

Review

Recent Achievements in the Synthesis of Cyclic Carbonates from Olefins and CO₂: The Rational Design of the Homogeneous and Heterogeneous Catalytic System

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Abstract: With the consumption of fossil fuels, the level of CO₂ in the atmosphere is growing rapidly, which leads to global warming. Hence, the chemical conversion of CO₂ into high value-added products is one of the most important approaches to reducing CO₂ emissions. Due to being simple, inexpensive and environmentally friendly, the direct synthesis of cyclic carbonates from olefins and CO₂ is a promising project for industrial application. In this review, we discuss the design of the homogeneous and heterogeneous catalytic system for the synthesis of cyclic carbonates from the reaction of olefins and CO₂. Usually, the catalyst contains the epoxidation active site and the cycloaddition active site, which could achieve the oxidation of olefins and the CO₂-insert, respectively. This review will provide a comprehensive overview of the direct synthesis of cyclic carbonates from olefins and CO₂ catalyzed by homogeneous and heterogeneous catalysts. The focus mainly lies on the rational fabrication of multifunctional catalysts, and provides a new perspective for the design of catalysts.

Keywords: CO₂; olefin; cyclic carbonate; oxidative carboxylation; catalyst design



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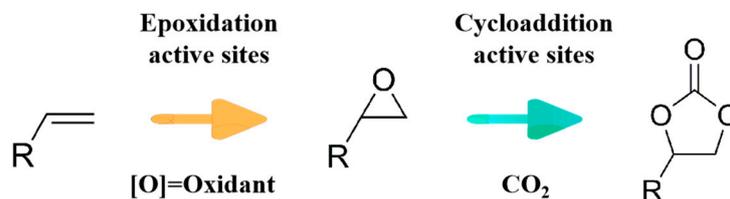
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1. Introduction

The use of CO₂ as a building block for the synthesis of high value-added chemicals has become an important current area of focus in CO₂ conversion [1]. As a cheap, non-toxic and renewable C1 resource, CO₂ has been successfully converted into many high value-added chemicals such as alcohols [2], carboxylic acids [3], formamides [4] and organic carbonates [5]. Considering environmental awareness and the atom-economic strategy, the direct synthesis of cyclic carbonates from CO₂ and epoxides may be an alternative way of utilizing CO₂. However, the high price of epoxides prevents the application of cycloaddition reaction of CO₂. As a result, direct one-pot preparation of cyclic carbonates from olefins and CO₂ has become an important issue for the conversion of CO₂ [6].

Recently, a lot of homogeneous and heterogeneous catalytic systems have been applied in the reaction of olefins and CO₂ [7]. Usually, these catalytic systems have two functionalized active sites: (i) the epoxidation active site for the oxidation of olefins; and (ii) the cycloaddition active site for the coupling reaction between epoxides and CO₂ (Scheme 1) [8,9]. However, how to design catalysts reasonably, and how to promote the synergistic catalysis effect, is a big challenge for the direct oxidative carboxylation between olefins and CO₂. Herein, we will try to give some suggestions on how to construct the multifunctional catalyst system in the synthesis of cyclic carbonates from olefins and CO₂.

This review will be divided into two major parts. The first part will give a summary of the homogeneous catalytic system in recent years, while the second part will focus on the heterogeneous catalytic system and the synergistic effect between the different catalytic moieties.

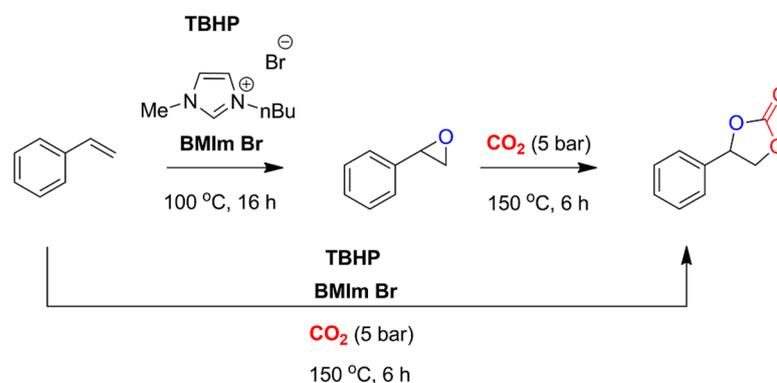


Scheme 1. Synthesis of cyclic carbonate from olefins and CO₂.

2. Homogeneous Catalytic System

2.1. Ionic Liquids Catalytic System

The straightforward synthesis of cyclic carbonates by direct oxidative carboxylation from olefins and CO₂ is a promising method of fixation and utilization of CO₂. Ionic liquids, with the advantages of negligible vapor pressure, unique solvation properties and the design-ability of anion and cation, have been widely used in the epoxidation and CO₂ cycloaddition [10–12]. However, constructing the multifunctional ionic liquids catalytic system with both catalytic ability for olefins epoxidation and CO₂ cycloaddition is still a big challenge. The direct formation of styrene carbonate (SC) from styrene and CO₂ by employing 1-*n*-butyl-3-methylimidazolium bromide (BMImBr) as the catalyst and tert-butyl hydroperoxide (TBHP) as an oxidant was achieved (Scheme 2) [13]. The one-pot reaction could give a moderate conversion and selectivity (Conv. 90% and Sel. 40%), while a slightly higher conversion and selectivity (Conv. 99% and Sel. 63%) could be obtained by the two-step reaction.



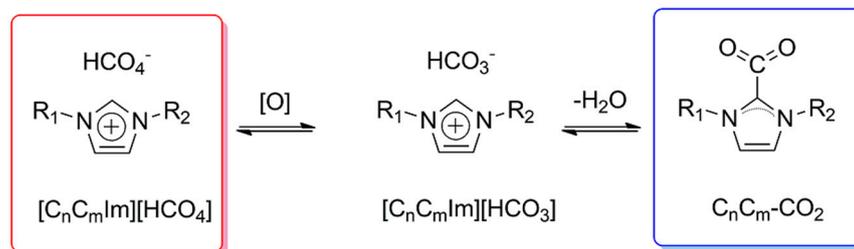
Scheme 2. Direct synthesis of cyclic carbonate from olefin and CO₂.

Due to the lack of the epoxidation active sites, the selectivity of styrene oxide is still low, which may significantly decrease the yield of SC. Considering that bicarbonate may react with hydroperoxide to form the active oxidant of peroxydicarbonate ion (HCO₄[−]) [14], Zhang et al. reported the synthesis of SC from styrene and CO₂ catalyzed by imidazolium hydrogen carbonate ionic liquids ([C_nC_mIm][HCO₃] ILs) [8]. Owing to the epoxidation active sites and cycloaddition active sites in [C_nC_mIm][HCO₃] (Scheme 3), the excellent yield of cyclic carbonates could be obtained by the one-pot reaction. Recently, Perosa et al. developed the tungstate assisted-tandem reaction system by combining ammonium tungstate ionic liquid catalyst ([N_{8,8,8,1}][WO₄]) and tetrabutyl-ammonium iodide ([N_{4,4,4,4}][I]), which could give a 94% yield of cyclic carbonate using H₂O₂ as oxidant under 10 bar CO₂ (Scheme 4) [15]. In contrast, aromatic and cyclic olefins such as styrene and cyclohexene suffered from easy overoxidation and consequent low selectivity towards the carbonates in the tungstate ionic liquid catalyst. Although the ionic liquids catalyst systems

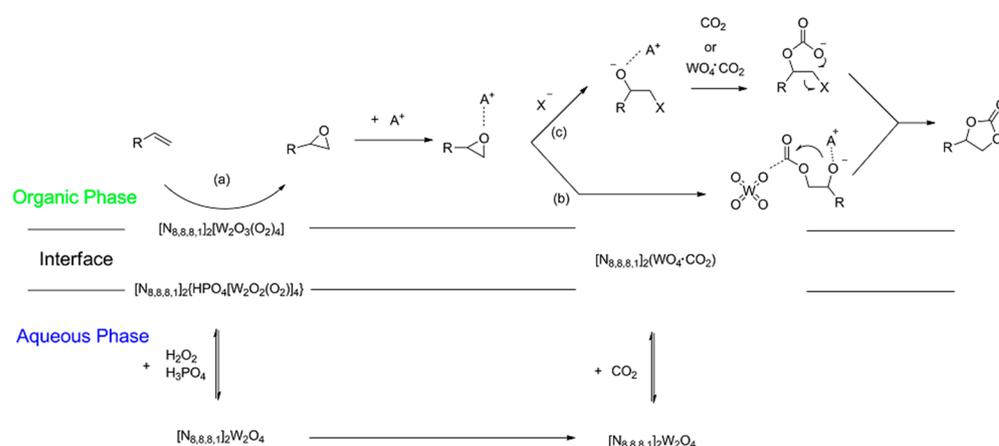
have good design ability, the development of highly efficient ionic liquids catalysts should be carefully designed.

