Pure Appl. Chem., Vol. 84, No. 3, pp. 621–636, 2012.
http://dx.doi.org/10.1351/PAC-CON-11-06-08

Chlorine-free catalysts for green synthesis of cyclic carbonates from carbon dioxide*

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Abstract: This article provides an overview on recent progress in the green synthesis of cyclic carbonates (CCs) from carbon dioxide (CO_2) catalyzed by chlorine-free catalysts. Special emphasis is placed on the synthetic routes and catalyst structures that govern the reactivity and selectivity.

Keywords: CO_2; catalysts; chlorine-free catalysts; cyclic carbonates; cycloadditions; green chemistry; green synthesis; structure–activity.

INTRODUCTION

Chemical fixation of carbon dioxide (CO_2) for reduction of its contribution to greenhouse gas effects and for further utilization as an industrial C_1 feedstock are of much interest from both scientific and practical perspectives because CO_2 is not only a greenhouse gas but also an inexpensive, nontoxic, nonflammable, naturally abundant, and biorenewable C_1 resource [1].

The synthesis of cyclic carbonates offers scope for promising technologies for chemical fixation and utilization of CO_2. The generic term "cyclic carbonate" (CC) refers to variously substituted 1,3-dioxolan-2-ones, and includes those derived from a number of simple industrial feedstocks that find application as excellent aprotic polar solvents, substrates for small-molecule synthesis, additives, antifoaming agents for antifreeze, and plasticizers [2]. Numerous syntheses of CCs from CO_2 have been described during the past 30 years [3]. Among them, a classical and industrial approach entails cycloaddition (or coupling) of CO_2 with epoxides. A remarkable variety of active initiators/catalysts such as metal and quaternary ammonium salts, phthalocyanine and salen complexes, ionic liquids, metal oxides, and immobilized molecular catalysts have been reported for this transformation so far. However, the toxicity of epoxides and complicated production processes coupled with high costs hamper their widespread use as starting materials. There are alternative routes for the synthesis of CCs, such as oxidative carboxylation of CO_2 with olefins [4], carboxylative cyclization of CO_2 with propargyl alcohols [5], and carboxylation of CO_2 and 1,2-diols [6]. Despite these extensive efforts, however, most catalysts used in these reactions contain halides, which severely limit their scope, owing to toxicity and attendant environmental pollution problems. The search for greener, environmentally friendly catalysts for the preparation of CCs from CO_2 is therefore of importance and interest from the ecological and economic points of view.

The synthesis of CCs from CO_2 has so far been included as part of more general overviews on inorganic, organic, or organometallic catalysts [7]. The purpose of this article is to give a thorough

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*[*Pure Appl. Chem.* **84**, 411–860 (2012). A collection of invited papers for the IUPAC project 2008-016-1-300 "Chlorine-free Synthesis for Green Chemistry".

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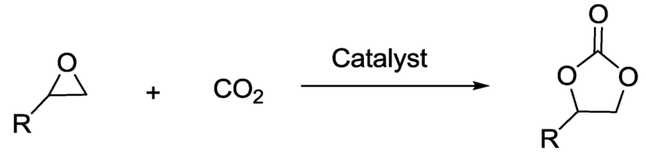
account of the current literature on green preparation of CCs from CO_2, with the aid of chlorine-free catalysts. The chlorine-free catalysts referred to here include all those compounds and complexes that are devoid of chloride, bromide, or iodide. The discussions are divided into sections based on synthetic routes and catalyst structures. Emphases are placed on the catalysts' structure–performance relationships.

CHLORINE-FREE CATALYSTS FOR SYNTHESIS OF CCs FROM CO_2 AND EPOXIDE

Cycloaddition of CO_2 with epoxides has received much attention since it is a classical and industrial way for the preparation of CCs from CO_2 (Scheme 1). In comparison with a remarkable variety of active initiators/catalysts containing halides described in the literature, only a few chlorine-free catalysts have been reported for this transformation.



