Catalytic Processes for Chemical Conversion of Carbon Dioxide into Cyclic Carbonates and Polycarbonates

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Abstract: Chemical fixation of CO_2 has received much attention because CO_2 is the most inexpensive and renewable carbon resource from the viewpoint of green chemistry and atom economy. The kinetic and thermodynamic stability of CO_2 molecule presents significant challenges in designing efficient chemical transformations based on this potential feedstock. Currently, cyclic carbonates and polycarbonates are both valuable products, and the coupling of CO_2 and epoxides is one of the most promising and eco-friendly methods for chemical conversion of CO_2 into cyclic carbonates and/or polycarbonates. In this review, we will mainly discuss the synthesis of polycarbonates or cyclic carbonates catalyzed by metal-salen complexes through adjusting the architecture of the ligands and optimizing reaction conditions, such as temperature, pressure, co-catalysts, epoxide concentration. Furthermore, the recent progress for the synthesis of cyclic carbonates *via* the coupling reactions of epoxides and CO_2 mediated by both homogeneous and heterogeneous catalysts is particularly reviewed.

Keywords: Chemical conversion, carbon dioxide, polycarbonate, cyclic carbonate, Metal-salen complex, homogeneous/heterogeneous catalyst.

INTRODUCTION

Since petroleum resources are predicted to be exhausted at the current rate of consumption, there is an ever-growing effort to develop new chemical processes using renewable

one of the promising methodologies in the utilization of CO_2 is the transformation of CO_2 into valuable polycarbonates and /or cyclic carbonates (Scheme **1**). Polycarbonates have a series of particular properties including strength, lightness,
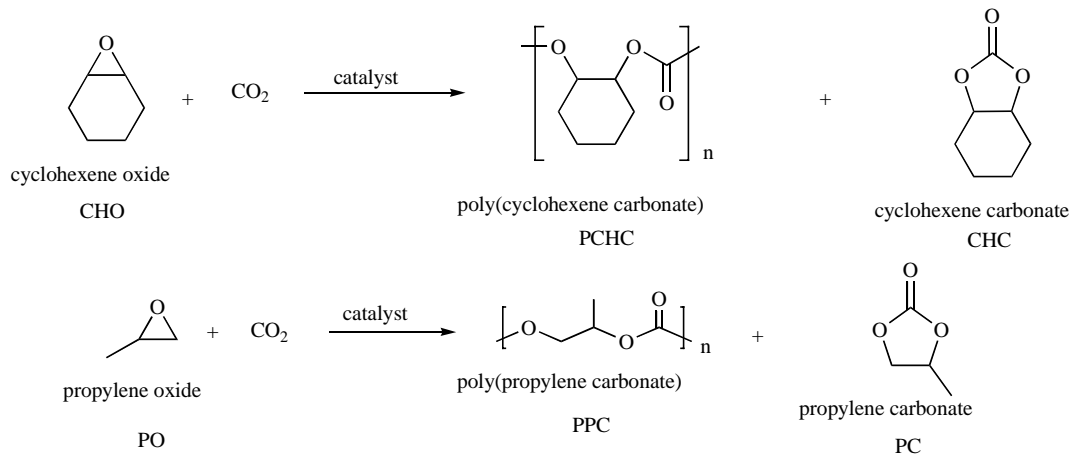
Scheme 1. Coupling of CO_2 and epoxides to afford polycarbonates and /or cyclic carbonates.

resources [1]. Carbon dioxide is drawing particular interest because it is an abundant, inexpensive, nontoxic and typical renewable resource [2]. The highly versatile nature of CO_2 has been exploited in numerous industrial applications, although the thermodynamic stability of CO_2 also hampered its utility as a reagent for chemical synthesis [3]. Particularly,

durability, high transparency, heat resistance, biodegradability and good electrical insulation; and being easily processed and colored. Therefore, these materials have been widely used in electronics, optical media, glazing and sheeting, the automotive industry, the medical and healthcare industry, and many other consumable goods [4a, b]. In addition, poly(propylene carbonate) (PPC) with high ether linkage content (80% ether) has shown excellent solubility in super-critical CO_2, a rare property for non-fluorinated polymers [4c]. On the other hand, organic cyclic carbonates such as ethylene carbonate and propylene carbonate (PC) are widely

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used for various purposes, for instance, electrolytic elements of lithium secondary batteries, polar aprotic solvent, monomers for synthesis of polycarbonates, and chemical intermediates for preparing medicines or agricultural chemicals [5].

Recently, much effort has been devoted to the coupling reaction of epoxide with CO_2 because of two important products produced in this reaction, *i.e.* cyclic carbonate and polycarbonate. As we known, there is a competitive direction towards formation of polycarbonates or cyclic carbonates (Scheme **1**). And the selectivity to polycarbonates or cyclic carbonates generally depends on the catalysts, additives, temperature, pressure, epoxide concentration. On the other hand, PPC could decompose uniformly and controllably to propylene carbonate below 250 ^{o}C, making it particularly useful as a binder for ceramics, adhesives, and propellants [6]. As for catalysts, the copolymerization is mainly catalyzed by (salen)-metal, whereas the cycloaddition is usually promoted by so-called Lewis-acidic and basic bifunctional catalysts such as quaternary ammonium and phosphonium salts, ionic liquids, Cs-loaded zeolite and alumina, lanthanide oxychloride, main-group and transition-metal complexes, and alkali metals salts [8]. Although great progress in fixation of CO_2 and epoxide has been made, only one specific review by Darensbourg [8d] in 1996 was reported. The aim of this review is to demonstrate the synthesis of polycarbonates or cyclic carbonates catalyzed by (salen)-metal through adjusting the architecture of the ligands and optimizing reaction conditions, such as temperature, pressure, co-catalysts, epoxide concentration. Furthermore, the recent progress for the synthesis of cyclic carbonates *via* the coupling reactions of epoxides and CO_2 mediated by both homogeneous and heterogeneous catalysts is particularly reviewed. Please note that this is a brief discussion on this topic, rather than a comprehensive account for developments in the area; thus, we apologize in advance to anyone who believes their contributions have been omitted.

## (SALEN)-METAL CATALYSTS FOR THE SELECTIVE FORMATION OF POLYCARBONATES OR CYCLIC CARBONATES

The production of five-membered cyclic carbonates from CO_2 has been industrialized since the 1950s. However, many new methodologies have been still developed. Especially, the fixation of the CO_2 by (salen)-metal complexes has seen significant progress. And (salen)-metal catalysts originally evolved from the metal porphyrinate catalysts. Typically, (salen)-metal offers following advantages: 1) salen ligands are easily synthesized in contrast to porphyrins; 2) the modular construction of salens from diamines and salicyladehydes enables easily tuning of steric and electronic properties. Accordingly, metal-salen catalysts are widely used for the fixation of CO_2 with epoxides. The origin of the metal-catalyzed copolymerization of carbon dioxide and epoxides could be traced back to the seminal work of professor Inoue and co-workers [7]. They employed several dihydric sources, such as water, resorcinol, dicarboxylic acids, and primary amines, in combination with $ZnEt_2$ for copolymerization of PO and CO_2. Although the activities of the initial catalytic systems were low, their work stimulated the development in this important area. Thus, many groups commit themselves to salen-catalyzed polymerization reaction, such as Kuran's, Soga's, Coates's, Darensbourg's group and etc. [8]. Herein,

we would like to demonstrate selective reactions of CO_2 with epoxides towards copolymerization or cycloaddition controlled through different metal-salen complexes systems employed.

(Salen)Cr for the coupling of CO_2 and epoxides

The utilization of Cr-salen complexes was inspired by Jacobsen's success with their application in asymmetrically ring-opening reactions of epoxides [9]. Mechanistically, Jacobsen showed a key reaction step is the formation of a chromium–alkoxide bond through a bimetallic initiation process. Subsequently, if CO_2 could insert into this type of bond, the utilization of (salen)Cr^{III} complexes as a cycloaddition or copolymerization catalyst would be reasonable.

For the coupling of CO_2 and epoxides to provide cyclic carbonates, Nguyen's group [10] first used a series of (salen)Cr complexes (**1a** to **1d**, Fig. (**1**)) with (dimethylamino)pyridine (DMAP) as catalysts for synthesis of cyclic carbonates. Compound **1d** exhibited the highest catalytic activity among all the catalysts. And the reactions were carried out at approximately 0.34 MPa of CO_2 pressure and 75-85 ^{o}C in the presence of 1 equiv of DMAP with TOFs (turnover frequency) ranging from 127-254 h^{-1}.
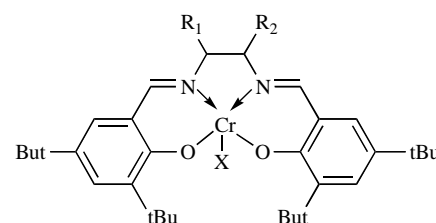
1a: R^1 and R^2 = trans - $(CH_2)_4$ -, X = Cl
1b: R^1 = CH_3, R^2 = H, X = Cl
1c: trans, R^1 = R^2 = Ph, X = Cl
1d: meso, R^1 = R^2 = Ph, X = Cl
1e: R^1 = R^2 = H or $(CH_2)_4$ -, X = Cl or N_3
1f: R^1 = R^2 = H, trans - $(CH_2)_4$ - or Ph, X = NO_3

Fig. (1). (Salen)Cr catalysts for the coupling of CO_2 and epoxides.

Then, García and co-workers [11] successfully realized the separation of the catalysts from the reaction mixture and the reuse of the (salen)-metal catalyst in the coupling reaction of CO_2 and epoxides to provide cyclic carbonates. As shown in Fig. (**2**), the supported catalysts were prepared by grafting the active species similar to **1a** onto an insoluble support like silica. The reaction was carried out under supercritical conditions (10 MPa and 80 ^{o}C) in the presence of Et_3N or N-methyl-imidazole (10 μl) with approximate 100 % selectivity and moderate yields. Baiker's group [12] also reported the similar strategy to perform catalysts recycling.

