbonate. r.t.—room temperature.

#	Catalyst	Catalyst Loading	Conversion/Yields	Temperature	CO_2 Pressure	Time	Reference
		(mol%)	(%)	(°C)	(MPa)	(h)	
1	**2**	2	85 (Y)	90	1.0	6	[40]
2	**4**	0.93	94 (Y)	100	0.4	24	[41]
3	**6**	10	86 (Y)	r.t.	0.1	24	[42]
4	**7**	10	99 (Y)	r.t.	0.1	24	[42]
5	**8**	2	61 (Y)	100	1.0	4	[43]
6	**9**	2	98 (Y)	100	1.0	4	[43]
11	**14**	0.45	96 (Y)	115	1.62	5	[49]
12	**15d**	0.5	82 (Y)	110	2.5	4	[51]
13	**16b**	0.3	39 (C)	125	4.0	3	[52]
14	**18g**	0.43	99 (C)	150	8.0	3	[54]
15	**19**	0.14	53 (C)	150	4.0	3	[55]
17	**20**	0.25	98 (C)	120	2.0	5	[57]
18	**ILs@mSiO$_2$**	0.26	89 (C)	120	2.0	8	[58]

2.1.3. Phosphonium- and Pyridinium-Functionalized Silica

In 2006, the catalytic activity of phosphonium halides toward the synthesis of propylene carbonate was highly improved via their immobilization onto silica [59]. Sakakura et al. introduced an example of a synergistic organic–inorganic hybrid material where the inorganic support simplified the catalyst separation and promoted the catalytic activity of the organic sites at 100 °C and 10 MPa CO_2. A few years later, Sakai et al. prepared a hybrid material via the coupling of 3-(triethoxysilyl)propyltriphenylphosphonium bromide and mesoporous silica [60]. Here again, the organic and inorganic moieties showed a synergistic effect on catalytic activity. The pore size of silica was found to influence the overall performance of the catalyst; mesoporous silica with a mean pore size of 19 nm displayed higher activity than silica with a mean pore size of 6 nm. The catalytic tests were carried out under solvent- and metal-free conditions at 90 °C, 1 mol.% loading of catalyst, for 6 h. Furthermore, the hybrid catalyst was tested with several epoxides (TOF values lower than 2 h^{-1}) and recycled in the reaction between CO_2 and 1,2-epoxyhexane up to 10 times, still retaining its activity.

Silica-supported pyridinium salts were proposed as heterogeneous catalysts for the synthesis of cyclic carbonates. In 2009, Baba et al. reported silica-supported 4-pyrrolidinopyridinium iodide prepared via quaternization of 4-pyrrolidinopyridine with silica-supported alkyl iodide [61]. This material was employed in the coupling of CO_2 with epoxides under solvent-free conditions and atmospheric pressure of carbon dioxide at 100 °C. The solid retained its catalytic activity for four cycles for the synthesis of styrene carbonate. The versatility of this material was examined with five different epoxides affording TOF values of 4–14 h^{-1}.

In a more recent study, Yang and co-workers proposed for the first time the efficient immobilization of cationic zinc porphyrin complexes on mesoporous SBA-15 via a simple one-pot route by refluxing 5,10,15,20-tetrakis(4-pyridyl)porphyrin zinc(II) (Zn-TPy), SBA-15, and 3-(trimethoxysilyl)propyl bromide in toluene, dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), or tetrahydrofuran (THF) [62]. The bifunctional solid material with both a Lewis acid site and nucleophile (bromide or iodide) catalyzed the CO_2 conversion into cyclic carbonates under solvent-free conditions at 120 °C and 1.5 MPa. Compared with its homogeneous counterpart, the solid catalyst resulted more active than the homogeneous system with Zn-TPy as a Lewis acid and tetra-*n*-butylammonium bromide (TBAB) as a nucleophile (TOF = 927 h^{-1} vs. 370 h^{-1}). This suggests that the closely connected Lewis acid and Br^- in the solid material could enhance their cooperation during the catalytic process.

2.2. Metal–Organic Framework (MOF)-Based Catalysts

Metal–organic frameworks (MOFs) are a class of structured solids obtained via coordination among transition metal cations or clusters (called secondary building units—SBU) and organic linkers (OL) often endowed with carboxylic or amino groups. By varying the combination of the selected OL/SBU, as well as the synthesis conditions, different crystalline porous networks can be obtained [63,64]. These solids possess a series of interesting features such as extremely high specific surface area, large pore volume, ordered three-dimensional (3D) structure and elevated adsorption properties, making them interesting candidates for applications in materials science [65–68]. Some examples of MOF systems, together with their specific surface areas, are reported in Figure 2 [69].

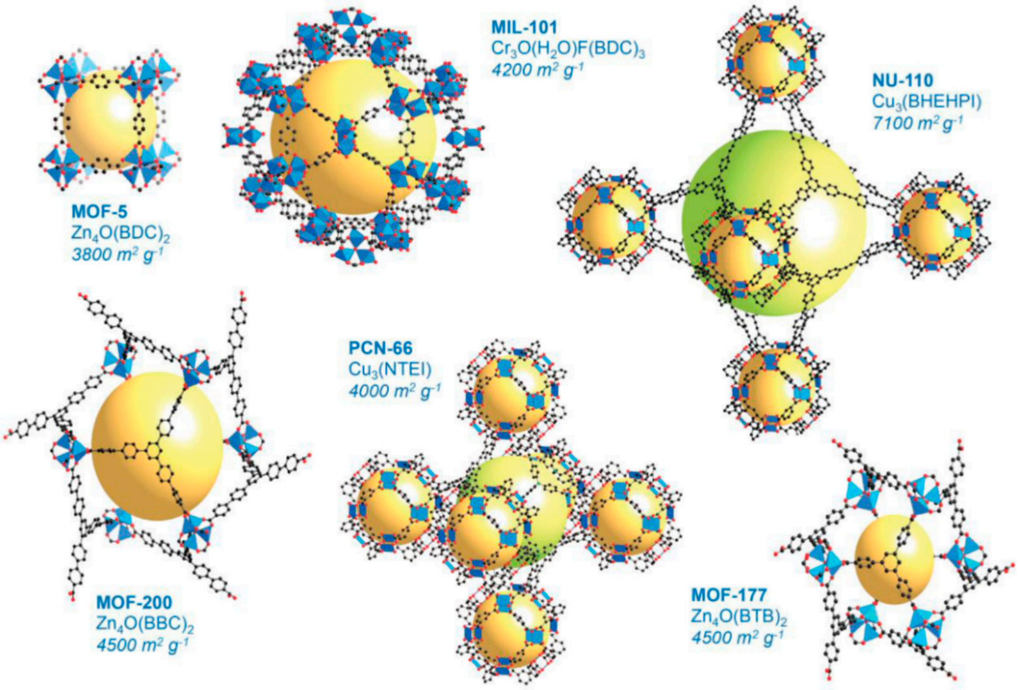
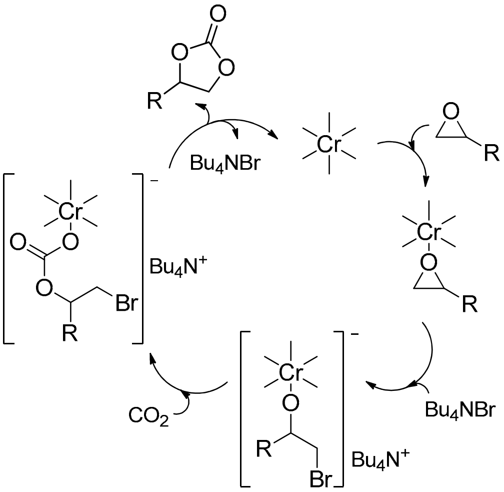