Scheme 1 Synthesis of monosubstituted CCs via cycloaddition of CO_2 with terminal oxiranes.

Organic catalysts

In 2003, Shi et al. reported that non-metal Lewis acid phenols (**1–3**) were efficient catalysts for the synthesis of CCs from the cycloaddition of CO_2 and epoxides such as 1,2-epoxyhaxane, 1,2-epoxybutane, propylene oxide, styrene oxide, and epichlorohydrin in the presence of various organic Lewis bases such as 4-dimethylaminopyridine (DMAP), pyridine, **1**, 8-diaza-bicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), and triethylamine (NEt_3) (Fig. 1) [8]. It was proved that the combination of phenol and amine was the best catalytic system. Under 3.6 MPa of CO_2 and 120 °C for 48 h, the **1c**/DMAP system showed the highest activity for the cycloaddition of CO_2 and propylene oxide, affording propylene carbonate (PC) with 98 % yield. A mechanism was proposed in which the Lewis base amine and the Lewis acid phenol work together to open the ring of epoxide and then CO_2 insert to form CC.

Activated by various organic bases, some Schiff bases, including binaphthyldiamino (**4**), ethyldiamino (**5**), cyclohexyldiamino (**6** and **7**), could promote the coupling reaction of CO_2 with almost all of the terminal epoxides to produce the corresponding CCs with high yields and high selectivities (Fig. 1) [9]. In comparison, the **6**/DMAP catalytic system gave an 84 % yield of PC under 3.6 MPa of CO_2 and 120 °C for 48 h, while the sterically hindered catalyst **4** or the catalyst **7**, which had no phenolic hydroxyl group in the presence of DMAP, showed lower yields of about 25 and 14 %, respectively. Specially, these catalytic systems were stable and could be easily recovered.

N,*N*-Dimethylformamide (DMF) (**8**) catalytic system was demonstrated to be active for the reaction of CO_2 with styrene oxide under a supercritical CO_2 ($scCO_2$) (Fig. 1) [10]. The catalytic activity significantly depended on the CO_2 pressure. With the increasing pressure of CO_2, the yield first increased and reached a maximum about 85 % at 7.9 MPa of CO_2 under 150 °C for 24 h. Further increasing CO_2 pressure, however, resulted in the sharp decrease of activity. DMF was also found to be effective for the synthesis of CC from CO_2 and epoxide under 5.0 MPa of CO_2, affording 95 % yield of 1-chloro-2,3-epoxypropane carbonate at 110 °C for 15 h [11]. Moreover, the catalytic activity of DMF could be significantly enhanced by the addition of a catalytic amount of water. Similarly, DMAP (**9**) alone could also catalyze the reaction of CO_2 with propylene oxide under 3.6 MPa of CO_2 and 120 °C for 4 h, preparing PC with 92 % yield (Fig. 1) [12]. A mechanism was suggested that the lone