On the other hand, many groups such as Jacobsen [13], Kruper [14], Holmes [15], and Darensbourg [16] devoted themselves to the development of copolymerization of epoxides and CO_2 utilizing (salen)Cr as a catalyst. Particularly, Darensbourg's group developed the air-stable, effective chiral catalyst (**1a**) for the coupling of cyclohexene oxide and carbon dioxide to afford poly(cyclohexene carbonate) (PCHC), along with a small quantity of its *trans*-cyclic carbonate. The TON (turnover number) and TOF increased by over 3-fold upon adding of 5 equiv of the Lewis base cocata-
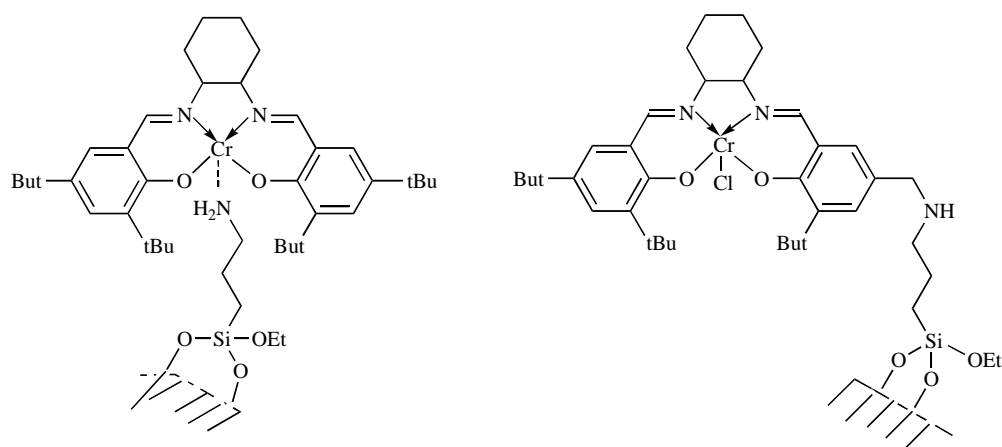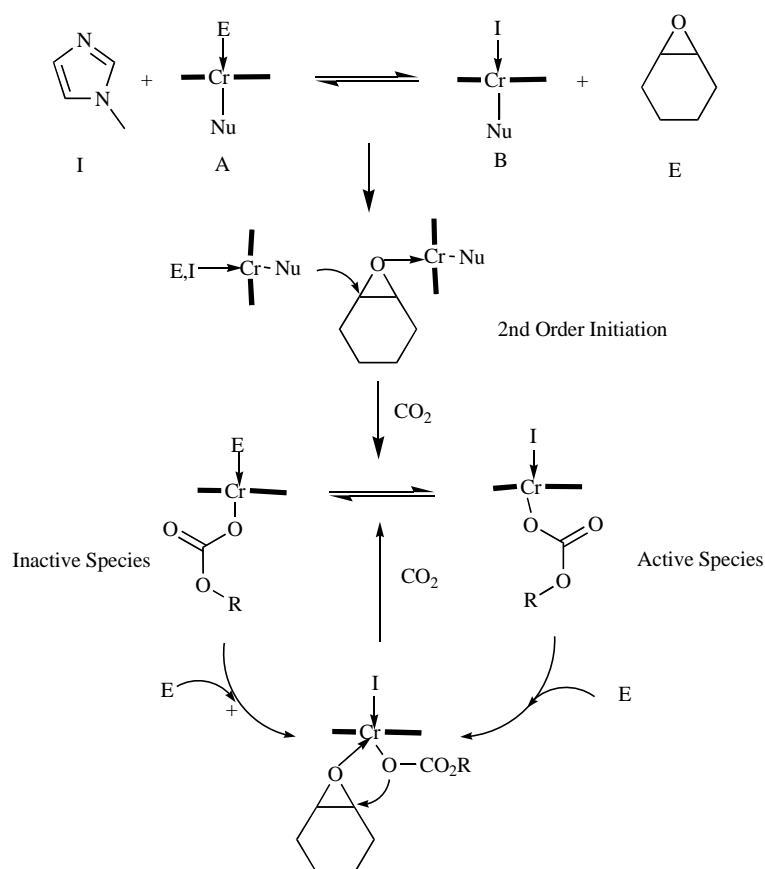
Fig. (2). Silica supported (salen)Cr.

Scheme 2. Mechanism for copolymerization.

lyst, such as *N*-methyl imidazole. They also proposed a detailed mechanism as shown in Scheme **2**, wherein the rate of copolymerization is dictated by two separate equilibria. The first equilibrium involves the initial second-order epoxide ring opening and is inhibited by excess amounts of co-catalyst. The second equilibrium involves the propagation step and is enhanced by excess co-catalyst. This gives the co-catalyst both a positive and negative effect on the overall rate of copolymerization [16].

In order to further understand copolymerization process, Darensbourg's group studied the role of the initiator and co-

catalyst [17], the effects of the substituents on the salen ligand, co-catalyst loading [16a] and the pressure of carbon dioxide [18]. First, the rate of copolymerization depends on both the electron-donating ability of the salen ligand and the co-catalyst such as, N-heterocyclic amines, phosphines, and ionic salts [17]. Second, comparative kinetic measurements show the activation energies determined for PC and PPC formation are 100.5 and 67.6 Kj·mol^{-1}, respectively. The corresponding activation energies for cyclohexene carbonate (CHC) and PCHC production is 133 and 46.9 Kj·mol^{-1}. This could account for the large quantity of cyclic carbonate pro-
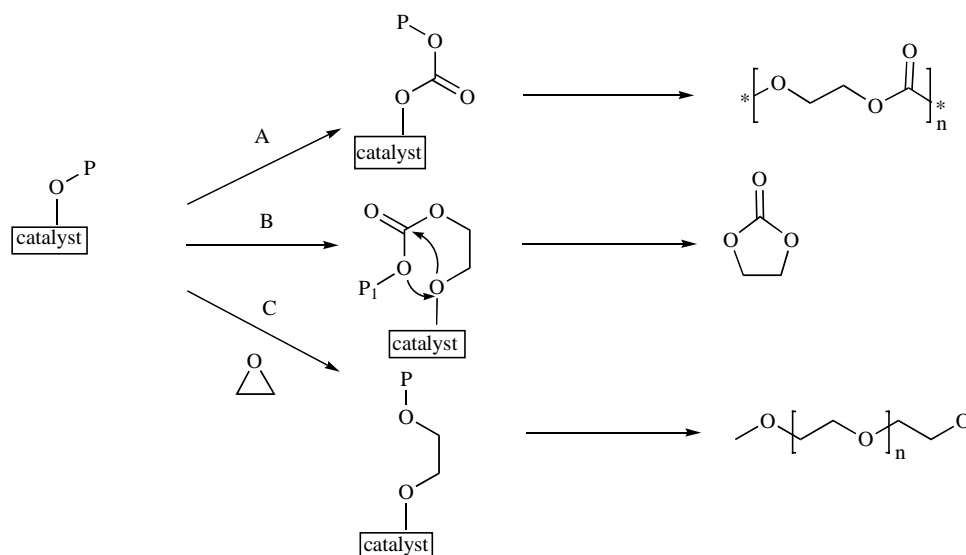
**Scheme 3.** The mechanism for the formation of different products.

duced at elevated temperatures, while relative more amount of polycarbonate generated at lower reaction temperature. Because cyclic carbonates are more thermodynamically stable than polycarbonates [19], one of pathways for cyclic carbonate formation during the copolymerization reaction would be through a unimolecular depolymerization reaction of the polymer-catalyst complex, *i.e.*, a backbiting mechanism (Scheme **3**, path B) [20]. Third, carbon dioxide insertion into the (salen)Cr-alkoxide intermediates after epoxide ring-opening, is shown to be a rate-limiting step at pressures below 35 bar. Higher pressure of carbon dioxide results in catalyst / substrate dilution, and thus causes the rate of copolymerization decreased. On the other hand, the formation of cyclic carbonate is inhibited as the CO_2 pressure increases [18]. Fourth, initiation step takes place *via* second-order activation (Scheme **2**). And the use of an azide (N_3) initiator increases activity substantially compared to chloride, due to its strong nucleophilicity. Conversely, electron-donating groups result in higher turnover frequencies while maintaining high CO_2 incorporation in the isolated polymer. Recently, Darensbourg's group also reported that a tetramethyltetraazaannulene complex incorporating a Cr^{III} metal center was shown to be highly active toward the copolymerization of cyclohexene oxide and CO_2 to afford PCHC in the presence of [PPN]N_3 [PPN$^+$ = bis(triphenylphosphoranylidene)ammonium] as a co-catalyst at 80 ^{o}C [21].

Meanwhile, to explore precise control polymer stereochemistry during the copolymerization of CO_2 and epoxides, Lu and co-workers [22] developed a two-component catalyst system composed of (salen)Cr (**1a** and **1f**) and an organic base as the co-catalyst, and various poly(propylene carbonate)s (PPC)s with different head-to-tail linkages (from ~ 60 % to 93 %) from (*rac*-PO) and CO_2 were obtained. A (salen)CrX complex with a low nucleophilic axial X anion and a conjugated cyclic diamine backbone, combined with a sterically hindered strong organic base, is an ideal binary catalytic system for the copolymerization of CO_2 and *rac*-PO. The produced polycarbonate has relative high head-to-tail connectivity and > 99% carbonate linkages. The polymer

chain end group (initiating and chain growth species) was continuously determined at various times by electrospray ionization mass spectrometry (ESI-MS). The results indicate that the sterically hindered strong organic base primarily plays an initiator of polymer-chain growth in the copolymerization process.