Figure 2. Schematic representation of some metal–organic framework (MOF) structures. BDC = 1,4-benzenedicarboxylate; BTB = 1,3,5-benzenetribenzoate; BBC = 4,4′,4″-[benzene-1,3,5-triyltris(benzene-4,1-diyl)]tribenzoate; NTEI = 4,4′,4″-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl)triisopthalate. Reproduced from Reference [69]. Creative Commons Attribution 3.0 License.

All the abovementioned characteristics, together with the possibility of fine-tuning the metal organic architecture, allow explaining the use of MOF structures in fields ranging from gas adsorption and storage to drug delivery, magnetism, and luminescence, among others. Moreover, the interaction between the organic linker and the metal clusters or ions is not always perfect. The defects generated in the MOF structure do not constitute a drawback since they can act as Lewis acid sites paving the way to a broad window of applications in catalysis.

Within the frame of the conversion of CO_2 for the synthesis of cyclic carbonates, MOFs are largely employed as co-catalysts, often in combination with ammonium or imidazolium salts [24,70]. Their use allows decreasing the reaction temperature, usually below 125 °C, and generally working under mild reaction conditions.

Zalomaeva et al. [71] explored the use of Cr-MIL-101 in the presence of tetrabutylammonium bromide (CTABr) as co-catalysts for the conversion of the challenging substrate styrene oxide. Their investigation covered a temperature range between room temperature (25 °C) and 125 °C. Improved carbonate yields (33%) compared to analogous experiments performed only in the presence of TBABr (2% conversion), as well as of $Cr(acac)_3$/TBABr (3% conversion), were achieved in the presence of the Cr-MIL-101/TBABr catalytic couple at room temperature after 24 h. Scheme 17 describes one possible reaction mechanism in which the Cr centers of the Cr-MIL-101 play the role of a Lewis acid, coordinating the oxygen of the epoxide which subsequently undergoes ring opening via nucleophilic substitution of the Br^- at the less-hindered carbon.



Scheme 17. Proposed reaction mechanism over MIL-101/ tetra-*n*-butylammonium bromide (TBABr) catalysts [71].

Ma and co-workers [23] reported the use of MOF-like structures as versatile catalysts for the syntheses of propylene and other mono-substituted cyclic carbonates. In this work, the authors presented a crystal engineering approach in which the synthesis of a Cu(II)-based metal–macrocyclic framework (MMCF-2) as a novel MOF (Figure 3) was successfully achieved. An almost total conversion of propylene oxide was obtained after 48 h at room temperature and under 1 atm CO_2 in the presence of the MMCF catalyst and 6.5 mol.% (with respect to the epoxide) of tetrabutylammonium bromide.

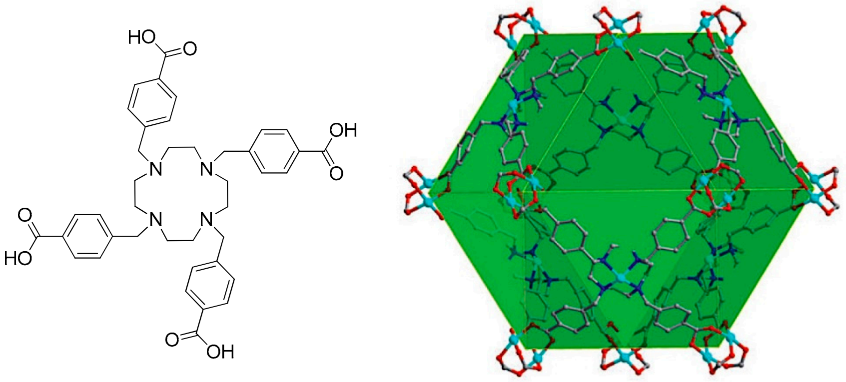


Figure 3. The organic linker used to obtain the metal–macrocyclic framework (MMCF-2) structure (on the left) and the cuboctahedral cage of the corresponding metal–macrocyclic framework (on the right). Adapted from Reference [23]. Copyright (2014) Wiley-VCH.

Another highly efficient catalyst at room temperature [72] was described by Park et al. A Zn-glutamate-based MOF was synthesized and used in the reaction between CO_2 and both propylene oxide (PO) and methylaziridine (MeAz). As the authors mentioned in the manuscript, the addition of an ammonium salts to the reaction mixture was needed since MOF structures alone never show activity at low temperature. Almost quantitative conversion and full selectivity were obtained with both PO (92% conversion) and MeAz (94% conversion) at room temperature and in the presence of TBABr (up to 10 mol.%).

With the objective of further increasing the affinity through CO_2, various MOF-bearing nitrogen-rich compounds were reported. Zhao and co-workers prepared a highly porous MOF, incorporating both nitrogen-rich triazole functionalities and exposed Lewis acid metal salts. In this case, Cu(II) ions were chosen, together with an octacarboxylate ligand (Figure 4a), for the design of an MOF structure made up of two neighboring Cu(II) bridged by four carboxylate groups from the OLs to give paddle-wheel Cu_2 clusters (Figure 4b). Single-crystal X-ray analysis was employed to identify the structure and to prove the presence of Cu_2 paddle-wheel clusters [37]. As claimed by the authors, the obtained MOF displayed a size-dependent reactant selectivity, resulting as extremely active in the presence of small-sized epoxides such as propylene oxide (96% carbonate yield after 48 h at room temperature in the presence of 10 mol.% TBABr). On the other hand, the carbonate yield dropped dramatically when epoxides such as 1,2 epoxyoctane, 1,2-epoxydodecane, or 2-ethyl-hexyl glycidyl ether were used as starting materials. The authors attributed the decreased catalytic performance to the large size of the latter epoxides.