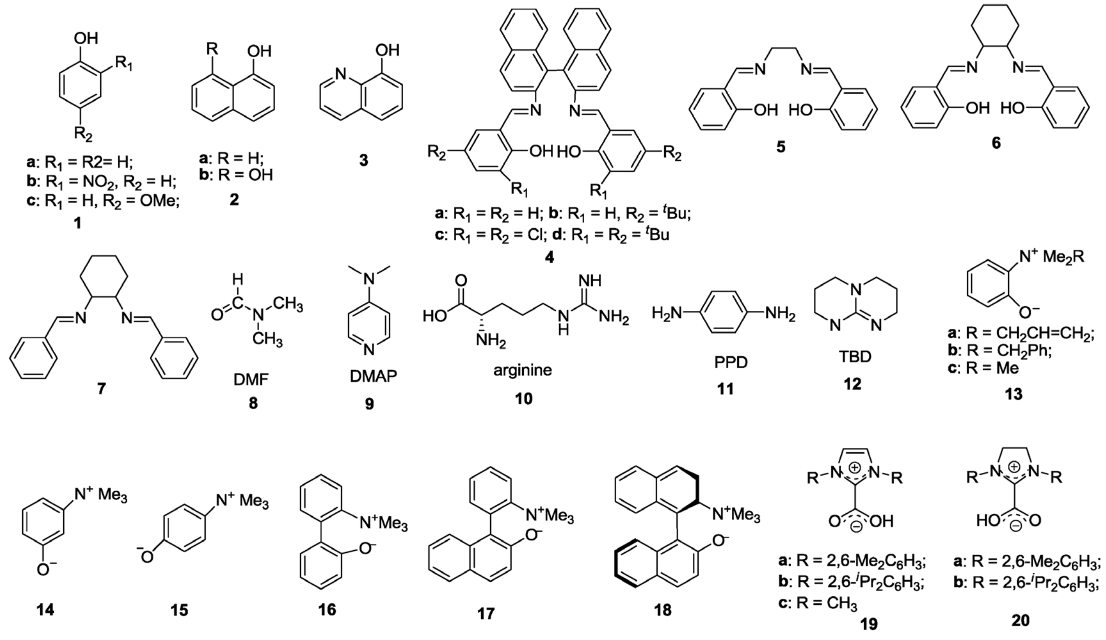


Fig. 1 Examples of typical nonmetallic, chlorine-free organic structures under recent investigation for catalytic activity.

pair on the pyridyl nitrogen of a single DMAP molecule attacks the epoxide ring following subsequent insertion of CO_2.

Other organic amines such as monoethanolamine, bis-(3-aminopropyl)-amine, *o*-phenylenediamine, oleyamine, 2-aminobenzylamine, arginine (**10**), *p*-phenylenediamine (PPD) (**11**), and 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) (**12**) were also reported to serve as single-component catalyst for the coupling reaction of CO_2 with propylene oxide (Fig. 1) [13]. Among them, TBD showed the highest activity, yielding 100 % of PC under 5 MPa of CO_2 and 150 °C for 24 h. The conjugated "N=C–N" structure of TBD was proposed to play an important role for its high catalytic activity.

Some bifunctional organic catalysts bearing an ammonium betaine framework (**13–18**) were investigated as metal-, halogen-, and solvent-free catalysts for the coupling reaction of CO_2 with epoxides such as 1,2-epoxyhaxane oxide, 1,2-epoxyoctane, propylene oxide, styrene oxide, methyl glycidyl ether, and epichlorohydrin (Fig. 1) [14]. Among them, catalyst **14** showed the highest activity under 1 MPa of CO_2 and 160 °C for 24 h, affording CCs with ca. 99 % yields.

A series of zwitterionic NHC-CO_2 compounds (**19–20**) were also used as effective catalysts for the preparation of CCs from CO_2 and epoxides (e.g., propylene oxide, styrene oxide, 1,2-epoxybutane, epichlorohydrin, 1,2-epoxyhaxane oxide) (Fig. 1) [15]. In contrast, catalyst **19b** exhibited the highest activity at 2.0 MPa of CO_2 and 120 °C for 24 h, giving 100 % of PC. It was suggested that the significantly increasing activity was due to the intermolecular cooperative catalysis of these binary components.

Metal oxide catalysts

In 1997, Yoshihara et al. first reported that magnesium oxide (MgO) displayed high activity and excellent stereoselectivity for the reaction of CO_2 and epoxides [16]. Under an atmosphere of CO_2 and 135 °C for 12 h, 60 % yield of (*R*)-styrene carbonate (SC) with 99 % selectivity was obtained when