(Salen)Co for the Coupling of CO_2 and Epoxides

Jacobsen *et al.* have demonstrated that (salen)Co^{III} complexes can also serve as catalysts for the ring-opening of epoxides with a variety of nucleophiles. With the develop-
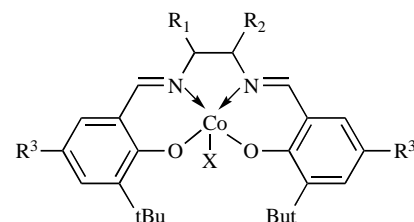
2a: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = Cl

2b: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = O_2CCCl_3

2c: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = EtO_2C^-

2d: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = Br, X = OAc

2e: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = H, X = OAc

2f: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = OAc

2g: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = OTs

2h: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = OTf

2i: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = BF_4

2j: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = NO_3

2k: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = I

2l: R^1 and R^2 = trans - $(CH_2)_4^-$, R^3 = tBu, X = $OBzF_5$

2m: R^1 and R^2 = (1R, 2R) - trans - $(CH_2)_4^-$, R^3 = tBu, X = 2, 4-dinitrophenoxy

2n: R^1 and R^2 = (1R, 2R) - trans Ph, R^3 = tBu, X = O_2CCCl_3

2o: R^1 = (R) - CH_3, R^2 = H, X = O_2CCCl_3, R^3 = tBu

Fig. (3). (Salen)Co catalysts for the coupling of CO_2 and epoxides.

ment of (salen)Cr in the fixation of the CO_2 and epoxides, the (salen)Co complexes have attracted increasing attention because of its stability and low toxicity. He and co-worker firstly reported the coupling of ethylene oxide and CO_2 to provide ethylene carbonate using (salen)Co and 1 equiv of *n*-Bu_4NBr at 15-16 MPa of CO_2 pressure at 110 °C with TOF of 1320 h^{-1} [23]. After that, Shi and co-workers described the production of various cyclic carbonates from the corresponding epoxides and CO_2, using binaphthyldiamino salen type catalysts including binaphthyldiamino (salen)Co^{II} complex. The yields of propylene carbonate achieved 80 and 91 %, respectively, in the presence of the catalyst and 2 equiv of DMAP or Et_3N at 100 °C [24]. Subsequently, Nguyen's group [25] demonstrated a chiral (salen)Co^{III} catalyst (**2a**, Fig. (**3**)) for the synthesis of several kinds of cyclic carbonates in high yields in the presence of the chiral (salen)Co and 2 equiv of DMAP at a CO_2 pressure of 2.068 MPa and 100 °C.

Meanwhile, many reports about synthesis of optically active propylene carbonate appear. Lu and co-workers [26] first described the preparation of optically pure cyclic carbonates from racemic epoxides by a catalytic kinetic resolution process involving several chiral (salen)CoX complexes and quaternary ammonium halides. And the reaction of racemic propylene oxide with 0.55-0.60 equiv of CO_2 was catalyzed by 0.1 mol % of (salen)Co$^{III}(O_2CCCl_3)$ complex **2b** and 0.1 mol % of *n*-Bu_4NBr under solvent-free conditions. Propylene carbonate was obtained with enantioselectivity (50.5 %) within 2 h at room temperature.

Notwithstanding, higher enantioselectivity was achieved by Yamada and co-workers, they employed a catalyst system including chiral (salen)Co (**2c**) and Et_2NSiMe_3 for the coupling of CO_2 and N,N'-diphenylaminomethyloxirane to the corresponding cyclic carbonate [27]. Pursuant to the above research results, Berkessel's group [28] and Kim's group [29] separately reported different binary catalyst system for the production of enantiomerically enriched propylene carbonate.

On the other hand, Coates [30] reported that the discrete cobalt complexes were used as catalysts for the copolymerization of CO_2 and epoxides. Complexes **2d-2f** were found to provide PPC in >99 % selectivity with 90-99 % carbonate linkages in the absence of a co-catalyst. And the results markedly depended on reaction conditions and the R substituent of the salen ligand. Complex **2d** was shown to be the
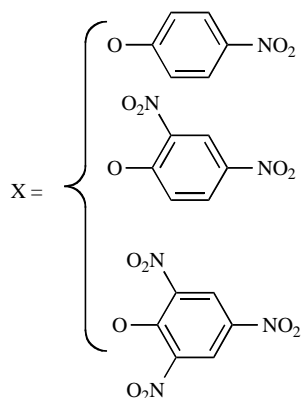
most active catalyst among the derivatives. Subsequent to the original report by Coates, Lu and co-workers [31] found complex **2f** with 1 equiv of *n*-Bu_4NBr was active for the copolymerization of propylene oxide and CO_2 at ambient temperature and 2 MPa CO_2 pressure, with a TOF for polycarbonate and cyclic carbonate of 228 h^{-1}. However, the selectivity to polycarbonate was just 3 %. Interestingly, the selectivity (78-99 %) was remarkably enhanced by replacing acetate with the axial ligands (X) in Fig. (**4**).

After the work of the coupling of CO_2 and epoxides to give cyclic carbonates using (salen)Co and DMAP as the catalyst system [25], Nguyen's group reported a series of (salen)CoXs (**2a**, **2f** to **2k**) with Lewis base catalyzed the reaction to provide poly(propylene carbonate). And the most active catalyst system contained X = NO_3 (**2j**) along with 2 equiv of DMAQ (*N,N'*-dimethylaminoquinoline) [32]. Coates and co-worker followed their preliminary work and designed a series of (salen)CoX [X = Br or pentafluorobenzoate ($OBzF_5$)] catalysts for the alternating polymerization of PO and CO_2. And the optimal catalytic system is (R,R)-(salen)Co$OBzF_5$ (**2l**) with [Ph_4P]Cl or [PPN]Y (Y = Cl or $OBzF_5$), exhibiting TOF up to 720 h^{-1} for *rac*-PO / CO_2 copolymerization and producing PPC with greater than 94 % head-to-tail connectivity under 0.689 MPa CO_2 pressure and 22 °C [33]. Another important research on the polymerization of epoxides and CO_2 is the work of Nozaki's group at 2006 [34]. They employed a salen ligand containing a piperidinium end-capping arm (Fig. (**5**)), and the piperidinium arm controlled the formation of cyclic carbonate by protonating the anionic polymer chain when it dissociated from the cobalt center. The quantitative conversion of propylene oxide to copolymer was achieved and also allowed for the production of block terpolymers under 60 °C and 1.4 MPa CO_2 pressure.
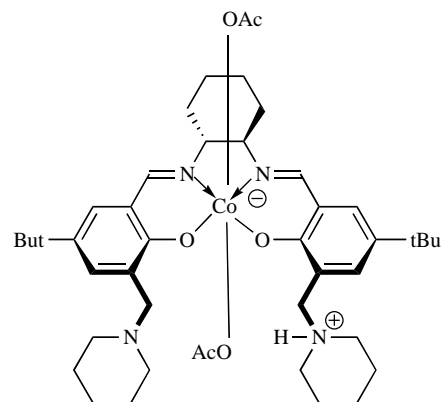

Fig. (5). Co-salen complex containing a piperidinium.

Although the asymmetric alternating copolymerization of cyclohexene oxide and CO_2 has been first demonstrated by Nozaki [35] using organozinc-chiral amino alcoholate catalysts for several years, many groups still readily pay much attention to the process. Among the achievements, Lu and co-workers [36] made great progress. They have extensively examined the asymmetric alternating copolymerization of *rac*-propylene oxide and CO_2 in the presence of chiral (salen)CoX (**2b**, **2m** to **2o**) with *n*-Bu_4NX or PPNX salts or a strong nitrogen base as co-catalyst. The effects of varying the salen ligand, axial ligand, and co-catalyst on the activity,

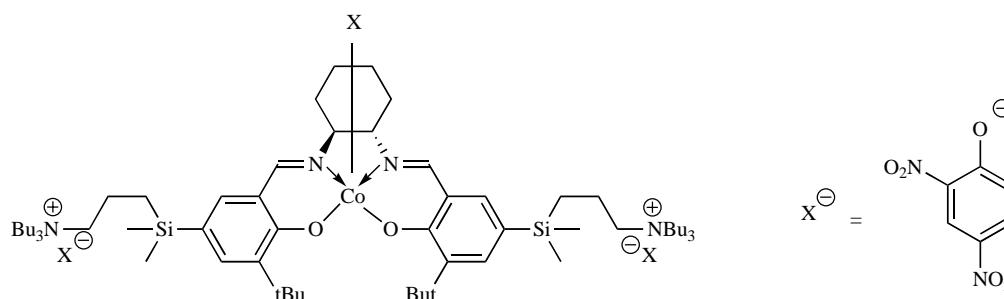**Fig. (4).** The axis of NO_2 instituted.

Fig. (6). (salen)Co complex containing an ammonium salt.

selectivity for copolymer formation, and enantio- and stereo-selectivity were assessed. The results showed that the best binary catalyst system combined a bulky chiral (salen)CoX complex containing a poor X leaving group and a co-catalyst composed of an X anion with poor leaving ability or a sterically encumbering strong organic base with low metal-binding ability. With such a binary catalyst system, for example, the complex **2n**, 1 equiv of [PPN]Cl, and the *rac*-propylene oxide could afford poly(propylene carbonate) with a TOF of 568 h^{-1}, >99 % selectivity for copolymer and 96 % head-tail linkages under the conditions of 1.5 MPa CO_2 and 25 °C. The binary catalyst system was also observed to asymmetrically copolymerize cyclohexene oxide and CO_2 to provide copolymer with > 99% carbonate linkages and 36.6 % ee (enantiomeric excess) at ambient temperature. Electron ionization mass spectrometry was employed for monitoring the copolymer chain growth process, which was initiated primarily by the cocatalyst. Besides, Coates's group also investigated several (salen)MX complexes as the catalysts for the asymmetric alternating copolymerization of cyclohexene oxide and CO_2. The best catalyst for the production of copolymer noted in the study was (R, R)-(salen)CoOBzF$_5$ (**2l**) and 1 equiv of [PPN]Cl, affording a TOF of 440 h^{-1} under 70 °C and 0.68 MPa CO_2 pressure. The presence of a [PPN]Cl as cocatalyst, however, resulted in a loss in syndio-specificity [37].

Nonetheless, most of the above catalytic processes involve binary systems, which are absolutely indispensable to achieve the catalytic cycle. Very recently, Lee and co-workers [38] firstly reported a (salen)Co complex (Fig. (6)) containing a metal center and an ammonium salt showed high activity even at high temperature and high [epoxide] / [catalyst] ratio. A very high TOF (up to 3500 h^{-1}) and TON (up to 14 500) were gained.