Catalyst for epoxidation

Catalyst for cycloaddition



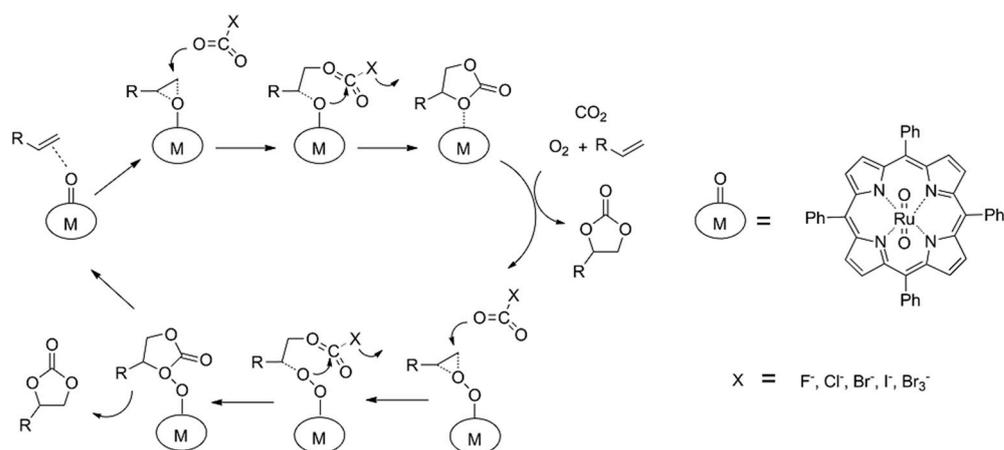
Scheme 3. The bifunctional catalyst of $[C_n C_m Im][HCO_3]$.



Scheme 4. Schematic representation of the main mechanistic pathways for the formation of cyclic carbonate. A^+ represents a Lewis acid or Brønsted acid.

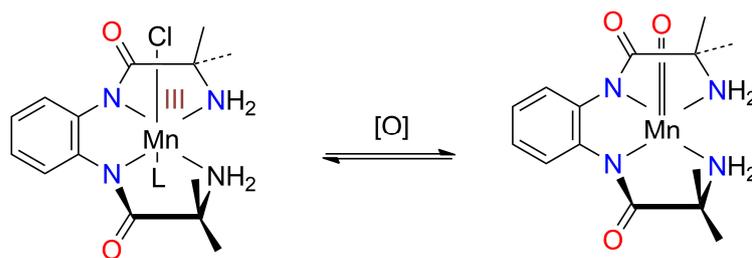
2.2. Metal Complex Catalytic System

It is well-known that some catalysts are inspired by nature and a lot of biological biomimetic catalyst has been applied in the olefin epoxidation reaction [16,17]. Hence, the direct oxidative carboxylation of olefins and CO_2 by a metal complex catalytic system seems to be an efficient method. Jing et al. reported the one-pot synthesis of synthesis carbonate from styrene, O_2 and CO_2 with dioxo(tetraphenylporphyrinato) ruthenium $[Ru(TPP)(O)_2]$ /quaternary onium salt [18]. The $[Ru(TPP)(O)_2]$ can transform the oxygen atom from the catalyst to form the epoxide which could act as a substrate for the coupling reaction with CO_2 (Scheme 5). It is well known that the selectivity of the epoxidation reaction has a great impact on the yield of cyclic carbonate. For example, the yield of styrene carbonate was only 3.6% with benzoic acid (55.3%) and benzaldehyde (37.5%) as major products when using a $Fe(TPP)Cl$ as a comparable catalyst [18]. However, the $Ru(Salen)(PPh_3)_2$ catalyst showed a 40.7% yield of styrene carbonate under the same conditions, which meant that the new active site of $Ru(Salen)(O)$ could generate from the $Ru(Salen)(PPh_3)_2$ in situ. As a result, the suitable oxidative property and coupling property in the catalyst may play an important role in the catalyst design.



Scheme 5. Proposed mechanism of aerobic oxidative carboxylation of olefins.

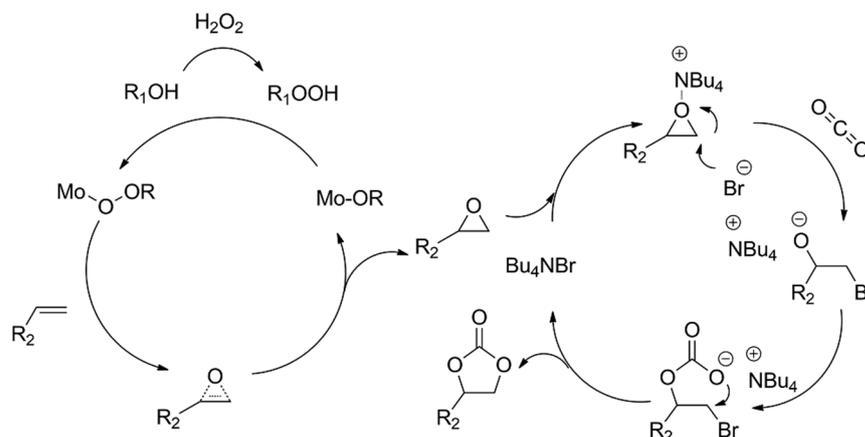
The functionalization of the ligand of metal-complex could have a great effect on the conversion and selectivity of the reaction, which could be an alternative method to optimize catalyst design. Ghosh et al. developed a manganese (III) complex of an amido-amine ligand/tetrabutylammonium bromide (TBAB) catalytic system, which could efficiently convert the alkene to the epoxide and further react with CO₂ to form cyclic carbonate in the presence of CO₂ and TBHP [19]. The high selectivity of the epoxide may originate from the transformation of the manganese (III) complex of an amido-amine ligand to a non-heme high-valent manganese-oxo intermediate in situ (Scheme 6). Besides, the Lewis acidity in the manganese (III) complex could also accelerate the CO₂ cycloaddition reaction. Based on recent research, the one-pot synthesis of cyclic carbonate catalyzed by the biomimetic transition metals (such as Fe, Mn, Ru) catalytic systems usually includes two parts. Firstly, the metal center is oxidized to form the oxo species, which could act as an intermediate to oxidize the olefin. Secondly, the coupling reaction between the epoxides and CO₂ is conducted. Although the homogeneous catalytic system showed excellent activity in the olefins epoxidation and CO₂ cycloaddition respectively, the integration of the epoxidation active sites and cycloaddition active sites is not easy work.



Scheme 6. Structure of manganese (III) complex of an amido-amine ligand and high-valent manganese-oxo intermediate.