DMF was used as solvent. It was found that the CO_2 pressure had no effect on the yield of CC. Subsequently, some Mg–Al mixed oxides obtained by calcining hydrotalcite were reported to catalyze the cycloaddition of CO_2 with epoxides [17]. These Mg–Al mixed oxides not only exhibited high activities and excellent stereoselectivities under an atmosphere of CO_2, but also were reusable. The most active catalyst was the Mg–Al mixed oxide with the Mg–Al ratio of 5. Under 0.5 MPa of CO_2 and 400 °C for 24 h using DMF as solvent, this catalyst afforded 90 % yield of SC, which is much higher than 38 % yield of SC obtained by a physical mixture of MgO and Al_2O_3 under the same conditions. The outstanding activity of the Mg–Al mixed oxide was accounted to the cooperative effort of acid–base sites derived from the Mg–O–Al bonds, which located in a neighbor position on the surface. Cs-doped Al_2O_3 was also investigated for the synthesis of CCs from CO_2 and epoxides [18]. A 24 % yield of ethylene carbonate was obtained under 3.7 MPa of CO_2 and 150 °C for 3 h by use of the Cs–Al_2O_3 system for the coupling reaction of ethylene oxide and CO_2. The proximity of Lewis acid sites to base sites in the surface of oxide was suggested to play an important role in the reaction process.

Recently, a series of Zn–M–Al–O (M = Mg, Ca, Sr, and Ba) ternary systems fabricated via calcination of the corresponding hydrotalcite precursors were indicated as effective catalysts for the coupling reaction of CO_2 with propylene oxide [19]. Among these catalytic systems, the Zn–Mg–Al–O with Zn–Mg ratio of 4 exhibited the highest activity and selectivity under 2.5 MPa of CO_2 and 140 °C for 12 h, affording 89 % yield of PC with 99 % selectivity. A mechanism was proposed, in which both acidic and basic sites were necessary for the cycloaddition. Moreover, the catalytic activity depended on the rate of activation of CO_2 at basic sites. Furthermore, the Zn–Mg–Al–O catalyst could be readily reused and recycled without any loss of activity.

Another acid–base bifunctional catalyst of cesium–phosphorous–silicon mixed oxide (Cs–P–Si oxide) reported by Sakakura could efficiently promote the cycloaddition of CO_2 and propylene oxide under 8 MPa of CO_2 and 200 °C for 8 h to produce 94 % yield of PC with more than 99 % selectivity [20]. For the Cs–P–Si oxide catalyst, however, the addition of DMF slightly decreased the activity, affording PC with lower yield (92 %) and selectivity (92 %) under the same conditions. Similarly, a combined complex Cs_3PO_4 was also proved as a highly efficient and non-halogen homogeneous catalyst for this reaction.

In 2003, Aresta et al. demonstrated that Nb_2O_5 was an effective catalyst for the coupling reaction of CO_2 and styrene oxide [21]. The catalytic activity was dependent on the pressure of CO_2. An 80 % yield of SC was achieved under 5 MPa of CO_2 at 135 °C for 12 h by use of DMF as solvent, which is much higher than those obtained by Mg and its mixed oxides. The solvent played an important role in the carboxylation process. For example, amides such as DMF and dimethylacetamide (DMA) could promote the reaction process, while a relatively low yield was obtained if xylene, diglyme, or toluene was chosen as solvent.

Polyoxometalate catalysts

Polyoxometalates (POMs), a class of large-cluster polyoxoanions consisting of both metal ion (Mo, W, V, Nb, and Ta) and oxo ligand, have attracted much attention as environmentally and economically attractive catalysts [22]. So far, a number of POMs have been synthesized, and their reactivities have been extensively studied in acid and oxidation catalysis reactions (Fig. 2). In contrast, little is known about their catalytic performances in the coupling reaction of CO_2 with epoxides [23].