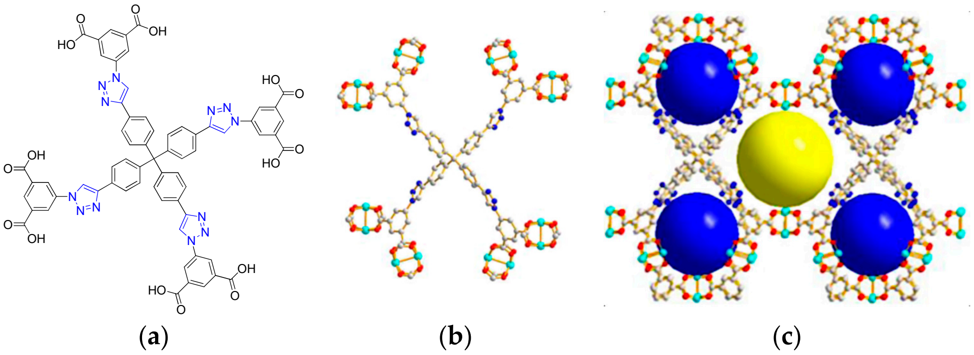
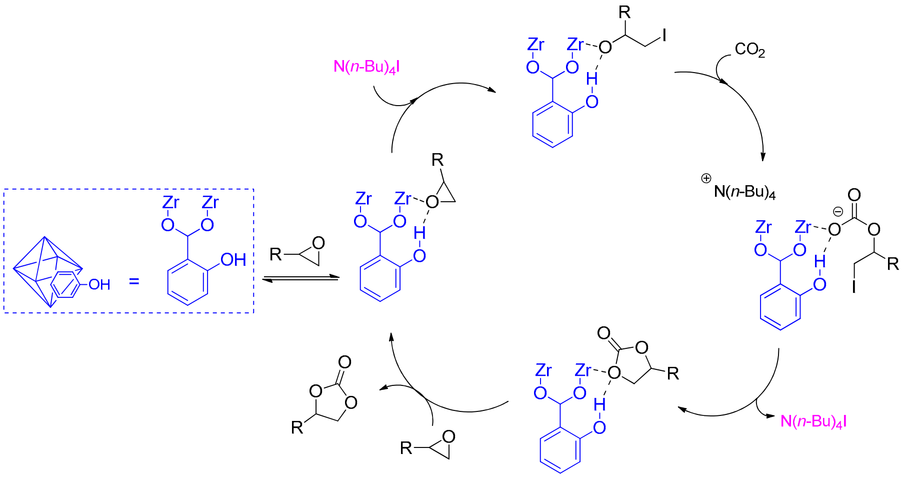


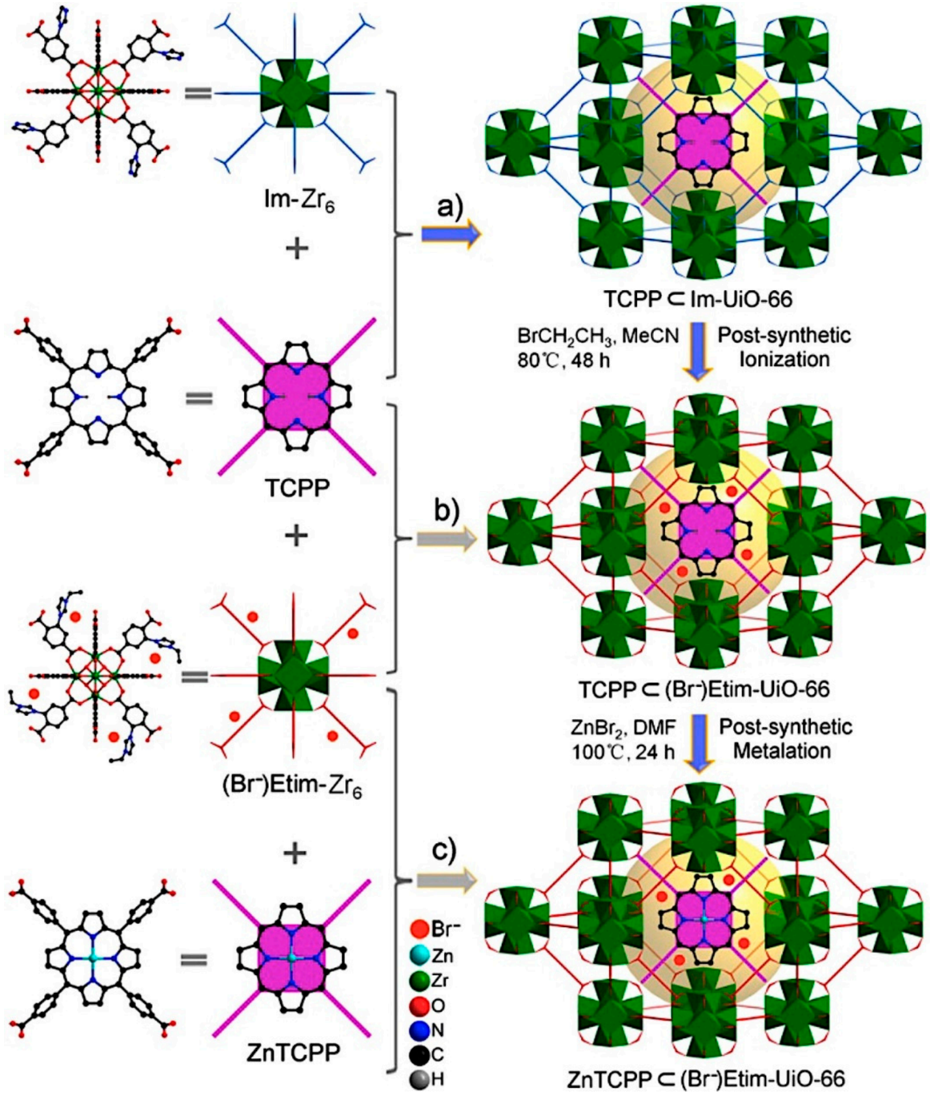
Figure 4. Octacarboxylate moiety used as an organic linker (**a**), and schematic representation of the coordination of the organic linker (OL) with unsaturated Cu_2 paddle-wheel centers (**b**) together with a three-dimensional (3D) view of the MOF porous structure (**c**) in which two different porosities (in yellow and blue) are evidenced. Adapted from Reference [37]. Copyright (2016) American Chemical Society.