Meanwhile, our group [39] designed a single component bifunctional cobalt-salen complex containing a Lewis acidic metal center and a quaternary phosphonium salt unit anchored on the ligand (Fig. (7)) effectively catalyzes the synthesis of cyclic carbonates from CO_2 and epoxides without the utilization of additional organic solvents or co-catalysts under 4 MPa (pressure of CO_2) and 100 °C.

(Salen)Al/Mn for the Coupling of CO_2 and Epoxides

Compared with Manganese, the activity of aluminum as the Lewis acidic center would be better for the coupling of epoxides and CO_2 to provide polycarbonates or cyclic carbonates. He and Lu reported the synthesis of cyclic carbonates from CO_2 and epoxides using (salen)AlX and tetraalkylammonium salts [39-41]. They examined the coupling of ethylene oxides and CO_2 with the catalyst (**4a**, Fig. (8)), and the TOF reached 2220 h^{-1} when (salen)AlCl and *n*-Bu$_4$NBr were used as catalysts under 110 °C and 15-16 MPa CO_2 pressure [40]. Then Lu followed the work and made a much in-depth insight. The scope of the substrate was extended to ethylene oxide, propylene oxide and styrene oxide. The reaction of epoxides and CO_2 were catalyzed by (salen)AlX and *n*-Bu$_4$NY binary system at 0.6 MPa and 25 °C, affording cyclic carbonates in good yield and 100 % selectivity [41]. Additionally, they also found that the (salen)AlEt (**4b**)/18-crown-6-KI catalyzed the coupling of (S)-propylene oxide and CO_2 to provide (S)-propylene carbonate in >99 % ee at 25 °C and 0.6 MPa of CO_2 pressure [42].
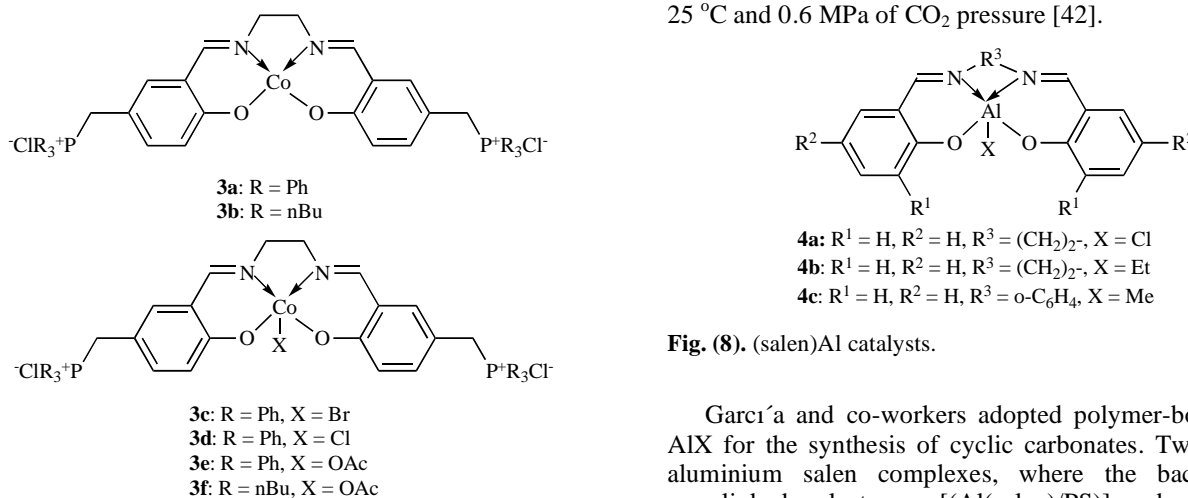

3a: R = Ph
3b: R = nBu

3c: R = Ph, X = Br
3d: R = Ph, X = Cl
3e: R = Ph, X = OAc
3f: R = nBu, X = OAc

Fig. (7). Single component bifunctional cobalt-salen complexes.

4a: R^1 = H, R^2 = H, R^3 = (CH$_2$)$_2$-, X = Cl
4b: R^1 = H, R^2 = H, R^3 = (CH$_2$)$_2$-, X = Et
4c: R^1 = H, R^2 = H, R^3 = o-C$_6$H$_4$, X = Me

Fig. (8). (salen)Al catalysts.

García and co-workers adopted polymer-bound (salen) AlX for the synthesis of cyclic carbonates. Two polymeric aluminium salen complexes, where the backbones are crosslinked polystyrene [(Al(salen)/PS)] and poly(ethylene
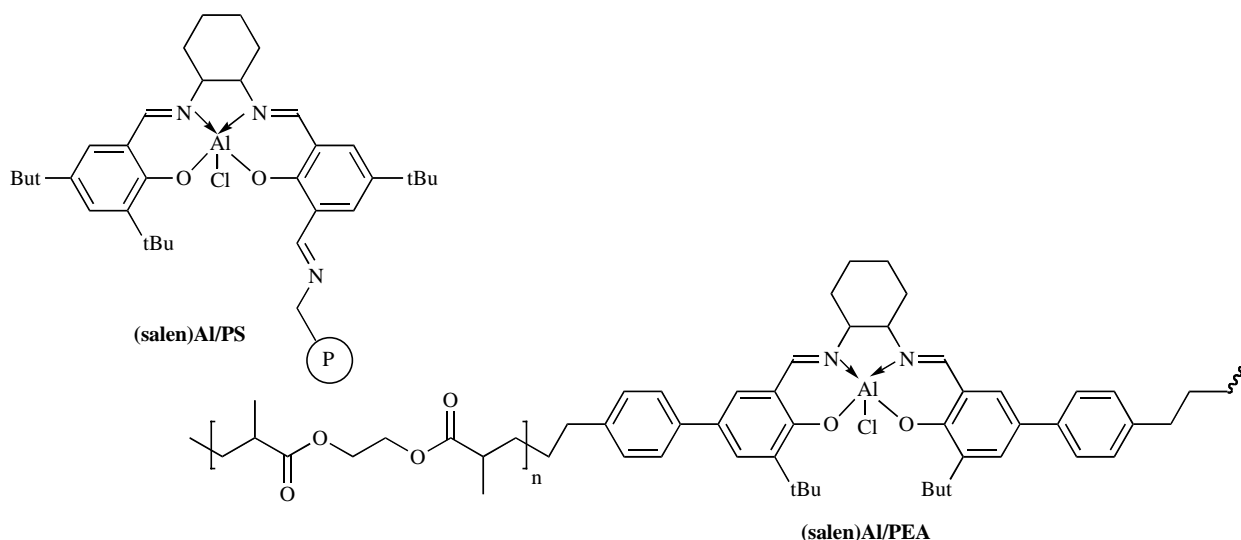
Fig. (9). Polymer-bound (salen)AlX.

glycol bismethacrylate) [(Al(salen)/PEA)] (Fig. (**9**)), were used for the coupling reaction [43].

In the case of (salen)Al used as catalysts for the copolymerization, there are only few reports because of the lower activity. After the work of Chisholm and Zhou [44], Darensbourg and coworkers [45] investigated a series of (salen)AlX as the catalysts for the copolymerization reaction. Aluminum prefers electron-withdrawing groups on the salen ligands, thereby being active toward production of polycarbonates. This is to be contrasted with the results observed for the (salen)CrX systems, where electron-donating salen ligands greatly enhanced the activity of (salen)Cr complexes. Under identical reaction conditions, the activity of (salen)AlX is poorer than that of (salen)CrX. Inoue and coworkers [46] have also examined (salen)AlX and ammonium salts binary catalyst system for copolymerization of cyclohexene oxide and CO_2. The copolymerization catalyzed by **4c** / Et_4NOAc system took place smoothly and achieved the yield of 96 % in 24 h under CO_2 (5 MPa) and 80 °C.

Recently, Baiker and co-workers reported several (salen)MnX (including simple ligands and axis linked SiO_2) catalytic system for the coupling of CO_2 and epoxides to give cyclic carbonates. Besides, Darensbourg's group [47] also evaluated the ability to couple CO_2 and cyclohexene oxide in the presence of (acacen)MnX (acacen: N,N'-bis(acetylacetone)-1,2-ethylenediimine) and a variety of co-catalysts. These complexes proved to be inactive; however, valuable information related to the coordination chemistry of these manganese Schiff bases was elucidated. Of importance, mechanistic findings from comprehensive studies of structurally related to (salen)CrX and (salen)CoX strongly support the requirement of six-coordinate metal species for the effective copolymerization of CO_2 and epoxides. In the case of these Mn^{III} complexes, it was determined that a five-coordinate species in chloroform or toluene solution is greatly favored over a six-coordinate species even in the presence of 20 equiv or more various Lewis bases. Significantly, epoxide monomers such as propylene oxide and cyclohexene oxide display no tendency to bind to these (acacen)MnX derivatives. Only in excessive quantities of

heterocyclic amines such as pyridine, DMAP, and DBU (1, 8-diazabicyclo[5.4.0]undec-7-ene), a six-coordinate Mn derivative was observed in solution.

CATALYSTS EXCEPT (SALEN)-METAL FOR THE FORMATION OF CYCLIC CARBONATES

Homogeneous Catalysts

Homogeneous catalysts generally show higher catalytic activity and selectivity, so many catalytic systems have been developed for cyclic carbonate synthesis, mainly including onium salts or metal halide, ionic liquid, muti-component bifunctional catalysts, polyoxomentalates and others.