In 2004, Manikandan et al. first reported that a Zn-substituted sandwich-type POM $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$ (Zn-POM) (**21**) in combination with a Lewis base DMAP displayed very high activity and selectivity for the coupling reaction of CO_2 with various epoxides such as epichlorohydrin, propylene oxide, or butylene oxide to form CCs in CH_2Cl_2 [24]. Under 0.4 MPa of CO_2 and 140 °C for 3 h using DMAP as solvent, the conversation of epichlorohydrin could reach to 97 %, yielding epichlorohydrin carbonate (EC) with 98 % selectivity. In comparison, this catalytic sys-

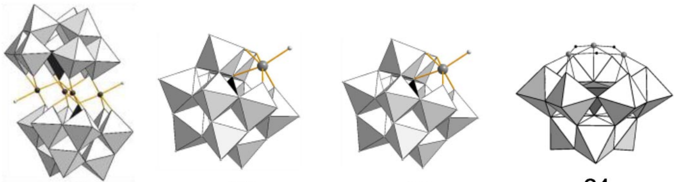


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Fig. 2 Examples of typical POM chlorine-free structures under recent investigation for catalytic activity.

tem completely converted 100 % of propylene oxide under 0.4 MPa of CO_2 and 160 °C for 12 h, affording PC with 97 % selectivity. The cooperative effect between Zn-POM and DMAP was proved to exist in this catalytic system. The two Zn ions bonded with five WO_6 octrahedra and a water molecule were believed to be active species for the CO_2 cycloaddition. The epoxide was activated by Lewis acidic site (Zn^{2+}), and CO_2 was activated simultaneously by DMAP, leading to the formation of CCs. Moreover, the Zn-substituted POM part of the catalytic system could be separated easily and reused with high conversion and selectivity, and was also active even in the absence of any organic solvent.

In 2005, Sakakura et al. described the green synthesis of CCs via the coupling reaction of CO_2 and epoxides by use of chlorine-free and single-component catalysts tetrabutylammonium salts of transition-metal-substituted α-Keggin-type silicotungstates $[(n\text{-}C_7H_{15})_4N]_x[\alpha\text{-}SiW_{11}MO_{39}]$ (**22**), M = Fe(III), $x = 0$; M = Mn (II), Co(II), Ni(II), Cu(II), Zn(II), $x = 1$ [25]. The catalytic activity was significantly influenced by the type of transition metal and the counteraction used. When DMF was used as solvent, $[(n\text{-}C_7H_{15})_4N]_6[\alpha\text{-}SiW_{11}O_{39}Co]$ exhibited the highest activity under 3.5 MPa of CO_2 and 150 °C for 2 h, affording 83 % of PC with excellent selectivity above 99 %. In contrast, the Ni(II)- and Fe(III)-substituted POMs showed the moderate activities, whereas the Cu(II) analogs were inert for the synthesis of PC under the same conditions. A postulated mechanism was proposed, where the carbon atom of CO_2 first coordinates to the substituted transition metal to afford an oxygen anion, and then the resulting oxygen anion attacks the less bulky carbon atom of epoxide to open the ring.