The synthesis of various Zr-based MOFs (UiO-66) bearing different groups (–NH_2, –NO_2, –OH, –Cl, –Br, –OH, –OMe, –naphtyl) was successfully achieved employing properly functionalized terephthalic acids and $ZrCl_4$ [73]. The catalysts were compared by selecting the conversion of propylene oxide as a benchmark reaction. The UiO decorated with hydroxyl moieties (UiO-OH) showed the best performance at high temperature (140 °C). However, when the reaction temperature was lowered to 50 °C, the non-substituted UiO-66 displayed the highest carbonate yield. All the catalytic tests were performed in the presence of an ammonium halide (1 mol.%). The proposed reaction mechanism for the reaction catalyzed by UiO-OH involves a synergic activation of the epoxide via coordination of the oxygen of the three-membered ring with the Zr center, together with the formation of a hydrogen bond with the –OH group in close spatial proximity, as reported in Scheme 18.



Scheme 18. Possible synergic activation mechanism for the synthesis of cyclic carbonates in the presence of UiO decorated with hydroxyl moieties (UiO-OH) catalyst [73].

Other more complex MOF structures prepared employing Zr-based SBUs and displaying both Zn porphyrin (having four carboxyphenyl extremities) and imidazolium moieties incorporated in the structure were obtained by Huang, Cao, and co-workers (Scheme 19) [74]. While the importance of having imidazolium functionalities in the structure is clear, the incorporation of Zn porphyrin as an additional source of Lewis acid (together with the Zr clusters) may be questionable. However, a comparison between similar catalysts bearing or not bearing Zn in the structure allows evidencing a comparable carbonate yield but better selectivity than the former catalyst. The versatility of the best catalyst was tested using various epoxides as reactants. Good conversions were achieved after 14 h at 140 °C. Despite the relatively high temperature compared to the abovementioned examples, it should be noted that, in this case, no additional ammonium salts were added as catalysts under homogenous conditions. The reaction was catalyzed by one bifunctional heterogeneous catalyst.



Scheme 19. Schematic step-by-step synthesis approach for the preparation of the final ZnTCPP ⊂ (Br$^-$) Etim-UiO-66 catalyst. ZnTCPP refers to the [5,10,15,20-tetrakis(4-carboxyphenyl)-porphirinato]Zn(II) units, while Etim stands for ethyl imidazolium. In the figure, Im-Zr$_6$ and (Br$^-$) Etim-Zr$_6$ represent, respectively, the imidazole- and imidazolium-functionalized Zr$_6$ clusters. Reproduced from Reference [74]. Copyright (2018) American Chemical Society.

Another interesting class of MOF is represented by the structures prepared from chiral organic linkers. Jiang, Ren, and co-workers reported the preparation and catalytic activity of a chiral salen-based MOF obtained using CuI and the properly designed Ni-salen moiety [75] (Figure 5a).

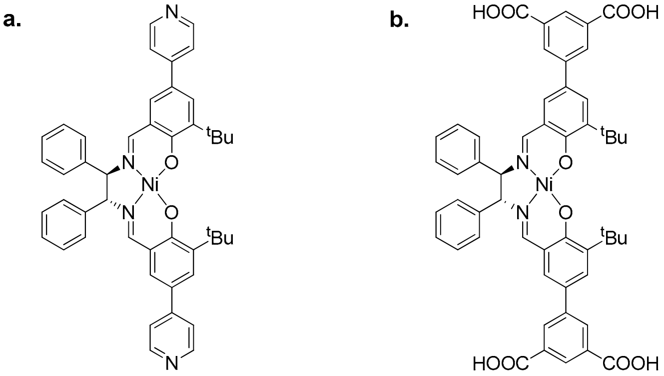


Figure 5. Chiral organic linkers based on metallosalens functionalized with pyridine (**a**) or 3,5 dicarboxyphenyl (**b**) moieties.

The crystal structure of the novel MOF was also achieved. The solid proved to be active in the conversion of styrene oxide, as well as epichlorohydrin and other monosubstituted epoxides such as 1,2-epoxyhexane and 1,2-epoxyoctane. In the presence of a challenging substrate such as styrene oxide (SO), good conversions (84%) were achieved after a 12-h reaction and employing TBABr (0.5 mol.%) as a homogeneous co-catalyst at the temperature of 100 °C. Importantly, the catalytic tests were also performed using carbon dioxide contaminated with water and with a mixture of SO_2/H_2O, with no evident lowering of the catalytic performance. Unfortunately, despite the use of a chiral linker, no enantiomerically enriched mixture of cyclic carbonate was obtained. The versatility of the solid was further proven in the presence of other epoxides such as epichlorohydrin (ECH), 1,2-epoxyhexane, and 1,2-epoxyoctane, which, under the previously mentioned reaction conditions, gave 99%, 65%, and 42% conversion, respectively. The same authors recently published the synthesis of a similar chiral MOF in which the salen-based linker display a higher number of coordination sites (Figure 5b). This synthesis was performed with the objective of improving the stability and, subsequently, the reusability of the final solid [76]. Moreover, this last catalyst displayed improved performance, giving rise to higher yields at lower temperature (80 °C) in a 12-h reaction with 0.5 mol.% TBABr as a co-catalyst. In this case, carbonate yields superior to 90% were obtained in presence of SO and EHC, whilst 1,2-epoxyhexane and 1,2-epoxyoctane produced 89% and 82% cyclic carbonates, respectively.