In addition to the biomimetic transition metals, selective epoxidation of olefins by alkyl hydroperoxide catalyzed by d⁰ transition metal complexes (Mo(VI), V(V) and Ti(IV)) has been used in the epoxidation reaction [20]. Hu et al. found that a MoO₂(acac)₂-quaternary ammonium salt catalytic system could achieve the direct synthesis of cyclic carbonates from olefins and CO₂ with TBHP as an oxidant [21]. The one-pot synthesis of cyclic carbonates contained two separate reactions catalyzed by the different active sites. During the epoxidation process, the formation of the alkyl-peroxo M-OOR intermediate could coordinate with the olefin to form a three-membered transition state (Scheme 7). After the transformation of oxygen from M-OOR to olefin, epoxide could be obtained. In the following cycloaddition process, the oxygen atom of the epoxide was activated by the [n-Bu₄N]⁺ cation of the TBAB and then the nucleophilic Br⁻ attacked the less hindered

carbon atom of the epoxide to form an oxygen anion intermediate. The oxygen atom of the oxygen anion intermediate nucleophilic attacked the carbon atom of CO₂ affords the alkyl carbonate intermediate, which was stabilized by the [n-Bu₄N]⁺ cation. Finally, the cyclic carbonate was obtained after the ring closure reaction and the catalyst and TBAB were regenerated.



Scheme 7. The proposed mechanism of the oxidative carboxylation of olefins catalyzed by the MoO₂(acac)₂/TBHP-TBAB system.

Table 1 summarizes the homogeneous catalytic system for the conversion of olefins and CO₂ to cyclic carbonates. Compared with the different homogeneous catalyst systems, it is found that using the polyoxometalates or metal complexes may be a benefit for the epoxidation reaction and the quaternary ammonium salts may promote the cycloaddition reaction (Table 1, entries 3 and 4). Although ionic liquids have good design ability and can integrate the epoxidation active site and cycloaddition active site into one catalyst, the yield of cyclic carbonates must continue to improve (Table 1, entries 1 and 2). Interestingly, we found that the reaction temperature had a significant influence on the yield and selectivity of cyclic carbonates during the one-pot reaction [8]. With the increasing temperature, the selectivity of cyclic carbonates is decreasing, which indicates that the high temperature is not beneficial for the epoxidation reaction, and the main byproduct is benzaldehyde. If benzaldehyde is formed, the subsequent CO₂ cycloaddition cannot take place. Besides, the pressure of O₂ is also an important reaction parameter. The high pressure of O₂ may lead to over-oxidation and the byproducts such as benzaldehyde, benzoic acid and acetophenone [19]. As we know, the CO₂ cycloaddition is hard to achieve, which means that the CO₂-insert reaction is unfavorable under low pressure of CO₂. However, further increasing the pressure of CO₂ may decrease the yield of cyclic carbonates. Hence, utilization of O₂ as an oxidant and without the addition of a co-catalyst is still a huge change for the direct oxidative carboxylation between olefins and CO₂.

Table 1. The direct oxidative carboxylation of olefins catalyzed by the homogeneous catalytic system.

Entry	Catalyst	Co-Catalyst	Oxidant	CO ₂ (bar)	T (°C)	t (h)	Conv. ^a (%)	Sel. ^b (%)	Yield ^c (%)	Ref.
1	BMIImBr	–	TBHP	5	150	6	90	40	36	[13]
2	[C ₁ C ₄ Im][HCO ₃]	–	TBHP	20	65	30	91.2	82.3	75.1	[8]
3 ^d	[N _{8,8,8,1}] ₂ [WO ₄]	[N _{4,4,4,4}]I	H ₂ O ₂	1	85	3/5	–	–	94	[15]
4	[Ru(TPP)(O) ₂]	TBAI	O ₂	11	30	48	–	–	89	[18]
5	Fe(TPP)Cl	TBAI	O ₂	11	30	48	–	–	3.6	[18]

Table 1. Cont.

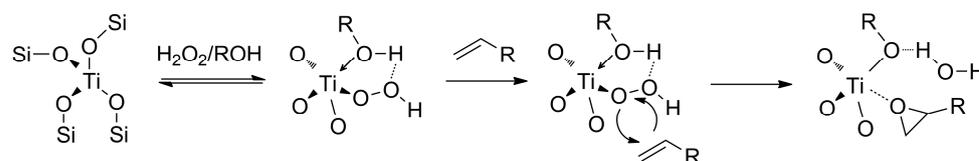
Entry	Catalyst	Co-Catalyst	Oxidant	CO ₂ (bar)	T (°C)	t (h)	Conv. ^a (%)	Sel. ^b (%)	Yield ^c (%)	Ref.
6	Ru(Salen)(PPh ₃) ₂	TBAI	O ₂	11	30	48	–	–	40.7	[18]
7	Mn(III)-complex	TBAB	TBHP	17	100	6	–	–	43	[19]
8 ^e	MoO ₂ (acac) ₂	TBAB	TBHP	30	100/140	1/1	–	–	68	[21]

^a Conversion of styrene. ^b Selectivity towards styrene carbonate. ^c Yield of styrene carbonate. ^d substrate: 1-decene, the reaction performed at 85 °C for 3 h followed by the raw addition of [N_{4,4,4,4}]I and CO₂ without any intermediate work-up. The reaction was further performed for 5 h. ^e 100 °C and 1 h for epoxidation reaction and 140 °C and 1 h for cycloaddition reaction.

3. Heterogeneous Catalytic System

3.1. Zeolite Catalytic System

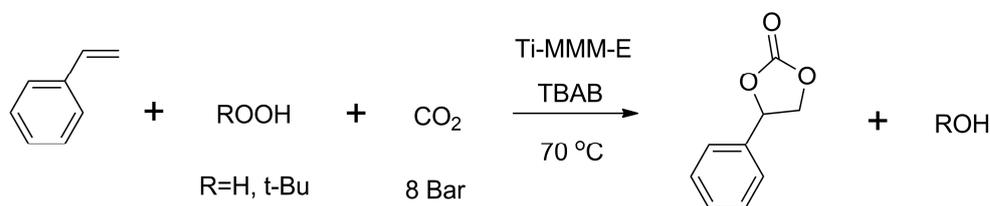
Due to the facile and efficient recovery of the catalyst from the reaction mixture, the heterogeneous method has shown enormous potential in industrial application. Zeolites, the microporous crystalline materials, attract a lot of attention in catalysts due to their tunable catalytic properties and shape selectivities [22]. Recent studies have found that a series of titanosilicate sieves (TS-1 [23], Ti-Beta [24], Ti-MWW, etc. [25]) reveal excellent selective oxidation during the epoxidation reaction. The real active sites of the oxidation reaction could be ascribed to the transformation of the tetrahedrally coordinated titanium atoms to Ti-OOH species [26,27], which may further react with olefins to selectively produce the epoxides (Scheme 8). After adding co-catalyst or functionalized modification of the titanosilicate sieves, the direct oxidative carboxylation of olefins and CO₂ can proceed. Srivastava et al. first reported the synthesis of cyclic carbonates from olefin, oxidant (H₂O₂ and TBHP, respectively) and CO₂ catalyzed by the microporous titanium-silicalite-1 (TS-1) and mesoporous Ti-MCM-41 [28]. With Ti-MCM-41/TBHP and 4-dimethylaminopyridine (DMAP) as a co-catalyst, a 33% yield of SC can be obtained under 6.9 bar CO₂ and 120 °C through two steps reaction. He et al. prepared a quaternary ammonium modified delaminated titanosilicate (Del-Ti-MWW-N⁺Bu₃Br[−]) which gave a moderate yield (48% for cyclic carbonate) in a one-pot reaction using H₂O₂ as an oxidant [29]. However, the pore blocking by heavy byproducts may lead to a decrease in catalytic activity and selectivity. Therefore, the development of highly efficient, easily recyclable and hierarchical porous catalysts for the direct synthesis of cyclic carbonates from olefins and CO₂ may overcome these problems.