Onium Salts or Metal Halide

Quaternary ammonium salts are currently used as cheap and efficacious homogeneous catalysts for the industrial preparation of cyclic carbonates. In 2002, Caló and coworkers [48] reported cyclic carbonate synthesis from CO_2 and oxiranes using the tetrabutylammonium halides as solvents and catalysts. They demonstrated that the epoxide dissolved in molten tetraalkylammonium salts bearing halides as counterions are converted into cyclic carbonates under atmospheric pressure of CO_2. The reaction rate depends on the nucleophilicity of the halide ion as well as the structure of the cation. The mechanism is shown in Scheme **4**.
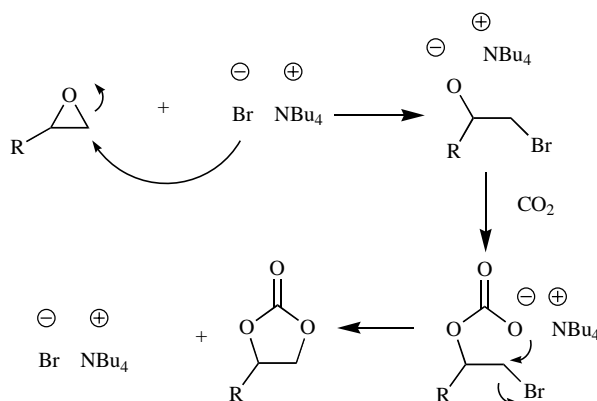
Scheme 4. Mechanism for cycloaddition reaction.

Lau and his co-workers [49] reported coupling reaction of CO_2 with epoxide catalyzed by PPN salts to yield cyclic carbonates. The results demonstrated that the off-the-shelf reagent PPN$^+$Cl$^-$ and PPN-manganese carbonylates [PPN]$^+$[Mn(CO)$_4$L]$^-$ (L = CO, PPh$_3$) were good catalysts for the coupling reactions of CO_2 with neat epoxides without the use of organic solvents to afford cyclic carbonates. PPN salts with weak nucleophilic anions such as PPN$^+$BF$_4^-$ and PPN$^+$OTf$^-$ were, however, inactive for the coupling reactions.

Takeshi Endo [50] reported catalytic activity of various salts in the reaction of 2, 3-epoxypropyl phenyl ether and CO_2 under atmospheric pressure. The results indicated that only halide salts give high catalytic activity, and the order of intrinsic activity was found to be as follow: chloride > bromide > iodide, which is the order of nucleophilicity of the anion. In addition, the order of the activity was found to be lithium salts > sodium salt > benzyltrimethylammonium salt, which is in accordance with the order of the Lewis activity of the cation. Kinetic analyses showed that the carbon dioxide pressure has no effect on the reaction rate. They also thought the reaction proceeds *via* nucleophilic attack of halide to oxirane to form β-haloalkoxide which reacted with CO_2 followed by cyclization.

Sakakura and coworkers [51] developed a new procedure for recycling homogeneous catalyst. Polyfluoroalkyl phosphonium iodides, Rf$_3$RPI (Rf = C$_4$F$_9$C$_2$H$_4$, C$_6$F$_{13}$C$_2$H$_4$, C$_8$F$_{17}$C$_2$H$_4$; R = Me, Rf), catalyzed propylene carbonate synthesis from propylene oxide and CO_2 under supercritical CO_2 conditions, where propylene carbonate was spontaneously separated out of the supercritical CO_2 phase. The Rf$_3$RPI catalyst could be recycled with maintaining a high CO_2 pressure and temperature by separating the propylene carbonate from the bottom of the reactor followed by supplying propylene oxide and CO_2 to the upper supercritical CO_2 phase in which the Rf$_3$RPI remained.

Ionic Liquid

Over the last decade, growing attention has been devoted to the use of ionic liquids (ILs) as catalysts and solvents for organic synthesis, a fact manifested by the increasing rate at which papers on this topic are being published. The unique ILs also have been widely applied to the cycloadditon of CO_2 and epoxides. Deng [52] reported cycloaddition of carbon dioxide to propylene oxide catalyzed by room temperature ionic liquids based on 1-*n*-butyl-3-methylimidazolium and *n*-butylpyridinium salts without any additional organic solvents. The 1-*n*-butyl-3-methylimidazolium tetrafluoroborate was the most active catalyst with almost 100 % selectivity, and a suitable CO_2 and propylene oxide molar ratio was needed for high conversion. The ionic liquid also could be recyclable.

Ikushima and co-worker [53] established a rapid and effective synthetic method of propylene carbonates using a supercritical carbon dioxide (scCO$_2$) / ionic liquid system. The reaction catalyzed by 1-octyl-3-methylimidazolium tetrafluoroborate achieved nearly 100 % yield and 100 % selectivity within 5 minutes, whose TOF value was 77 times larger than those reported before. They observed the phase behavior through high-pressure view cell under the same pressure and temperature condition, and a marked increase in the concentrations of CO_2 and epoxide in 1-octyl-3-methylimidazolium tetrafluoroborate phase under scCO$_2$ region was considered to achieve nearly 100 % yield even at shorter reaction time.

Muticomponent Catalyst

The aim of muticomponent system is to explore much more efficient catalyst system. Kim [54] reported Imidazolium zinc tetrahalides, (1-R-3-methylimidazolium)$_2$ ZnX$_2$Y$_2$ (R = CH$_3$, C$_2$H$_5$, *n*-C$_4$H$_9$, CH$_2$C$_6$H$_5$; X = Cl, Br; Y = Cl, Br), prepared by reacting ZnX$_2$ with (1-R-3-methylimidazolium)Y, were found to have surprisingly high activities for the coupling reaction of CO_2 and ethylene oxide or propylene oxide to produce corresponding cyclic carbonate. The catalytic activity of imidazolium zinc tetrahalide was greatly influenced by the nature of halide groups bonded to the zinc center. The catalytic activity was found in the order of [ZnBr$_4$]$_2^-$ > [ZnBr$_2$Cl$_2$]$_2^-$ >> [ZnCl$_4$]$_2^-$. The TOF increased with increasing temperature, but remained almost unchanged with the increase of pressure.

Fujita and co-workers [55] developed ZnBr$_2$/*n*-Bu$_4$NI as a highly efficient binary catalyst for the synthesis of styrene carbonate (SC) from styrene oxide and CO_2 under supercritical conditions. In a very short reaction time (30 min) and even at a mild reaction temperature (80 ^{o}C), 100 % selectivity and nearly 100 % yield of SC were obtained; the TOF value obtained was 46 times larger than those before reported under similar conditions. The effects of the ZnBr$_2$/*n*-Bu$_4$NI ratio, types of cation and anion, and other reaction conditions on the reaction were also investigated.

Nguyen and Jing [56] reported SnCl$_4$-organic base as highly efficient catalyst system for coupling reaction of CO_2 and epoxide. On the basis of co-catalyst screening among DBU, DMAP, Pyridine, NEt$_3$ (triethylamine) and DABCO (1,4-diazabixyxlo[2.2.2]octane); they found SnCl$_4$-DBU was the best catalysts for the coupling reaction of CO_2 and various epoxides to furnish cyclic carbonates by which CO_2 could be easily introduced into organic molecules under very mild conditions. They also proposed a mechanism in terms of *in situ* ^{119}Sn NMR investigations.

He and co-workers [57] described various cyclic carbonates from epoxides and CO_2 catalyzed by the binary catalytic systems composing of aluminum phthalocyanine (PcAlCl) and base co-catalysts, such as tributylamine, 1-methylimidazole and triphenylphosphine. Under the employed conditions, cyclic carbonates were produced nearly quantitatively from CO_2 and the corresponding epoxides. The reaction appeared to be temperature dependent, and was also affected by the amount of base co-catalyst in the binary catalytic systems. The catalyst could be reused for several recycles without the obvious loss of activity. In contrast to PcAlCl, other divalent metal phthalocyanines (MtPc) did not show high catalytic activities towards the reaction. Their activities were in the order: PcAlCl > MgPc > FePc >> NiPc or CoPc.

Fujita disclosed the synthesis of styrene carbonate from styrene oxide and CO_2 with various catalyst systems including metal halides and ionic liquids [58]. The total conversion of SO and the selectivity for SC strongly depended on the catalyst systems. The highest SC yield of 93 % could be achieved at a low temperature of 80 ^{o}C for 1 h with a catalyst system of ZnBr$_2$ and [C$_4$-mim]Cl at a molar ratio of 1 : 2. A
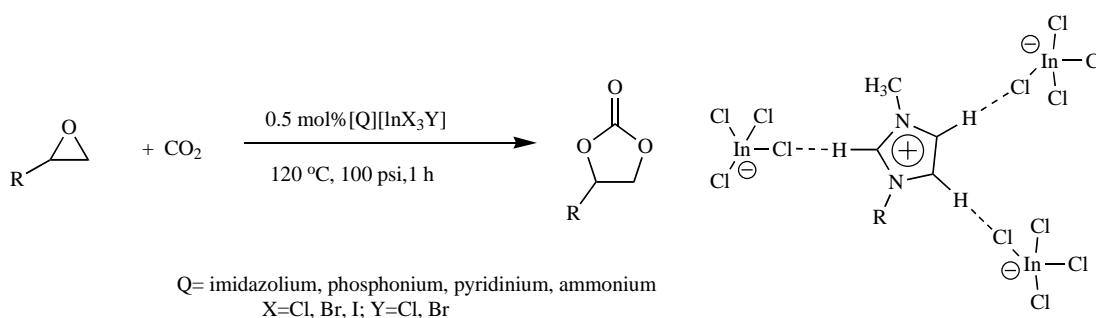
**Scheme 5.** Synthesis of cyclic carbonates catalyzed by tetrahaloindate^{III}-based ionic liquid.

CO_2 pressure of 4 MPa was optimal but elevated pressures had no positive effects on this SC synthesis.

Varma and co-workers [59] reported tetrahaloindate^{III}-based ionic liquids in the coupling reaction of CO_2 and epoxides to produce cyclic carbonates (Scheme **5**).

The microwave-assisted reactions of InX_3 with $[Q]Y$ produced a series of tetrahaloindate^{III}-based ionic liquids (ILs) with a general formula of $[Q][InX_3Y]$ (Q = imidazolium, phosphonium, ammonium, and pyridinium; X= Cl, Br, I; Y=Cl, Br). The reaction of CO_2 with a variety of epoxides was examined in the presence of these ILs, wherein tetrahaloindate^{III}-based ILs was found to exhibit high catalytic activities. The experimental evidence supported the significant role of H-bonding interactions in the $[Q][InX_3Y]$-catalyzed coupling reactions. The plausible reaction mechanism based on the ^1H and ^{13}C NMR studies was also proposed for the formation of propylene carbonate (Scheme **6**).