Within the MOF family, an interesting subclass is constituted by the zeolitic imidazolate framework (ZIF), in which the metal typically used in MOF structures plays the role of silicon and the imidazolate mimics the role of oxygen [77] in the well-known zeolite solids. ZIF structures recently attracted considerable interest due to their large surface area and high porosity combined with exceptional mechanical, thermal, and chemical stability [78]. It is considered that the difference between ZIF- and MOF-based architectures stands in the combination of all these different features. The high affinity of the ZIF solids toward CO_2 motivated various researchers to test the activity of these materials in the conversion of carbon dioxide. Park et al. described the use of ZIF-95 as a catalyst in the chemical fixation of CO_2 into propylene oxide to give the corresponding cyclic carbonate [79]. Good conversions were achieved at 80 °C in the presence of TBABr as a co-catalyst after a 2-h reaction. In the absence of a co-catalyst, a drastic drop in conversion was observed. However, a high propylene carbonate yield was achieved in the absence of ammonium salts, raising the reaction temperature and employing a longer reaction time (24 h). The same group reported the preparation of a ZIF-90 structure incorporating aminopyridinium iodide (IL-ZIF-90) units (Figure 6) which were subsequently employed as catalysts in the synthesis of cyclic carbonates [77]. The activity of ZIF-90 and Il-ZIF-90 was compared, choosing the reaction between CO_2 and propylene oxide. As expected, the novel IL-ZIF-90 solid displayed better performance (97% conversion) than the corresponding ZIF structure without the aminopyridinium iodide moiety (51% conversion). More interestingly, the IL-ZIF-90 showed higher activity compared to a catalytic mixture containing ZIF-90 and aminopyridinium iodide separately (65% conversion). Despite the reaction temperature being higher than the previously reported examples (120 °C), it is important to underline that the reaction time was 3 h, and no ammonium or imidazolium salts under homogeneous conditions were added to the reaction mixture. IL-ZIF-90 constituted the sole (bifunctional) heterogeneous catalyst. A study concerning the activity of the novel catalyst under different conditions in terms of pressure, temperature, catalyst loading, and reaction was also performed. The solid resulted as stable after four consecutive cycles.

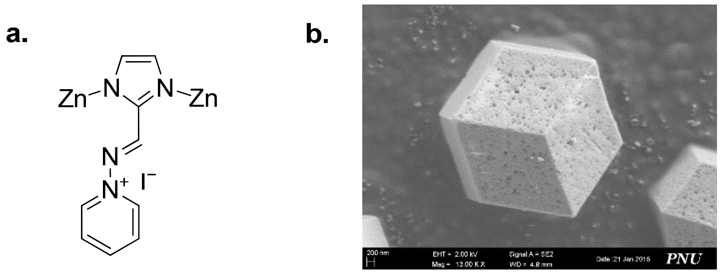
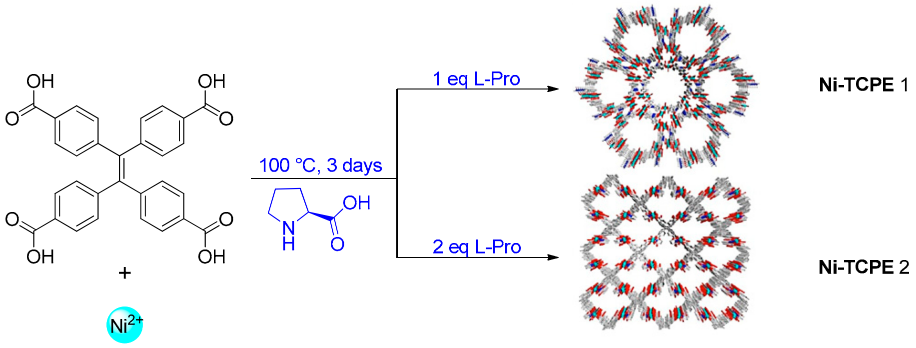


Figure 6. Schematic representation of the secondary building unit (SBU)/OL building unit of the ZIF-90 structure incorporating aminopyridinium iodide (IL-ZIF-90) in which the imidazole moieties coordinate the Zn centers and the aminopyridine iodide functionalities are incorporated as pendant (**a**). Scanning electron microscopy images of the IL-ZIF-90 solid (**b**). Adapted from Reference [77]. Copyright (2016) Royal Chemical Society.

Some attempts to construct different MOF-based architectures can be also found in literature. As an example, Duan et al. [80] reported the preparation of Ni-based single-walled metal–organic nanotubes using a tetrakis(4-carboxyphenyl)ethylene (TCPE) unit as a backbone (Scheme 20). The final assembled structure displays a tubular morphology with an exterior wall diameter of 3.6 nm and an internal section of 2.1 nm. Two tubular assemblies were obtained depending on the equivalent of L-proline (L-Pro) added in the synthesis mixture.



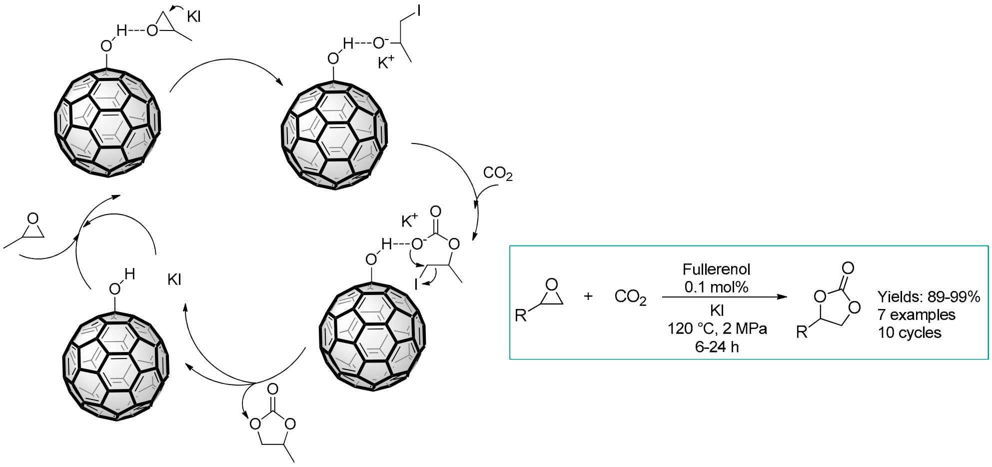
Scheme 20. Synthesis conditions and view of the two Ni-based single-walled metal–organic nanotubes. Adapted from Reference [80]. Copyright (2015) American Chemical Society.

The final solids displayed excellent catalytic activity in the conversion of carbon dioxide employing various epoxides as reactants, with Ni-TCPE-1 showing slightly better performances. All the catalytic reactions were performed at 100 °C in presence of 1.5 mol.% (with respect to the substrate) TBABr. Almost quantitative conversion and elevated turnover number (TON) were afforded for the synthesis of styrene carbonate after 12 h in presence of the best Ni-TCPE-1 catalyst. Moreover, the stability of the solid was proven in consecutive cycles. The slight loss of carbonate yield (99% at the first cycle and 85% at the fourth cycle) was attributed to the small amount of catalyst used.