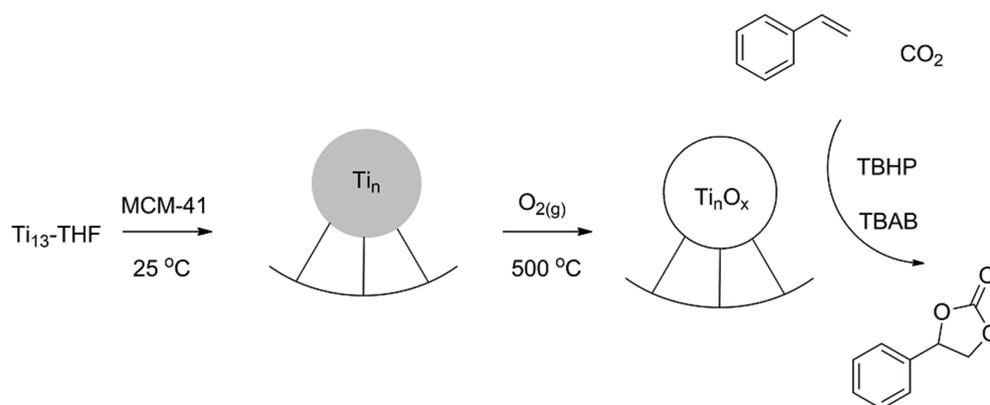
Scheme 8. Ti active sites and proposed mechanism for the epoxidation of olefins.

Because mesoporous materials have a larger pore size than microporous materials, some researchers have designed many mesoporous titanium-silicates applications in oxidative carboxylation of olefins with oxidants and CO₂ [20]. For example, Kholdeeva et al. prepared a mesoporous titanium-silicates Ti-MMM-E by evaporation-induced self-assembly (EISA) method [30]. The mesoporous titanium-silicates Ti-MMM-E exhibited superior catalytic performance in the one-step oxidation carboxylation of styrene and 4-methylstyrene with TBHP, TBAB and CO₂ under mild conditions (Scheme 9). Moreover, it was found that bromide ions in TBAB may occupy the Lewis acid sites and prevent styrene oxide from further oxidation to benzaldehyde in the presence of TBHP and Ti-MMM-E. To avoid pore blocking, Kholdeeva et al. explored a new method to prepare titanium-grafted mesoporous silica catalysts by metallic titanium clusters deposition on silica supports [31]. The non-single-site Ti(IV)_nO_x-like silica-supported catalyst (Ti_xO_n-MCM-41 and Ti_xO_n-MMM-2) from Ti₁₃ metal clusters deposited onto ordered mesoporous silicas showed a high yield

of cyclic carbonate. Compared with the traditional titanium-silicates, these grafted Ti_nO_x -silica materials had better accessibility to titanium active sites exposed on the surface of the catalyst (Scheme 10).

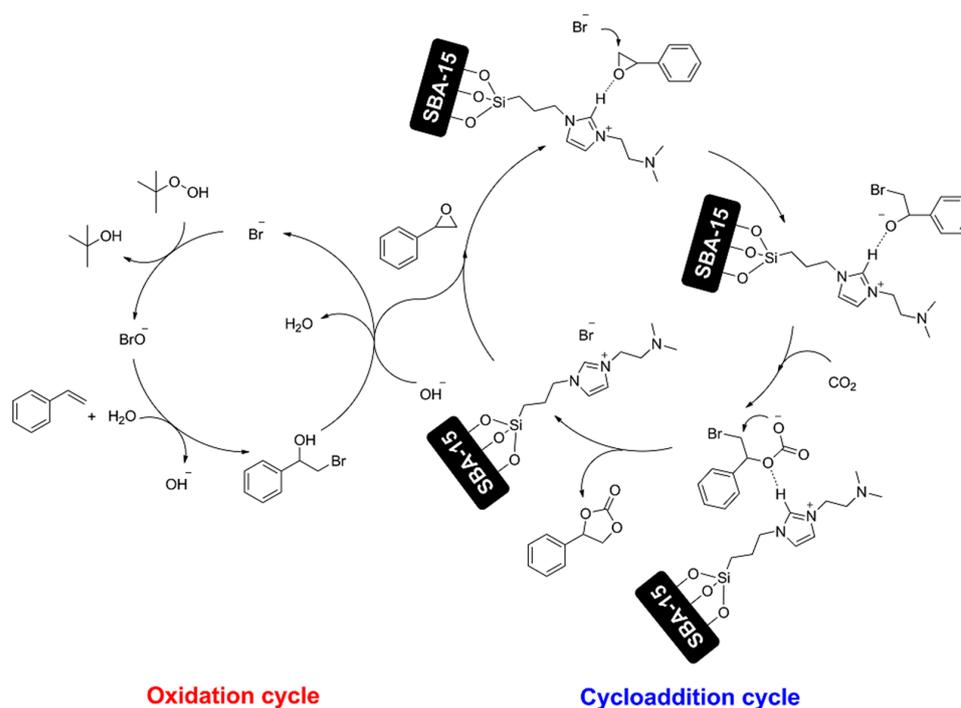


Scheme 9. Oxidative carboxylation of styrene over Ti-MMM-E.



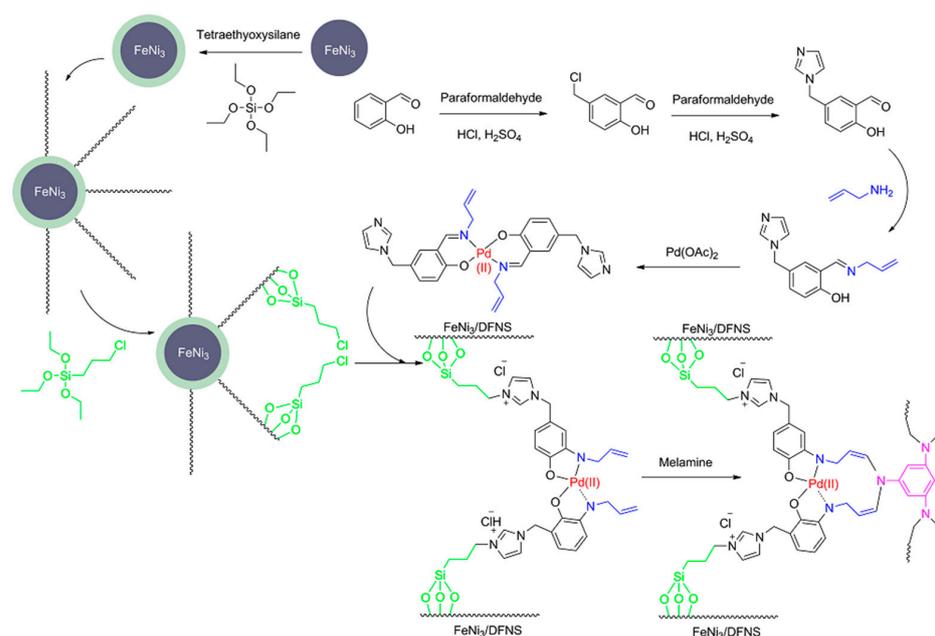
Scheme 10. Preparation sequence for Ti_nO_x -MCM-41 and the oxidative carboxylation of styrene over titanium-grafted mesoporous silica catalyst.

As we know, large pore size molecular sieves are beneficial for the substrate diffusion and the dispersion of the active sites. Since the well-ordered hexagonal mesoporous silica structures (SBA-15) with uniform pore sizes were discovered by Zhao et al. [32], SBA-15 has attracted increasing attention and is considered an important class of nanostructured support materials in heterogeneous catalysis [33]. Xu et al. reported amino-functionalized ILs@SBA-15 catalysts ($N(\text{CH}_3)_2\text{-[Im][Br]@SBA-15}$), which showed impressive catalytic activity for the one-pot synthesis of cyclic carbonates from olefins and CO_2 [34]. The dual function of the $N(\text{CH}_3)_2\text{-[Im][Br]@SBA-15}$ could not only catalyze the oxidation of olefins but also promote the CO_2 cycloaddition reaction (Scheme 11). In the oxidation cycle, Br^- was first oxidized by TBHP to hypobromite (BrO^-), which could act as an active [O] site to react with styrene to form bromohydrin. After the deprotonation of bromohydrin, styrene oxide was obtained, which was activated by the C2-H on the imidazole ring via the hydrogen bond interaction. Then the C-O bond in the styrene oxide caused polarization. Meanwhile, Br^- nucleophilic attached the less hindered carbon atom of the styrene oxide, forming an oxyanion intermediate. Subsequently, CO_2 may interact with the oxyanion intermediate to form a new alkyl carbonate compound. The cyclic carbonate can be obtained via the intramolecular ring-closure process. As a result, the synergistic effects between Br^- and $N(\text{CH}_3)_2\text{-[Im][Br]}$ effectively promoted the direct oxidative carboxylation reaction of olefins and CO_2 .