Xia and co-workers [60] presented a novel and effective Ni complex catalyst system for the cycloaddition reaction. The coupling of CO_2 and mono-substituted terminal epoxides or cyclohexene oxide to form cyclic carbonates under a Ni complex catalyst system without using additional organic solvents performed in excellent selectivity and TOF.

Shi and co-workers [61] described a method for chemical fixation of CO_2 by NaI /PPh_3 /$PhOH$. In the presence of catalytic amounts of sodium iodide, triphenylphosphine, and phenol, CO_2 could efficiently react with epoxides to give the corresponding five-membered cyclic carbonates in high yields. The mechanism of this reaction was also revealed by ^{31}P NMR spectroscopic data and deuterium labeling experiments. They [62] also showed Phenol could efficiently catalyze the reactions of terminal epoxides with CO_2 in the presence of catalytic amounts of various organic bases, such as DMAP, pyridine, DBU and triethylamine, to give the corresponding five-membered cyclic carbonate in high yields. *p*-
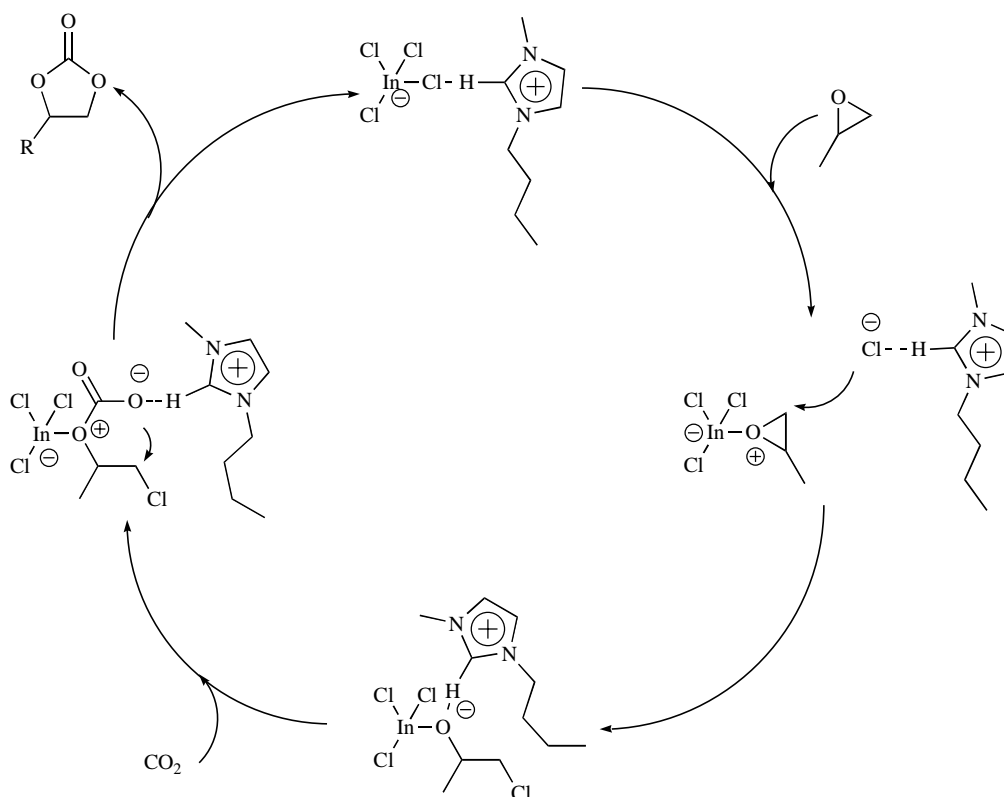
Scheme 6. Mechanism for coupling of epoxide and CO_2.

Methoxyphenol with DMAP was the best combination to give the cyclic carbonate in the highest yield.

Polyoxomentalates

The polyoxomentalates, mixed addenda and d-electron-transition-metal-substituted polyoxometalate complexes, were found many applications in catalysis because of the unusual versatility and tenability of these catalysts and their compatibility with environmentally and economically attractive conditions. Sakakura and coworkers [63] reported an efficient synthesis of cyclic carbonate from CO_2 catalyzed by polyoxometalate. Tetraalkylammonium salts of transition-metal-substituted polyoxometalates, such as $[(n-C_7H_{15})_4N]_6[\alpha-SiW_{11}O_{39}Co]$ and $[(n-C_7H_{15})_4N]_6[\alpha-SiW_{11}O_{39}Mn]$, efficiently catalyzed cyclic carbonate synthesis from CO_2 and epoxide. The catalytic activity was significantly influenced by the type of transition metal and the counter cation ($Co^{2+} \approx Mn^{2+} > Ni^{2+} > Fe^{3+} >> Cu^{2+}$; $(n-C_7H_{15})_4N^+ > (n-C_4H_9)_4N^+ >> K^+$). Co- or Mn- substituted catalysts required neither additional organic solvents nor additives. Thus, polyoxometalates are promising as non-halogen anionic components of catalysts for cyclic carbonate synthesis.

Manikandan and coworkers [64] reported a zinc-substituted polyoxometalate as an effective catalyst for cycloaddition of CO_2 to epoxides. A zinc-substituted sandwich-type polyoxometalate, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot46$ H_2O, in conjunction with a Lewis base, was found to be efficient for the cycloaddition of CO_2 with epoxides to form cyclic carbonates. The catalytic system could obtain near-quantitative conversion and high selectivity with or without organic solvents. The zinc-substituted polyoxometalate part of the catalyst system was heterogeneous, easy to separate after completion of reactions and reusable for many runs.

Others

Besides the above-mentioned, many other catalysts are also explored for cycloaddition reaction. Hua and coworkers [65] reported $Re(CO)_5Br$-catalyzed coupling of epoxides with CO_2 affording cyclic carbonates under solvent-free conditions. In the presence of a catalytic amount of $Re(CO)_5Br$, the coupling of epoxides with supercritical CO_2 without an organic solvent had afforded cyclic carbonates in good to excellent yields.

Kawanami [66] reported chemical transformation of carbon dioxide to styrene carbonate proceeds effectively under supercritical conditions with DMF even in the absence of any additional catalysts, giving a maximum yield of 85 % in the near-critical region.

Heterogeneous Catalysts

In homogeneous catalytic systems, the reactions can be efficiently carried out with high yields, but the toilsome purification procedures are inevitable and generally the catalysts are quite difficult to recover and recycle. However, in heterogeneous systems, the reaction mixture can be easily separated from one another by simple filtration, and in some cases the catalysts can be reused several times, thus bestowing on heterogeneous systems more conveniently potential applications in industry. As for the coupling of CO_2 and epoxide, the heterogeneous catalysts used mainly include metal oxides, silica-supported catalysts, polymer-supported catalysts and others.

Metal Oxide

Hydrotalcites are found to be excellent catalysts for many reactions. Yoshida and his co-workers [67] first reported the Mg-Al mixed oxides from calcinations of hydrotalcites acted as efficient catalysts for the addition of CO_2 with various epoxides under mild conditions. In addition, the mixed oxide with the Mg / Al ratio of 5 calcined at 400 °C showed the highest catalytic activity. The unique catalyst performance was due to the cooperative action of acid-base sites derived from the formation of Mg-O-Al bonds. And also, the catalysts could be reusable and exploited for many other organic reaction.

Polymer-Supported Catalysts

Our group aims at developing new protocols: one is that the catalyst homogeneously dissolved during the reaction and precipitates quantitatively in the separation stage, the other is anchoring the active species to solid support. We [68] reported organic solvent-free process for the synthesis of propylene carbonate from supercritical CO_2 and propylene oxide catalyzed by insoluble ion exchange resins. Insoluble ion exchange resins, one type of polystyryl supported catalysts containing an ammonium salt or amino group, and the polar macroporous adsorption resin, were efficient and reusable heterogeneous basic catalysts for the synthesis of propylene carbonate from propylene oxide and CO_2 under supercritical CO_2 conditions, which required no additional organic solvents either for the reaction or for the separation of product. A quantitative yield (99 %) together with excellent selectivity (99 %) was obtained. The purity of product separated directly by filtration from the reaction mixture, reached more than 99.3 % without further purification processes. The catalyst could be easily recovered and reused without significant loss of its catalytic activity.

Polyethylene glycol (PEG) and its derivatives are known to be inexpensive, thermally stable, recoverable, almost negligible vapor pressure, toxicologically innocuous and environmentally benign media for chemical reactions. Our group [69] reported PEG-supported quaternary ammonium salt was proved to be an efficient and recyclable homogeneous catalyst for solvent-free synthesis of cyclic carbonates from carbon dioxide and epoxides under supercritical conditions (Scheme **7**). Supporting Bu_4NBr on soluble polymer PEG_{6000} enhanced the catalytic activity. Furthermore, the catalyst can be reused over five times with no appreciable loss of catalytic activity and selectivity. We also [70] found the phosphonium halide-functionalized polyethylene glycol as efficient catalyst for synthesis of cyclic carbonate (Scheme **7**).
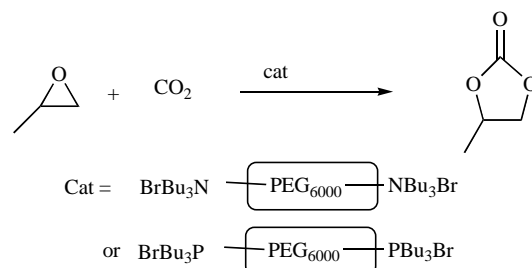
Scheme 7. Cycloaddition reaction catalyzed by PEG-supported quaternary ammonium or phosphonium salt.
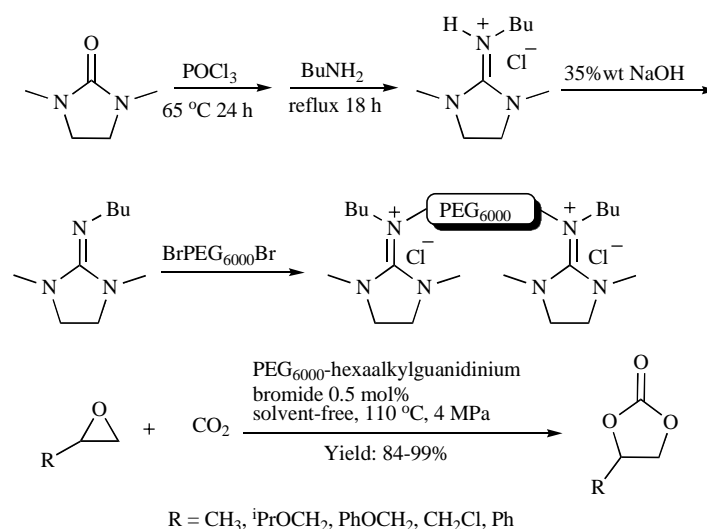
Scheme 8. Synthesis of PEG-supported guanidinium and its application to cycloaddition reaction.