2.3. Nanocarbon-Based Catalysts for CO_2 Conversion into Cyclic Carbonates

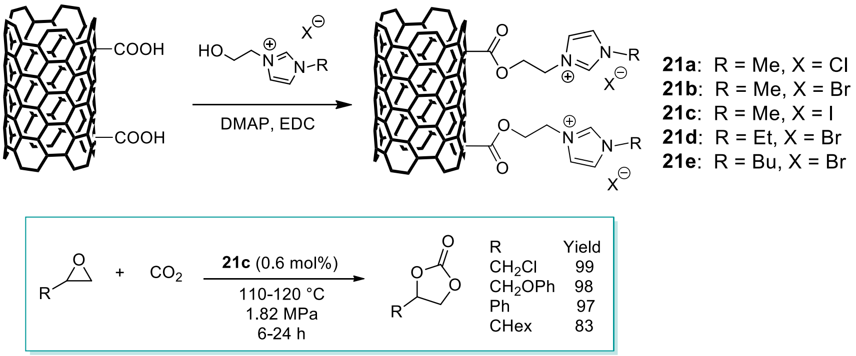
Carbon nanoforms (CNFs), or nanocarbons, represent a class of recent allotropes of carbon having nanometric dimensions whose functional properties strongly depend on the kind and tridimensional arrangements of their carbon atoms [81,82]. These nanomaterials can arrange into zero-, one-, two-, and three-dimensional (0D, 1D, 2D, and 3D) nanoobjects such as fullerene, carbon nanotubes, graphene, nanohorns, and nanodiamonds [83]. In the past few years, they were extensively studied in applications spanning photonics and optoelectronics, advanced electrodes, nanomedicine, etc. [84–88]. In recent years, CNFs emerged as suitable support for heterogeneous catalytic materials, due to their high chemical inertness, thermal stability, and mechanical resistance, along with an unconventional lightness [89]. In addition, CNFs are nanoobjects with well-defined structure and dimensions often displaying sharp size distribution, which allows for a homogeneous dispersion of the functionalities and active sites all over their surface, giving rise to reproducible properties. Furthermore, in given processes, CNFs participate in the catalytic cycle through specific interactions between the active catalyst or the substrates and the solid matrix via surface functionalities (e.g., acidic groups or other oxygenated groups) or by means of electronic interactions (e.g., π–π interactions) [90]. In this section, examples regarding the use of hybrid nanocarbons as catalysts in the chemical fixation of CO_2 to epoxides are highlighted, ordered from 0D to 3D CNFs.

In 2014, Cao, Song, and co-workers reported the synthesis of the fullerenol $C_{60}(OH)_{17}O_5 \cdot 28H_2O$, prepared via oxidation of C_{60} with ozone/hydrogen peroxide [91]. The fullerenol at ~0.06 mol.% was used as a heterogeneous catalyst for the synthesis of a series of cyclic carbonates, running the reactions at 120 °C with a CO_2 pressure of 2 MPa employing 1 mol.% KI as a co-catalyst for 5–24 h (Scheme 21). It is worth noting the synergetic effect of the two co-catalysts, since fullerenol or KI alone were not able to promote the title reaction, whereas their combination led to almost quantitative yields. TOFs of up to 1576 were obtained although without taking into account the presence of KI. The catalyst was easily recovered by centrifugation and reused in ten consecutive cycles with quite unchanged yields, showing high thermal and mechanical stability. A tentative mechanism was proposed in which fullerenol provides Lewis acid sites to activate the oxygen atom in the epoxide ring through hydrogen bonds, and the I^- anion operates a nucleophilic attack on the less sterically hindered carbon of the epoxide, resulting in ring opening. Then, the interaction between the alkoxy anion and CO_2 forms the corresponding alkyl carbonate anion, which gives rise to the cyclic carbonate through the intramolecular substitution of I^-.



Scheme 21. Mechanism of CO_2 fixation into epoxide catalyzed by KI and fullerenol.

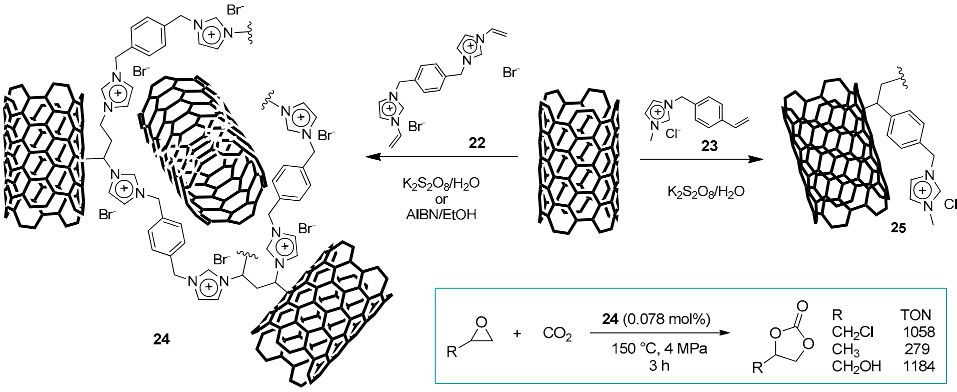
Carbon nanotubes possess high chemical and thermal stability, surface area, and tensile strength, and they are recently finding application in catalysis. In 2012, Park et al. employed oxidized multi-walled carbon nanotubes (MWCNTs) as support for immobilizing a series of imidazolium-based ionic liquids with different anions and alkyl chains through esterification of the carboxylic groups present on the nanotubes (Scheme 22) [92]. All the prepared hybrid materials featured high loading in ionic liquid (1.59–2.40 mmol/g) and showed good activity toward the cycloaddition of CO_2 to allyl glycidyl ether. Catalyst **21c** resulted as the most active and was applied for the conversion of a series of epoxides, being easily recycled five times with just a little loss in conversion.



Scheme 22. Imidazolium salts grafted onto carbon nanotubes for the synthesis of cyclic carbonates.

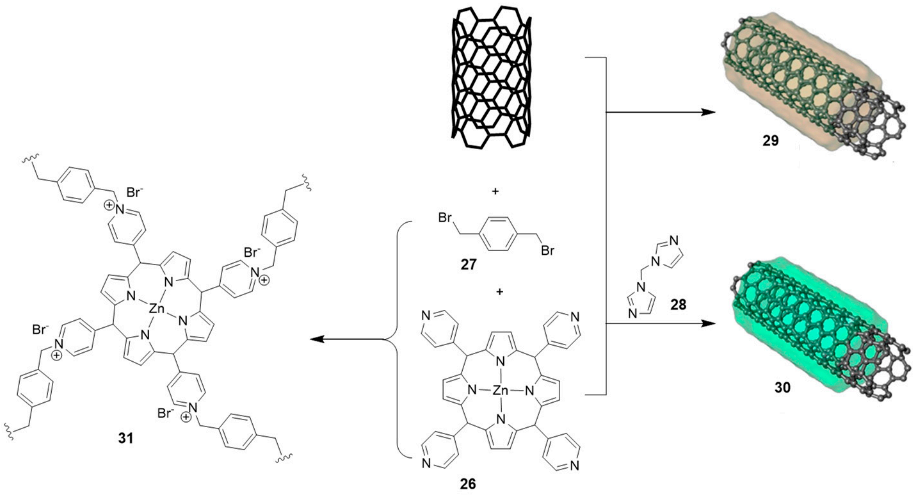
An analogous synthetic strategy was followed by Baj and co-workers for the preparation of MWCNTs endowed with quaternary ammonium salts, which displayed minor activity with respect to **21a–e** [93].