Scheme 11. Possible mechanism for the oxidative carboxylation of styrene and CO₂ over N(CH₃)₂-[Im][Br]@SBA-15.

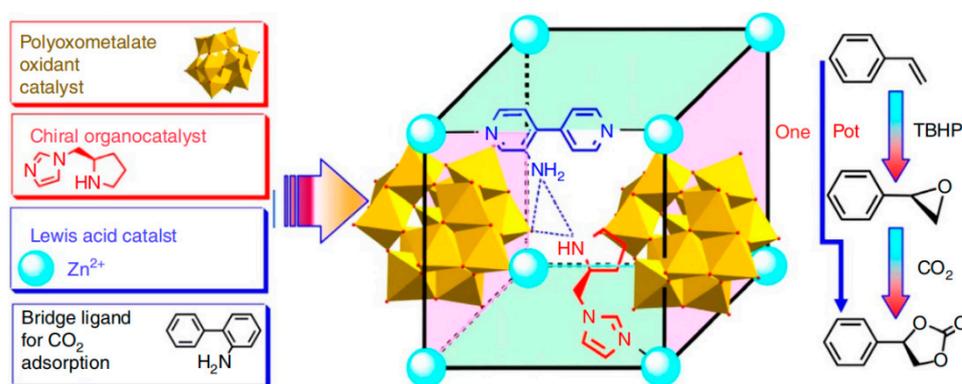
Dendritic fibrous nanosilica (DFNS), with the properties of morphology-controlled and intrinsic mesoporous characteristics, have been widely used in catalysis, gas capture, solar-energy harvesting, energy storage, and so on [35]. Sadeghzadeh et al. developed a melamine-Pd(II) Schiff base complex functionalized FeNi₃/DFNS core-shell NPs (FeNi₃/DFNS/salen/Pd(II) MNPs) (Scheme 12), which showed 94% yield of styrene carbonate even after 10 runs [36]. Recently, Motavalizadehkakhky et al. applied the DFNS-supported platinum (II) complexes (DFNS/Pt(II) NPS) in the synthesis of cyclic carbonate from olefins and CO₂ [37]. It was found that the Pt(II) complex in the DFNS played an important role in the direct oxidative carboxylation of CO₂ and styrene to styrene carbonate.



Scheme 12. Schematic illustration of the preparation of the FeNi₃/DFNS/salen/Pd(II) MNPs.

3.2. MOFs Catalytic System

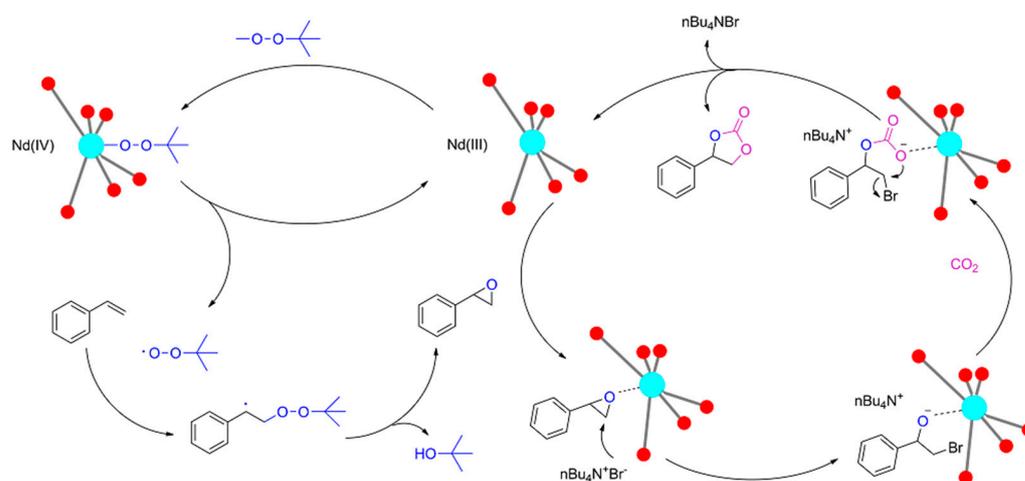
Metal-organic frameworks (MOFs), as a new kind of porous materials with high crystalline, high metal content, large surface area and tunable pore structure, have shown great potential applications in gas storage [38], energy storage [39] and catalysis [40]. Some pioneering research has been reported in the olefins epoxidation reaction and CO₂ cycloaddition reaction respectively [41–45]. The direct synthesis of cyclic carbonates from olefins and CO₂ catalyzed by MOFs usually contained two parts, including the epoxidation reaction and cycloaddition reaction [46]. As a result, combining these two reactions into one functionalized MOFs catalyst may not only avoid the co-catalyst but also promote the conversion and selectivity. Duan et al. used MOF as support and incorporated a pyrrolidine moiety as a chiral organocatalyst and a polyoxometalate as an oxidation catalyst (ZnW-PYIs, ZnW: ZnW₁₂O₄₀⁶⁻) for the direct synthesis of cyclic carbonates from olefins and CO₂ (Scheme 13) [47]. The oxygen-enriched surface of ZnW₁₂O₄₀⁶⁻ could accelerate the transformation of the catalytic precursors to the active intermediate of the epoxidation [48]. Meanwhile, pyrrolidine-2-yl-imidazole (PYI) could act as a cooperative catalytic site, which may enhance the activities of the oxidants and drive the catalysis asymmetrically [49]. Based on the synergistic effect, 72–92% yields of cyclic carbonates and 55–80% enantiomeric excesses were obtained with styrene and its derivatives in the presence of TBHP and TBAB. Compared with the polyoxometalate, Mn-porphyrin is also a suitable candidate for epoxidation reaction [50]. Nagaraja et al. constructed a 3D Mn(II)-porphyrin metal-organic framework ([{Mn₂(TCPP)·2H₂O}·DMF]_n, TCCP = 5,10,15,20-tetrakis(4-benzoate)porphyrin), which showed excellent selective capture of CO₂ and further transformed CO₂ and olefins to cyclic carbonates [51]. The non-metallated porphyrin linker in the [{Mn₂(TCPP)·2H₂O}·DMF]_n can adsorb two CO₂ molecules by the interaction of CO₂ and the pyrrole -N-H groups of the porphyrin linker through the -N-H—O=C=O bond. Moreover, the implantation of Fe(III) ions in the [{Mn₂(TCPP)·2H₂O}·DMF]_n can give 98% conversion of styrene with about 65% selectivity for cyclic carbonate under mild conditions. Similarly, Li et al. developed a molybdenum (VI) oxide incorporated cooperative catalyst (CuMo-BPY: Cu₃(μ₃-OH)₂(4,4'-BPY)(MoO₄)₂), which exhibited catalytic activity for the synthesis of cyclic carbonates through the two-step catalytic process [52]. The spatial matching between the Mo(VI) and alkaline μ₃-OH tricopper (II) cores could provide the compatibility with the Mo=O-activated epoxidation intermediate during the epoxidation reaction. In the CO₂ cycloaddition reaction, the μ₃-OH tricopper (II) core could increase the adsorption of CO₂ with the formation of a bidentate bridge or tridentate linear adsorption state [53], which could promote the CO₂-insertion reaction. Hence, improving the adsorption or desorption property of a catalyst can significantly influence the catalytic activity [54].



Scheme 13. The schematic representation of tandem catalysis for the asymmetric cyclic carbonate transformation from olefins and carbon dioxide.