In 2004, our group demonstrated that tetrabutylammonium salts of transition-metal-substituted 2-Wells–Dawson-type phosphotungstates $[(n\text{-}C_4H_9)_4N]xP_2W_{17}M(Br)O_{61}$ [M = Co(II), Cu(II), Mn(III)] could serve as efficient, single-component catalysts for the coupling reaction of CO_2 with epoxides without any solvent [26]. Recently, we investigated the tetraheptylammonium salts of transition-metal-substituted α-Keggin-type germanotungstates $[(n\text{-}C_7H_{15})_4N]_nGeW_{11}MO_{39}$ (**23**) (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, $n = 5$ or 6) as halogen-free and single-component catalysts for the coupling reaction of CO_2 and epoxides without any solvent [27]. The catalytic activity significantly depended on the transition metal and the countercation in germanotungstates. Under 3.0 MPa of CO_2 and 150 °C for 2 h, the activities of these germanotungstates gradually increase with transition metals in order of Mn > Zn > Co > Ni > Fe > Cu, and the most active catalyst was $[(n\text{-}C_7H_{15})_4N]_6GeW_{11}MnO_{39}$, which produced PC with 95 % yield. More recently, the tetrabutylammonium salts of tritransition-metal-substituted A-α-tungstogermanate $[(n\text{-}C_4H_9)_4N]_3H_7GeW_9M_3(H_2O)_3O_{37}$ (**24**) [M = Mn(II), Co(II), Ni(II), Cu(II)], which were obtained via a modified synthetic method using $(n\text{-}C_4H_9)_4NHSO_4$ in place of $(n\text{-}C_4H_9)_4NBr$ (TBAB) in order to avoid the possibly environmental pollution caused by the residual halogen ion in POMs when TBAB was used as the origin of cation, were synthesized in our group to serve as an absolutely halogen-free catalysts for the synthesis of CCs from CO_2 and epoxide without any cocatalyst and solvent [28]. The catalytic activities also depended on the transition metal introduced and decreased as following order: Mn > Co > Ni > Cu. Under 3.0 MPa of CO_2 and 150 °C, $[(n\text{-}C_4H_9)_4N]_3H_7GeW_9Mn_3(H_2O)_3O_{37}$ could convert 95 % of epichlorohydrin to EC in 3 h. In each case, however, the selectivity of CCs obtained was more than 98 %. The plausible mechanisms were proposed based on the previous researches.

Metal carboxylate catalysts

In 1984, Kuran et al. demonstrated the synthesis of EC from CO_2 with epichlorohydrin catalyzed by alkali metal salts such as potassium acetate (CH_3COOK), potassium carbonates (K_2CO_3), potassium phenolates (C_6H_5OK), or sodium carbonates (Na_2CO_3)/phase-transfer agent (crown ether) systems [29]. Among them, the K_2CO_3/18-crown-6 catalytic system showed the highest activity under 4 MPa of CO_2 and 120 °C for 48 h, affording almost 100 % yield of EC.

A Zn(II) pyridine-2-carboxylate (**25**)/1-methyl imidazole catalytic system could also promote the coupling reaction of CO_2 with various epoxides such as propylene oxide, butene oxide, styrene oxide, cyclohexene oxide to give the corresponding CCs with low yields (Fig. 3) [30]. Cocatalyst 1-methyl imidazole not only activated the epoxide due to its high nucleophilicity, but also served as good solvent since it could coordinate with the Zn center and enhance the solubility of the Zn carboxylate complex into the reaction mixture.

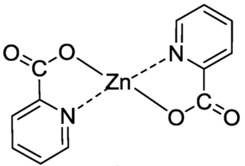

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Fig. 3 Examples of typical metal carboxylate chlorine-free structures under recent investigation for catalytic activity.

Metal hydroxy-containing catalysts

In 2002, Lermontov et al. found that the metal 8-hydroxyquinolinate complexes $M(Ox)_3$ (**26**) [M = Al(III), Cr(III), Fe(III)] in combination with triphenylphosphine oxide served as effective catalysts for the reaction of CO_2 and propylene oxide (Fig. 4) [31]. In contrast, the Fe and Al compounds were more active than the Cr analogue under 1.8 MPa of CO_2 and 155 °C for 5.5 h, affording about 92 % yields of PC.

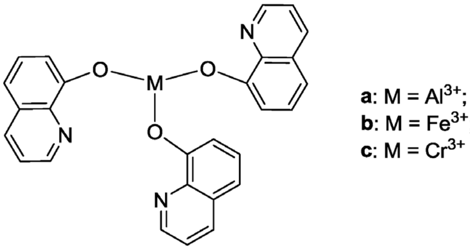

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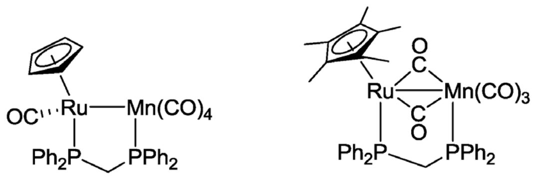
Fig. 4 Examples of typical metal hydroxy-containing chlorine-free structures under recent investigation for catalytic activity.