Another approach in order to immobilize ionic liquid like moieties onto carbon nanotube surfaces was recently reported by Gruttadauria, Aprile, and co-workers [94]. The direct radical polymerization of bis-vinylimidazolium chloride **22** and styryl imidazolium chloride **23** in the presence of single-walled carbon nanotubes (SWCNTs) gave rise to highly loaded SWCNT–polyimidazolium salt hybrids (Scheme 23) [94]. Raman spectra confirmed the covalent linking of polymer chains onto the nanotube surface and the Brunauer–Emmett–Teller (BET) specific surface area values were 100 $m^2 \cdot g^{-1}$ and 360 $m^2 \cdot g^{-1}$ for **24** and **25**, respectively. The hybrids were applied as catalysts in the conversion of carbon dioxide and a series of epoxides to the corresponding cyclic carbonates with a TON of up to 1184 and a TOF of 395 h^{-1} with no need for additional Lewis acid co-catalyst. Although both catalysts displayed analogous activity, **24** was easily reused for four runs with no deactivation, whereas **25** suffered significant leaching of polymer during the recycling.



Scheme 23. Single-walled carbon nanotube (SWCNT)–polyimidazolium salt hybrids **24** and **25** used as catalysts for the conversion of CO_2 and epoxides into cyclic carbonates.

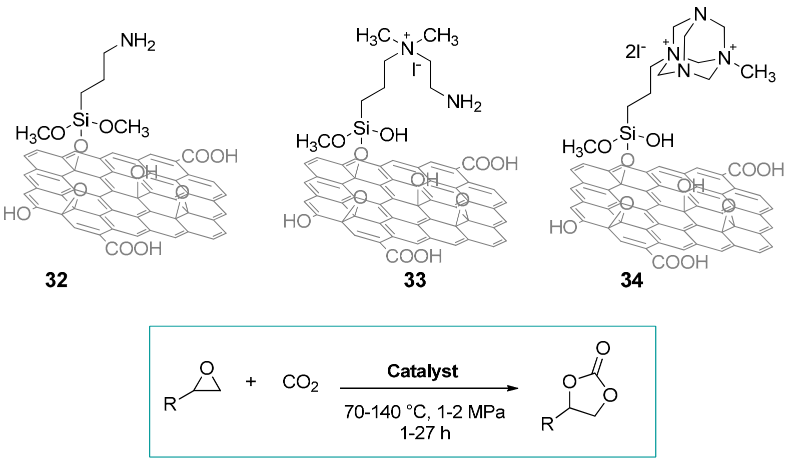
In 2017, Yang and co-workers followed a similar approach, supramolecularly coating MWCNTs with polyimidazolium bromide polymers, reacting 5,10,15,20-tetrakis(4-pyridyl)porphyrin zinc(II) **26**, 1,4-bis(bromomethyl)benzene **27**, and di(1H-imidazol-1-yl)methane **28** in the presence of CNTs (Scheme 24) [95]. In such a way, the obtained catalysts **29–31** displayed nucleophile bromide anions cooperatively working with the zinc(II) porphyrin as Lewis acids in the cycloaddition of epoxides and CO_2 under solvent-free conditions. The bifunctional materials showed enhanced catalytic activity, especially in comparison with the corresponding homogeneous counterpart, affording a TOF of up to 2602 h^{-1} with a substrate/catalyst ratio of 7100. Furthermore, after seven cycles, just minor loss of activity was shown with no leaching of Zn.



Scheme 24. Cationic porphyrin-based polymer-coated multi-walled carbon nanotubes (MWCNTs) **29** and **30** and MWCNT-free polymer **31** used for the synthesis of cyclic carbonates from CO_2 and epoxides.

Graphene oxide (GO) represents an ideal support material for catalysts thank to its 2D structure, which confers a high surface area. Moreover, once functionalized, GO may provide access to all the catalytic centers, avoiding mass transfer problems of the substrates. In addition, the presence in its structure of several oxygen-containing groups (–OH, –COOH, etc.) leads to a synergistic effect activating the CO_2 chemical fixation process by means of the instauration of hydrogen bonds with epoxide substrates. This fact was clearly demonstrated by Qu and co-workers, who used commercially available GO as a carbocatalyst (in the presence of DMF) for cyclic carbonate synthesis [96]. They found a direct correlation between the number of oxygenated groups and the catalytic activity of GO.

On the other hand, the oxygenated groups can be used as reactive species for the modification of GO with proper silanes. Condensation between 3-aminopropyltrimethoxysilane and GO gave the 3-aminopropyl-grafted GO **32**, which was used as a catalyst with the tetrabutylammonium iodide as a co-catalyst (TBAI) for the fixation of CO_2 into cyclic carbonates (Scheme 25) [97]. The presence of both oxygenated groups of GO and amine moieties afford several hydrogen-bonding donor sites able to provide a synergistic effect for the activation of CO_2 and epoxides. This robust and recyclable (up to seven cycles) heterogeneous catalytic system (**32**/TBAI 1 mol.%) allowed obtaining good results in terms of conversion into the corresponding cyclic carbonates using atmospheric pressure of CO_2 (0.1 MPa) at 100 °C in 27 h, although increasing CO_2 pressure up to 1 MPa permitted reducing the temperature and reaction time down to 70 °C and 12 h, respectively. Under these conditions, almost quantitative yields were obtained for a series of epoxides.

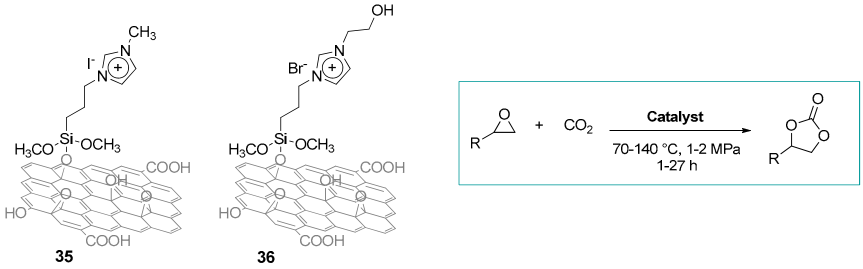


32 **33** **34**

Scheme 25. Modified graphene oxide (GO)-based hybrids for the synthesis of cyclic carbonates.