The rational design of multifunctional MOFs can achieve selective capture and conversion of CO₂ under mild conditions [55], but combining CO₂ capture with its conversion is

still a problem. Recently, Nguyen et al. prepared lanthanide-based metal-organic frameworks (MOF-590 and MOF-591), which showed good adsorption of CO₂ [56]. Additionally, MOF-590 revealed excellent catalytic activity for the one-pot oxidative carboxylation of olefins with CO₂. Usually, the oxidative carboxylation of styrene and CO₂ catalyzed by the MOF-590 consisted of two steps, including the epoxidation catalyzed by MOF-590/nBu₄NBr-TBHP and the cycloaddition catalyzed by MOF-590/nBu₄NBr (Scheme 14). The Nd³⁺ clusters of MOF-590 were first oxidized to Nd⁴⁺-peroxy species and Nd⁴⁺-peroxy species released a t-butoxy radical to oxidize styrene to obtain the styrene oxide through the peroxy intermediate [42]. Secondly, the styrene oxide was first coordinated by the Nd unit in the MOF-90 and the C-O bond in the styrene oxide was polarization and elongated. Then Br[−] attacked the less steric hindrance C atom in the styrene oxide forming the metal-coordinated bromoalkoxide intermediate, which was stabilized by the Nd unit. The metal-carbonate intermediates were formed by the insertion of CO₂ into the metal-coordinated bromoalkoxide intermediate. After the ring-closing reaction, styrene carbonate was formed and the MOF-590 and nBu₄NBr were regenerated.



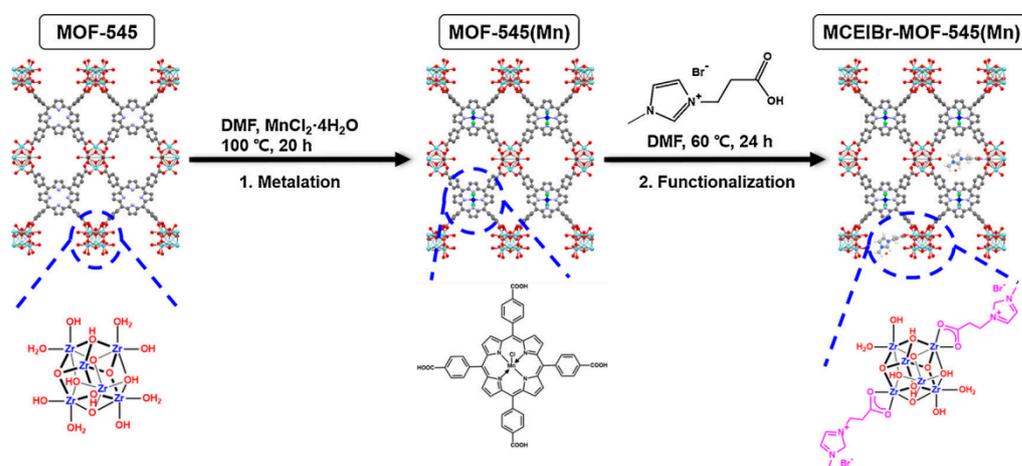
Scheme 14. Proposed mechanism for the oxidative carboxylation of styrene and CO₂ catalyzed by MOF-590.

To avoid the addition of a co-catalyst, Ahn et al. constructed a zirconium-based porphyrinic MOF-545 (Zr₆O₈(H₂O)₈(H₂-TCPP)₂) using a tetrakis(4-carboxyphenyl) porphyrin (H₂-TCPP) ligand and Zr₆ clusters, followed by Mn(III) metalation to the porphyrin units for the epoxidation reaction (Scheme 15) [57]. Then, 1-methyl-3-(2-carboxyethyl)imidazolium bromide (ImBr) ionic liquid was introduced to the Zr₆ clusters forming ImBr-functionalized MOF-545(Mn) (ImBr-MOF-545(Mn)) for the CO₂ cycloaddition reaction. The MOF-545 could act as a support platform that integrated the Lewis acidic Mn(III)/Zr(IV) ions and Br[−] in the adjacent position and exhibited a high yield of cyclic carbonates in the absence of any co-catalyst under mild reaction conditions.

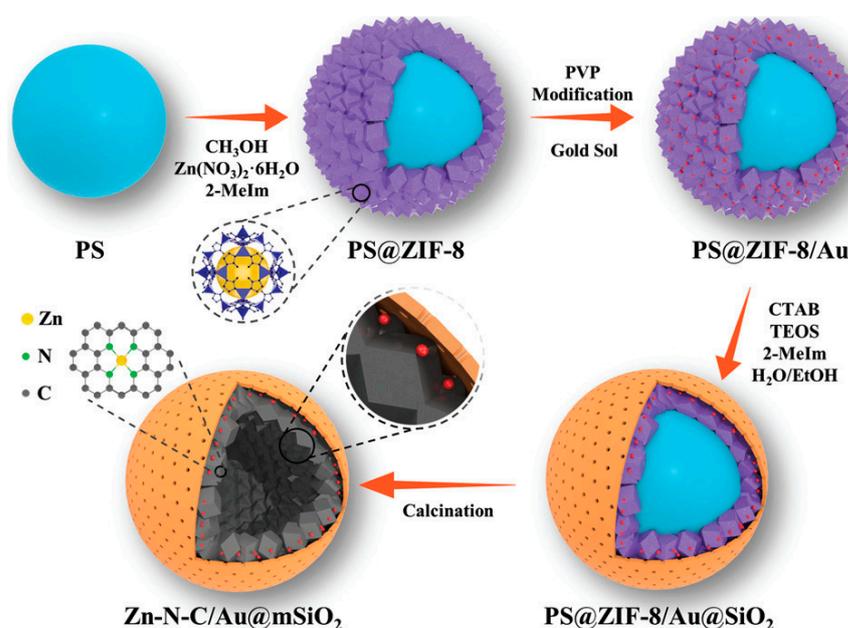
3.3. Metal Nanoparticles Catalytic System

Metal nanoparticles (NPs) or single-atom catalytic sites (SACs) have been widely used in a variety of catalytic reactions due to their excellent activity [58,59]. For example, Sun and co-workers prepared a series of Au-supported catalysts which could synthesize the cyclic carbonates from olefins and CO₂ [60,61]. They applied the Au/SiO₂-ZnBr₂/Bu₄NBr catalyst system for the preparation of cyclic styrene carbonate from styrene and CO₂ [60], which could give a 42% selectivity towards cyclic styrene carbonate under mild reaction conditions (80 °C, 1 MPa CO₂). Moreover, it was found that cumene hydroperoxide was a better oxidant than Bu₄NBr, indicating that choosing the suitable oxidation may have a significant effect on the yield of styrene carbonate. Using a strong basic resin R201 as support to replace the SiO₂, a 51% yield of styrene carbonate was obtained in the Au/R201

catalyst with anhydrous TBHP as an oxidant. The different catalytic activity between the Au/SiO₂-ZnBr₂/Bu₄NBr and Au/R201 catalyst may originate from the different particle sizes of Au nanoparticles, which may play important role in the epoxidation reaction. The work function of Au species with different atomicity is strongly dependent on the particle size [58]. The appropriate size of Au nanoparticles could enhance the selectivity of epoxides during the epoxidation reaction [62]. Recently, Zhang et al. fabricated a double-shell microencapsulated nanoreactor as a bifunctional catalyst for the one-pot synthesis of cyclic carbonates from olefins [63]. Au nanoparticles (NPs) were confined between an inter shell of nitrogen-doped porous carbon rich in Zn single-atom catalytic sites (SACs) and an outer shell of mesoporous SiO₂ (noted as Zn-N-C/Au@mSiO₂, Scheme 16). The synergistic catalysis of the ultrafine Au NPs and Zn SACs showed high catalytic efficiency and tandem catalytic function for the direct oxidative carboxylation from olefins and CO₂.