R = CH_3, $^iPrOCH_2$, $PhOCH_2$, CH_2Cl, Ph

The catalyst had high catalytic activity even under mild conditions, which was also easily recycled and reused. Moreover, the catalyst leaching and recycle could be detected by ^{31}P NMR.

Our group [71] recently reported a guanidinium bromide covalently bound to CO_2-philic polyethylene glycol (PEG) was proved to be a highly effective homogeneous catalyst for the eco-friendly synthesis of cyclic carbonates from CO_2 and epoxides under mild conditions (Scheme **8**), which required no additional organic solvents or co-catalyst. Notably, it was found that there was a pronouncedly cooperative effect between the catalyst part and the support part. Moreover, the catalyst was able to be reused with retention of high catalytic activity and selectivity.

We [72] also disclosed a quaternary ammonium salt covalently bound to chitosan (Scheme **9**) as an efficient and recyclable single-component catalyst for the synthesis of propylene carbonate (PC) from propylene oxide (PO) and CO_2 without any organic solvent or co-catalyst. The catalyst could be easily recovered by filtration and reused for at least five times without obvious loss of its catalytic activity.

Kim and co-workers [73] reported the poly(4-vinyl-pyridine)-supported zinc halide catalysts, prepared from a reaction of ZnX_2 and poly(4-vinylpyridine), exhibited high selectivity and activity for the coupling reaction of CO_2 and ethylene oxide or propylene oxide. Solid NMR characterization of the poly(4-vinylpyridine)-supported $ZnBr_2$ catalyst and its reaction product with propylene oxide and / or CO_2 showed that a pyridiniumalkoxy ion-bridged zinc bromide complex would function as an active species, such as in the homogeneous catalysis with L_2ZnBr_2 (L=pyridine or methyl-substituted pyridine).

Han and coworkers [74] reported CO_2 cycloaddition reactions catalyzed by an ionic liquid grafted onto a highly cross-linked polymer matrix. [VBIM]Cl (3-butyl-1-vinylimidazolium) could be supported on a DVB simply by co-polymerization of [VBIM]Cl and DVB (Scheme **10**). The polymer-supported ionic liquid was very active, selective, and stable for the cycloaddition of CO_2 to epoxides. Also, it could be easily separated from the products and reused.

Han and coworkers [75] demonstrated that the catalytic activity of polyaniline-HX (X=I, Br, Cl) (PANI-HI, PANI-HBr, PANI-HCl) for the cycloaddition of CO_2 and propylene oxide (PO) to produce propylene carbonate (PC) as shown in Scheme **11**. It was found that all the PANI salts were active for the reaction, and PANI-HI was most active and selective. The catalyst had great potential for industrial applications because it has some unusual advantages, such as its easy preparation, high activity, selectivity, stability, low cost, and simple separation from products.
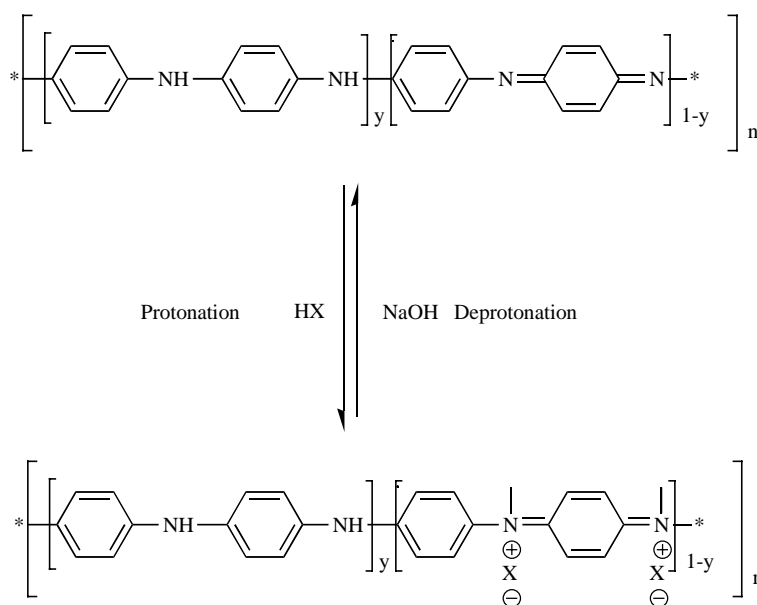
Silica-Supported Catalysts

Our group [76] disclosed a silica-supported quaternary ammonium salt as a recyclable and efficient catalyst for the

R: CH_3, CH_2CH_3, $CH_2CH_2CH_3$ X: Cl, Br, I
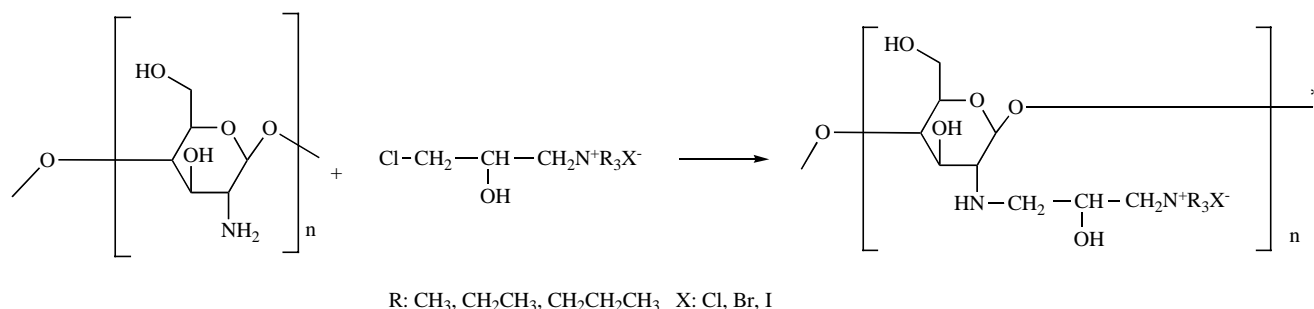
**Scheme 9.** Synthesis of chitosan-supported ammonium salts.
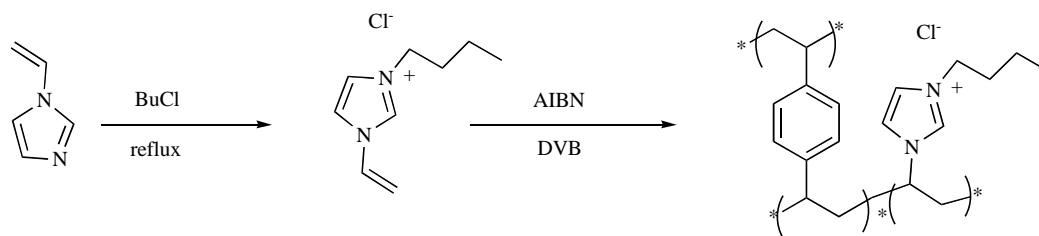
Scheme 10. Synthesis of ionic liquid polymer.

Scheme 11. Synthesis of polyaniline-HX.

synthesis of propylene carbonate from propylene oxide and CO_2 under supercritical conditions (Scheme **12**), which required no additional organic solvents either for the reaction or for the separation of product. Moreover, the catalyst can be easily recovered by a simple filtration and reused over four times without obvious loss of its catalytic activity.
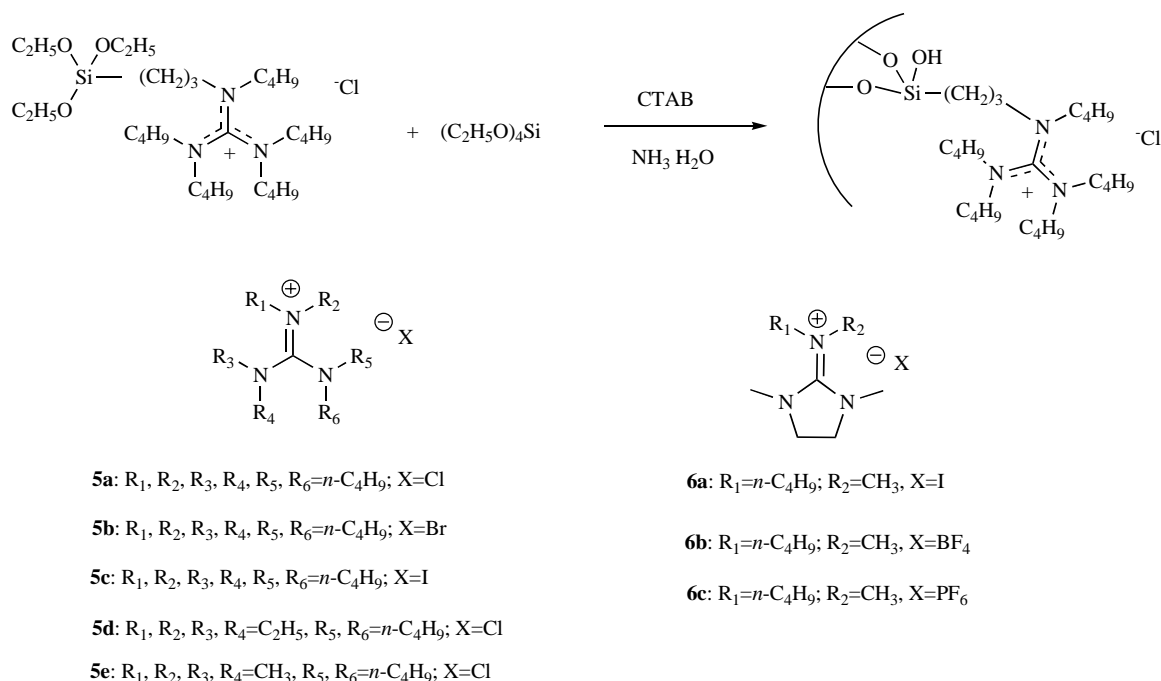
Cat. = Bu_4NBr, $[C_4min]^+[BF_4]^-$
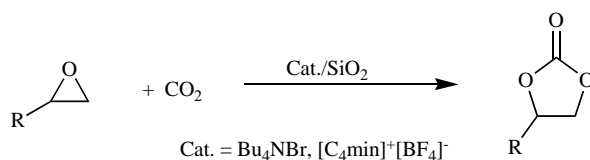
Scheme 12. Cycloaddition reaction catalyzed by silica-supported catalysts.