Yi, Yin, et al. reported the preparation through silylanization of two multi-functionalized catalysts **33** and **34** possessing quaternary ammonium iodide moieties (Scheme 25). These catalysts, characterized by the co-existence of quaternary ammonium salts, silanol groups, and primary (**33**) or tertiary amines (**34**), were designed for maximizing the synergistic effects between silanol groups and halide ions in activating the ring opening of the epoxides, while ensuring a good adsorption of CO_2 thanks to the action of amine groups with no need for supplementary co-catalysts [98,99]. Both catalysts allowed converting carbon dioxide into cyclic carbonates with an apparent similar catalytic activity within 4 h, using 2 MPa CO_2 at 120 °C for **33** and at 90 °C for **34**, and they were reused for five consecutive catalytic cycles without significant loss of activity.

Li et al. reported the preparation of a series of imidazolium-based IL grafted onto the surface of GO, used as active and recyclable catalysts for CO_2 cycloaddition to produce cyclic carbonates [100]. Hybrid material **35** endowed with iodide counteranions (Scheme 26) resulted as the best-performing catalyst (2 MPa pressure of CO_2 at 140 °C for 4 h), although 600 mg of modified GO were used for 15 mL of epoxide. It is worth noting that the fundamental role played in the co-catalytic process by the residual hydroxyl groups of GO acting as hydrogen-bond donors was highlighted, since their silylation resulted in a marked drop in the catalytic activity. The synergistic effect in accelerating the ring opening of epoxides by hydroxyl groups was further confirmed with the use of catalyst **36**, in which a hydroxyl functionalized IL was grafted onto GO (Scheme 26) [101]. In this case, higher conversions of propylene oxide into the corresponding carbonate were obtained with 0.35 mol.% catalyst at 140 °C in 4 h, showing the beneficial effect of hydroxyl groups in the imidazolium tag. Furthermore, it was possible to recycle catalyst **36** up to seven times without loss of activity.

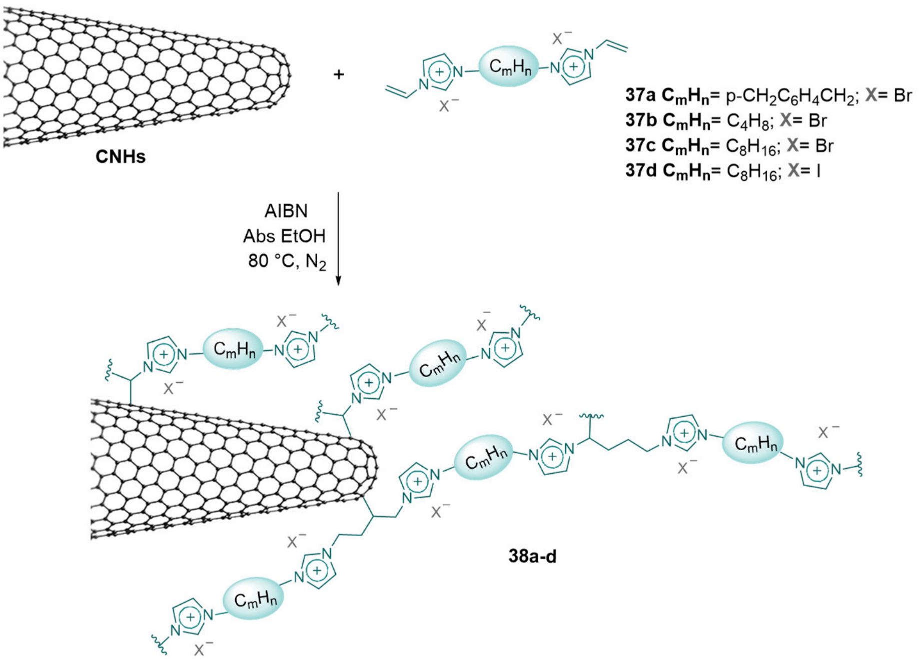


35 **36**

Scheme 26. Imidazolium-modified GO-based materials for the synthesis of cyclic carbonates.

Carbon nanohorns (CNHs) are an exotic nanocarbon constituted by graphene tubes closed with a horn-shaped tip with good thermal stability, micro- and mesoporosity, internal pore accessibility, and semiconducting properties. CNHs aggregate in a dahlia-like shape and they are very intriguing materials that share some features and chemistry resembling both that of fullerenes, due to the presence of the closed tips, and that of SWCNTs, thanks to their elongated shape [102].

The importance of the nanocarbon support of choice on the catalytic activity of the resulting hybrid was greatly evident when a series of polyimidazolium-functionalized CNHs was employed for the conversion of CO_2 and epoxides into cyclic carbonates [103]. These hybrid materials based on CNHs/cross-linked imidazolium salts were easily prepared using the direct radical polymerization of bis-vinylimidazolium salts **37a–d** in the presence of pristine CNHs (Scheme 27). CNH-based catalysts **38a–d** resulted as extremely active materials displaying an unprecedented increase in catalytic activity from the first to the sixth cycle in the reaction with styrene oxide (catalyst 0.22 mol.%, 4 MPa CO_2 at 150 °C for 3 h). In addition, a seventh cycle with epichlorohydrin resulted in an increased catalytic activity with respect to the first cycle with the same epoxide reaching a TON of up to 2819. The same behavior was not observed with the self-condensed polymer nor with the analogous SWCNT-based catalysts [94]. This finding was ascribed to the higher percentage of porosity of the reused catalyst that was probably caused by an additional cross-linking of residual double bonds during the catalytic reaction.



Scheme 27. Synthesis of imidazolium-functionalized carbon nanohorns (CNHs).

3. Conclusions

In the present review, we surveyed the development of heterogeneous catalytic systems for the conversion of carbon dioxide into valuable chemical products, namely cyclic carbonates. The environmental and societal impact of CO_2 emissions is receiving a lot of interest from both academia and industry. In this context, we gave a brief overview of an issue of paramount importance focusing on the one-pot reaction between carbon dioxide and epoxides. In particular, we report selected examples of hybrid materials based on mesoporous silicas, metal–organic frameworks, and carbon nanostructures as promising catalytic supports. Considering CO_2 mitigation as a global challenge, we hope that this work will encourage the development of novel ideas for the design and the application of recyclable catalytic systems with improved performance, leading to an optimization of the process.

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