Scheme 15. The synthetic procedure of ImBr-MOF-545(Mn) by post-synthetic Mn metalation followed by ImBr ionic liquid functionalization.

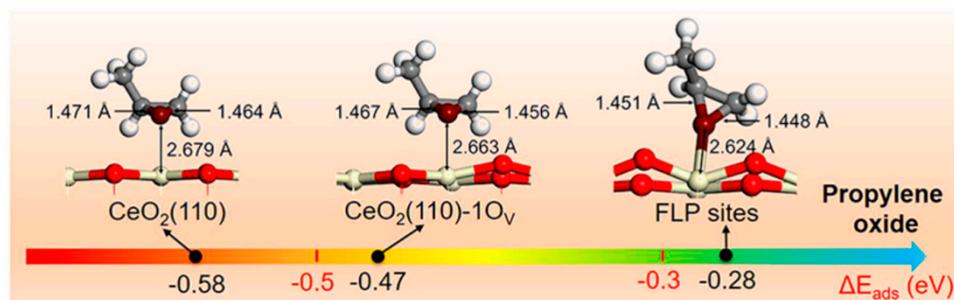


Scheme 16. Synthesis procedure of Zn-N-C/Au@mSiO₂.

3.4. Others

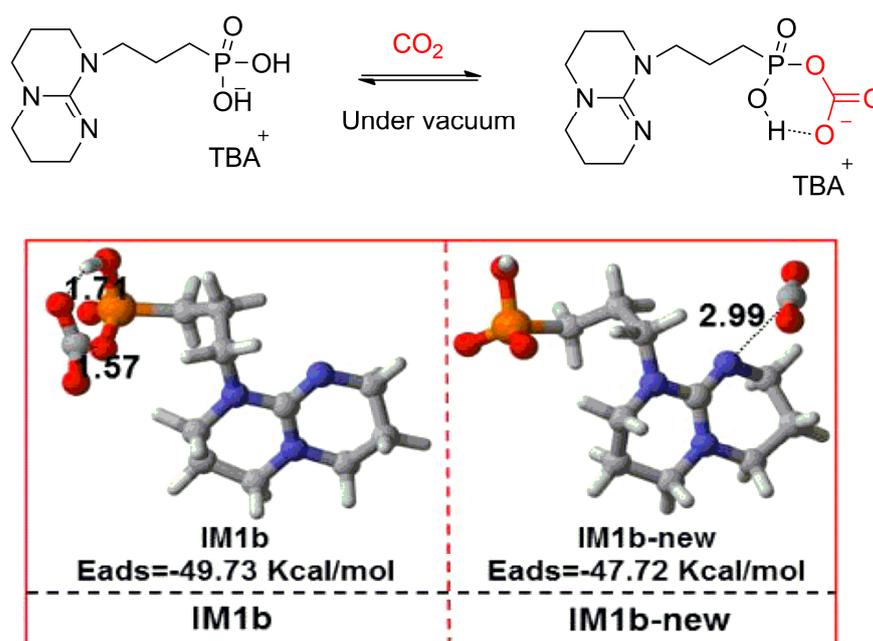
Frustrated Lewis pairs (FLPs) are combinations of Lewis acids and Lewis bases that are prevented from forming a stable adduct by steric or electronic hindrance [64].

Due to the sterically hindered Lewis acid and Lewis base, the FLPs have shown the ability in the activation and transformation of inert small molecules such as H_2 and CO_2 [65–67]. Qu et al. reported a defect-enriched CeO_2 with constructed interfacial FLPs (two adjacent $Ce^{3+} \cdots O^{2-}$), which could activate CO_2 via the interactions between C/Lewis basic lattice O^{2-} and the two O atoms in CO_2 /two adjacent Lewis acidic Ce^{3+} ions [68]. When increasing the surface of CeO_2 , an 88% yield of styrene carbonate can be obtained catalyzed by porous nanorods of CeO_2 (PN- CeO_2) under $80^\circ C$ and 24 h. The excellent performance of the selective tandem conversion of olefins and CO_2 to cyclic carbonates may derive from the efficient CO_2 activation for cycloaddition and weakening of the adsorption of in situ-produced epoxides to suppress their hydrolysis (Scheme 17).



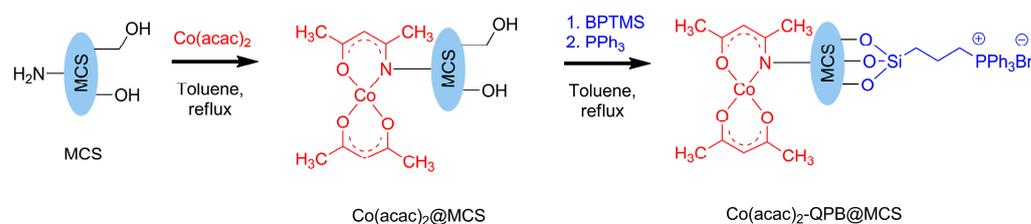
Scheme 17. Adsorption energy of propylene oxide on defective $CeO_2(110)$.

Hou et al. prepared the 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) functionalized phosphonate salts with different cations and applied them in the synthesis of styrene carbonate from styrene and CO_2 [69]. Experiment and DFT calculation demonstrated that TBA-TBD-P (TBA: tetrabutylammonium salts) could capture CO_2 by organic phosphate anion sites and the adsorption energy of TBA-TBD-P at phosphonate was ~ 2 Kcal/mol lower than that of the TBA-TBD-P with CO_2 being absorbed in nitrogen atom of TBD ring (Scheme 18). The formation of carboxyphosphate intermediate may be a crucial active intermediate species, which plays a key role in CO_2 activation and conversion. The TBA-TBD-P/ $ZnBr_2$ catalyst system showed a 69.6% yield of cyclic carbonates under mild conditions (0.1 MPa CO_2 , $80^\circ C$) with TBHP as an oxidant.



Scheme 18. The reaction procedure of TBA-TBD-P with CO_2 and calculated two different ways of activating CO_2 on TBA-TBD-P.

Considering the utilization of “carbon-neutral” resources, using a biomass-based catalyst for the synthesis of styrene carbonate from styrene and CO₂ may be a green and sustainable method. Due to the abundant hydroxyl groups in the biomass-based catalyst (such as cellulose, chitosan and lignin), these biomass-based catalysts have been applied in the CO₂ cycloaddition reaction [5,70–72]. Although the biomass-based catalysts exhibit excellent catalytic activity for the CO₂ cycloaddition reaction, how to introduce the epoxidation active sites in the biomass-based catalysts and achieve the direct synthesis of cyclic carbonates remains a big challenge. Jain et al. Fabricated magnetically separable chitosan (MCS) modified with Co(II) acetylacetonate and triphenylphosphonium bromide catalyst (Co(acac)₂-QPB@MCS) for the direct synthesis of cyclic carbonates from olefins and CO₂ with O₂ as an oxidant (Scheme 19) [73]. They used chitosan as a support platform to combine the epoxidation active site (cobalt(II) acetylacetonate complex, Co(acac)₂) and the cycloaddition active site (quaternary triphenylphosphonium bromide, P⁺Ph₃Br), which could achieve 73.1% yield of styrene carbonate. However, the yield of styrene carbonate was lower when using QPB@MCS alone or a physical mixture of Co(acac)₂@MCS and QPB@MCS (1:1) as a catalyst, which indicated that the covalent grafting of Co(acac)₂ and P⁺Ph₃Br moieties to MCS showed obvious synergistic catalytic effect during the one-pot reaction.



Scheme 19. Synthesis procedure of Co(acac)₂-QPB@MCS.