Our group [77] also reported a silica-supported ionic liquid as an efficient heterogeneous catalyst for solvent-free synthesis of cyclic carbonates from epoxides and CO_2 under supercritical conditions (Scheme **12**), which requires no additional organic solvents either for the reaction or for the separation of product. High yields with excellent selectivity were obtained. The purity of the product separated directly by filtration from the reaction mixture, reached 99 % without further purification process. Moreover, the catalyst can be easily recovered by filtration and reused over four times with slight loss of its catalytic activity.

Sartorio and coworkers [78] reported cycloaddition of CO_2 to epoxides over both homogeneous and silica-supported guanidine catalysts. They studied the coupling catalyzed by both homogeneous MTBD (7-methyl-1, 5, 7-triazabicyclo [4.4.0] dec-5-ene) and TDB (1, 5, 7-triazabicyclo [4.4.0] dec-5-ene) supported on MCM-41 mesoporous silica (Fig. (**10**)). The results showed the reaction catalyzed by heterogeneous MCM-41-TBD was slower than that with homogeneous MTBD, but offered the great advantage that the catalyst could easily be recovered and reused for at least three further cycles.

Zhang and coworkers [79] described that both homogeneous and a silica-supported hexaalkylguanidinium chloride were effective catalysts for CO_2 fixation to carbonate without any solvent under mild reaction conditions (4.5 MPa, 120 °C, 4 h). The silica-supported hexaalkylguanidinium chloride (Scheme **13**) showed the great advantage that it could be recycled easily at least 5 further times without any obvious decrease in its catalytic activity, after simple filtration.

Sakakura and coworkers [80] reported synergistic hybrid catalyst for cyclic carbonate synthesis. The catalytic activity of phosphonium salts towards cyclic carbonate synthesis from propylene oxide and CO_2 was remarkably enhanced by their immobilization onto silica that itself has no catalytic activity.
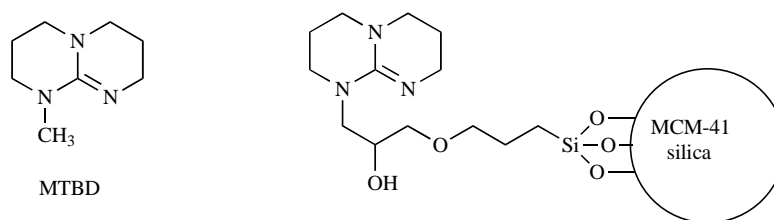
Fig. (10). Guanidine and silica-supportd guanidine.

Scheme 13. Guanidines and silica-supportd guanidine.

5a: R_1, R_2, R_3, R_4, R_5, R_6=n-C_4H_9; X=Cl

5b: R_1, R_2, R_3, R_4, R_5, R_6=n-C_4H_9; X=Br

5c: R_1, R_2, R_3, R_4, R_5, R_6=n-C_4H_9; X=I

5d: R_1, R_2, R_3, R_4=C_2H_5, R_5, R_6=n-C_4H_9; X=Cl

5e: R_1, R_2, R_3, R_4=CH_3, R_5, R_6=n-C_4H_9; X=Cl

6a: R_1=n-C_4H_9; R_2=CH_3, X=I

6b: R_1=n-C_4H_9; R_2=CH_3, X=BF_4

6c: R_1=n-C_4H_9; R_2=CH_3, X=PF_6

Han and coworkers [81] reported silica supported choline chloride / urea as a heterogeneous catalyst for cycloaddition (Fig. (**11**)). They studied the catalytic efficiency of ionic liquid (IL) choline chloride / urea supported on molecular sieves under different conditions. It was demonstrated that this biodegradable and green catalyst was very active and selective, and choline chloride and urea showed a synergetic effect in promoting these reactions. After reaction, the solid catalyst and the products could be separated easily.
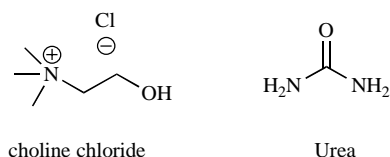
Fig. (11). Choline chloride and urea.

Sakai and coworkers [82] reported highly active and robust organic-inorganic hybrid catalyst for cycloaddition reaction. The best hybrid catalyst (Scheme **14**) was prepared by the coupling of 3-(triethoxysilyl)propyltriphenylphosphonium bromide and mesoporous silica, and the organic and inorganic moieties had a synergistic effect on catalytic activity. The pore size of silica was found to be important for catalysis. The solvent-free and metal-free reactions pro-

ceeded successfully under very mild conditions (1 MPa, 90 °C, 1 mol % loading of catalyst, 6 h), and the hybrid catalyst could be recycled ten times.
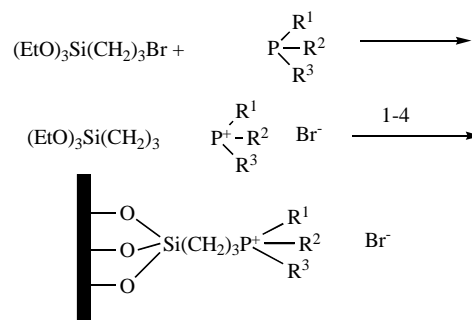
1. silica A   a: R^1= R^2 = R^3 = Ph
2. silica B   b: R^1= R^2 = R^3 =p-Me-C_6H_4
3. Toyonite   c: R^1 = R^2 = R^3 =p-F-C_6H_4
4. alumina   d: R^1= R^2 = Ph, R^3 = n-Bu

Scheme 14. Organic-inorganic hybrid catalyst.

Others

Sakakura and coworkers [83] reported cyclic carbonate synthesis from scCO$_2$ and epoxide over lanthanide oxychlo-

ride. From catalyst screening, they observed that Lanthanide oxychloride, especially SmOCl, was an efficient solid catalyst for synthesis of propylene carbonate. The process required no additional organic solvents and the product could be automatically separated out from the CO_2 phase.

Lau and coworkers [84] reported the coupling reaction of epoxides with CO_2 catalyzed by heterobimetallic Ru-Mn complexes. The heterobimetallic complexes [$(\eta^5$-$C_5H_5)$Ru (CO)(mdppm) Mn(CO)$_4$] and [$(\eta^5$-$C_5Me_5)$Ru(mdppm)(m-CO)$_2$Mn(CO)$_3$] (dppm= bisdiphenylphosphinomethane) have been prepared by reacting the hydridic complexes [$(\eta^5$-$C_5H_5)$Ru(dppm)H] and [$(\eta^5$-$C_5Me_5)$Ru(dppm)H], respectively, with the protonic [HMn(CO)$_5$] complex. The bimetallic complexes could also be synthesized through metathetical reactions between [$(\eta^5$-$C_5R_5)$Ru$^-$ (dppm)Cl] (R=H or Me) and Li$^+$ [Mn(CO)$_5$]$^-$. Although the complexes failed to catalyze the hydrogenation of CO_2 to formic acid, they catalyzed the coupling reactions of epoxides with CO_2 to yield cyclic carbonates.

Deng and coworker [85] demonstrated that polymer-immobilized nano-gold catalysts had unprecedented catalytic activity for coupling epoxide and of carbon dioxide, with TOF > 50000 mol / mol / h for the synthesis of cyclic carbonate.

CONCLUSIONS

Carbon dioxide can be regarded as an abundant and readily accessed atmospheric gas that could, in principle, be useful synthon for organic compounds. However, its inherent thermodynamic stability and kinetic inertness hinder the development of metal catalysts that achieve CO_2 activation and functionalization. Efforts to convert CO_2 to useful chemicals will inevitably rely on the active catalysts. Those findings reported in the literature open synthetic pathways for the selective synthesis of cyclic carbonate and polycarbonate from an abundant chemical feedstock and demonstrate that such CO_2 functionalization with high energy starting material like epoxides reaction is easily available.

Over the last decades, significant advances have been achieved in CO_2 and epoxide coupling chemistry which catalyzed by several kinds of (salen)-metal catalysts and others. Both polycarbonates and cyclic carbonates can be synthesized with high rates and high selectivity. The controlled formation of cyclic carbonates or / and polycarbonates could be achieved by adjusting the architecture of the ligands and the reaction conditions, such as temperature, pressure, co-catalysts, epoxide concentration. However, unlike the wide substrate scope for the production of cyclic carbonates, the range of epoxides that couples with CO_2 to afford alternating copolymers still remains quite limited. Copolymerizations remain mainly focused on cyclohexene oxide and propylene oxide. So the other co-monomer (limonene oxide, styrene oxide, *et al.*) could be promising substrates in the production of unique copolymers. In addition, only (salen)Cr/Co complexes have shown significant activity for the copolymerization of CO_2 and epoxides, while Mn and other transitional metals are rarely examined. Moreover, if there is an effective catalyst developed, which could selectively fix CO_2 in atmosphere, that would be much more promising.

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