Table 2 summarizes the heterogeneous catalytic system for the conversion of olefins and CO₂ to cyclic carbonates. It is found that most of the heterogeneous catalyst with good yields and selectivity towards the cyclic carbonates usually includes two important parts: (i) a high selectivity epoxidation active site for the oxidation of olefins, (b) the Lewis acid and base sites for the CO₂ cycloaddition reaction (Table 2, entries 10–17). In addition, the suitable catalyst support with high surface area, controllable pore size, and the easy diffusion of substrate molecules can accelerate the direct oxidative carboxylation of olefins with CO₂ (Table 2, entries 4–9). Interestingly, some of the heterogeneous catalysts integrating the different catalytic moieties show a higher catalytic activity than the physical mixture of the different catalytic moieties, which indicates that the stereoconfinement effect and the distribution of the different active sites can efficiently stabilize and transform the intermediates and promote the reaction (Table 2, entries 10–17).

Table 2. The direct oxidative carboxylation of olefins catalyzed by the heterogeneous catalytic system.

Entry	Catalyst	Co-Catalyst	Oxidant	CO ₂ (bar)	T (°C)	t (h)	Conv. ^a (%)	Sel. ^b (%)	Yield ^c (%)	Ref.
1 ^d	TS-1	DMAP	H ₂ O ₂	6.9	60/120	24/4	54.6	55.6	–	[28]
2 ^d	TiMCM-41	DMAP	TBHP	6.9	60/120	24/4	44.0	83.4	–	[28]
3 ^e	Del-Ti-MWW-N ⁺ Bu ₃ Br [−]	–	H ₂ O ₂	20	40/140	1/6	–	–	48	[29]
4	Ti-MMM-E	TBAB	TBHP	8	70	48	92	70	–	[30]
5	Ti _n O _x -MCM-41	TBAB	TBHP	8	70	48	89	40	–	[31]

Table 2. Cont.

Entry	Catalyst	Co-Catalyst	Oxidant	CO ₂ (bar)	T (°C)	t (h)	Conv. ^a (%)	Sel. ^b (%)	Yield ^c (%)	Ref.
6	Ti _n O _x -MMM-2	TBAB	TBHP	8	70	48	81	51	–	[31]
7	N(CH ₃) ₂ -[Im][Br]@SBA-15	–	TBHP	10	80	28	>99	–	79	[34]
8	FeNi ₃ /DFNS/sale/Pd(II) MNPs	aniline	TBHP	20	80	10	–	–	98	[36]
9	DFNS/Pt(II) NPS	aniline	TBHP	20	100	10	–	–	97	[37]
10	ZnW-PYIs	–	TBHP	5	50	120	–	–	92	[47]
11	[[Mn ₂ (TCPP)·2H ₂ O]·DMF] _n	TBAB	PhIO	8	50	24	47.3	39.3	–	[51]
12	Fe@[[Mn ₂ (TCPP)·2H ₂ O]·DMF] _n	TBAB	PhIO	8	50	24	98.6	65.3	–	[51]
13 ^f	CuMo-BPY	TBAB	TBHP	5	50/50	48/48	–	–	90	[52]
14	MOF-590	TBAB	TBHP	1	80	10	93	94	87	[56]
15	MOF-591	TBAB	TBHP	1	80	10	95	85	81	[56]
16	MOF-592	TBAB	TBHP	1	80	10	98	82	80	[56]
17	ImBr-MOF-545(Mn)	–	O ₂	5	60	10	99.1	94.8	–	[57]
18	Au/SiO ₂	TBAB/ZnBr ₂	CHP	10	80	4	76	42	–	[60]
19 ^g	Au/R201	–	TBHP	40	80/150	3/4	98.0	–	50.6	[61]
20	Zn-N-C/Au@mSiO ₂	TBAB	TBHP	1	80	12	93.2	–	92.9	[63]
21	PN-CeO ₂	TBAB	TBHP	20	80	20	81	93	–	[68]
22	TBA-TBD-P	ZnBr ₂	TBHP	1	80	10	99.2	70.2	69.6	[69]
23	Co(acac) ₂ -QPB@MCS	–	O ₂	30	100	4	95.2	73.1	69.6	[73]

^a Conversion of styrene. ^b Selectivity towards styrene carbonate. ^c Yield of styrene carbonate. ^d 60 °C and 24 h for epoxidation reaction and 120 °C and 4 h for cycloaddition reaction. ^e 40 °C and 1 h for epoxidation reaction and 140 °C and 6 h for cycloaddition reaction. ^f 50 °C and 48 h for epoxidation reaction and 50 °C and 48 h for cycloaddition reaction. ^g 80 °C and 3 h for epoxidation reaction and 150 °C and 4 h for cycloaddition reaction.

The reaction parameters such as oxidant, temperature and CO₂ pressure can significantly affect the activity and selectivity for both the epoxidation and cycloaddition reaction during the oxidative carboxylation of styrene. Usually, the organic oxidants (such as TBHP, CHP and PhIO) exhibit higher activity than H₂O₂ or O₂. For example, the oxidation of TBHP can enhance the interaction with the substrate and react with the catalyst forming the main driver of epoxidation [52]. Besides, the high temperature is a disadvantage in improving the selectivity of the epoxidation process. Hence, the low temperature is usually used for the epoxidation reaction (Table 2, entries 1–3, 13 and 19). However, the high temperature benefits the activation of CO₂ during the CO₂ cycloaddition reaction [29]. The high temperature of the direct oxidative carboxylation of olefins may lead to the over-oxidation of styrene oxide and polymerization of styrene [57]. It is found that the higher cyclic carbonates can be obtained with a higher initial CO₂ pressure (Table 2, entries 8 and 9). The higher CO₂ pressure can enhance the contact between CO₂ molecules and substrate, so it is necessary to develop the catalyst with a higher CO₂ capture capacity.

4. Conclusions and Perspectives

The direct oxidative carboxylation of olefins with CO₂ is an economic and sustainable strategy for the synthesis of cyclic carbonates. However, the one-pot reaction usually contains two different reactions: (i) the epoxidation reaction; (ii) the CO₂ cycloaddition

reaction and the optimal reaction conditions of these two reactions are obvious different. For example, the optimal reaction conditions of the epoxidation reaction are 50 °C with TBHP as an oxidant (Table 2, entry 19). However, the optimal reaction conditions of the CO₂ cycloaddition reaction can be obtained at 150 °C with 40 bar CO₂. Hence, how to combine these two different reactions into a one-pot reaction may be a huge challenge. Although utilization of two different catalysts can achieve the one-pot reaction, the low conversion and selectivity may prevent the large-scale reaction (Table 2, entries 1, 2 and 4–5). As a result, the integration of two different catalytic sites into one catalyst may be an alternative method to avoid the problems mentioned above (Table 2, entries 17 and 23).

In this review, we carefully investigate the method in the design of the homogeneous and heterogeneous catalytic system for the direct oxidative carboxylation of olefins with CO₂. Considering the oxidation reaction is the first step, the effectively transferring active [O] atom from oxidation to olefins via the epoxidation active site may play a significant role in the selectivity of the epoxides (Schemes 3 and 6). Compared with the TBHP, the use of H₂O₂ or O₂ as oxidation is safe and environmentally sustainable. However, using H₂O₂ or O₂ as oxidation needs well-designed epoxidation active sites such as POMs or Mn-porphyrin (Table 2, entries 10 and 17). The effective activation and transformation of active [O] species are important for the epoxidation reactions. For example, the high selectivity of epoxidation reaction with H₂O₂ as oxidation must activate H₂O₂ without radical production (Table 2, entry 3 and Scheme 8). The heterolytically cleaved the O-O band was a benefit for the epoxidation reaction. For the CO₂ cycloaddition reaction, the catalyst should both have the Lewis acid and Lewis base sites, which could activate the epoxides and CO₂ respectively (Table 2, entry 21). However, CO₂ is hard to convert due to its thermodynamically stable and kinetically inert. As a result, a high temperature or CO₂ pressure is used in the CO₂ cycloaddition reaction. However, a high temperature may affect the oxidation reaction in the first step because some by-products (acid or aldehyde) can be found at a higher temperature (Table 2, entries 1–3, 13 and 19). Therefore, the integration of the suitable epoxidation active site and cycloaddition active site into a porous material could be a benefit for the direct oxidative carboxylation of olefins with CO₂.

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