The hydroxyapatite-bound Zn complex (ZnHAP) in conjunction with a Lewis base represented good activity and selectivity for the coupling of CO_2 and epoxides in the absence of organic solvents [32]. As a Lewis base, DMAP was more efficient than other bases such as NEt_3, DBU, or pyridine. A 98 % yield of SC with 99 % selectivity was achieved by the ZnHAP/DAMP system under 5 MPa of

CO_2 and 100 °C for 20 h. The further addition of organic solvents significantly decreased the catalytic activity of this catalyst.

Metallocene catalysts

A series of well-defined heterobimetallic complexes $[(\eta^5\text{-}C_5H_5)Ru(CO)(\mu\text{-dppm})Mn(CO)_4]$ (**27**) and $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-dppm})(\mu\text{-}CO)_2Mn(CO)_3]$ (**28**) (dppm = bisdiphenylphosphinomethane) were developed by Lin as active catalysts for the coupling reactions of CO_2 with epoxides such as 1,2-epoxyhaxane, butadiene monoxide, cyclohexene oxide, propylene oxide, epifluorohydrin, epichlorohydrin, and epibromohydrin (Fig. 5) [33]. At 39.6 MPa of CO_2 and 100 °C for 2 h, catalyst **27** showed higher activity than catalyst **28**, preparing 13 % yield of epifluorohydrin carbonate. Two possible reaction pathways were proposed, however, both routes began with heterolytic cleavage of the Ru–Mn bond and coordination of an epoxide molecule to the Lewis acidic ruthenium center.



27 **28**

Fig. 5 Examples of typical metallocene chlorine-free structures under recent investigation for catalytic activity.

Metal salen and Schiff-base catalysts

Metal salen complexes have received much attention owing to their excellent catalytic property in the organic reaction and polymerization [34]. Until now, the salen complexes based on almost all of the transition and main-group metals had been synthesized. Among them, some complexes were investigated to be effective for the cycloaddition of CO_2 and epoxides. However, most of these salen-type catalysts involved halogen ions in view of their high nucleophilicity capable of attaching to the least-hindered carbon atom of the epoxide in the cycloaddition. Only a few chlorine-free metal salen catalysts were reported for the green synthesis of CCs from CO_2 and epoxides.

In 2003, Shi et al. explored the catalytic property of binaphthyldiamino salen-type complexes based on Cu(II), Co(II), and Zn(II) (**29**) for the coupling reaction of CO_2 and epoxides such as 1,2-epoxyhaxane, 1,2-epoxybutane, propylene oxide, styrene oxide, and epichlorohydrin in the presence of a catalytic amount of organic base as cocatalyst under 34 MPa of CO_2 and 100 °C for 2 h (Fig. 6) [35]. The results indicated that the unsubstituted complexes **29a–c** showed higher activities than the substituted analogs **29d** and **f** under the same conditions. As cocatalyst, Et_3N and DBU were better than DMAP, pyridine, or DABCO. By use of complexes **29a–b/**Et_3N systems, almost all of the mono-substituted terminal epoxides could be transferred to the corresponding CCs with yields ranging from 10 to 91 %. Moreover, these catalytic systems were stable and could be reused at least 10 times with no lost activity. A Lewis acid and Lewis base cocatalyzed mechanism was suggested.

The Cu salen complexes (**30–31**) also showed good activities for the cycloaddition of CO_2 with epoxides such as propylene oxide and epichlorohydrin (Fig. 6) [36]. Under 0.7 MPa of CO_2 at 120 °C for 4 h, catalyst **31** showed higher activities than catalyst **30**, affording 72 % yield of EC and 34 % yield of PC.

Recently, a series of metal Schiff-base complexes containing Si $[M(L_n)_2]$ [M = Pd(II), Co(II)] (**32**)/DMAP systems exhibited high activities and excellent selectivities for the cycloaddition of CO_2

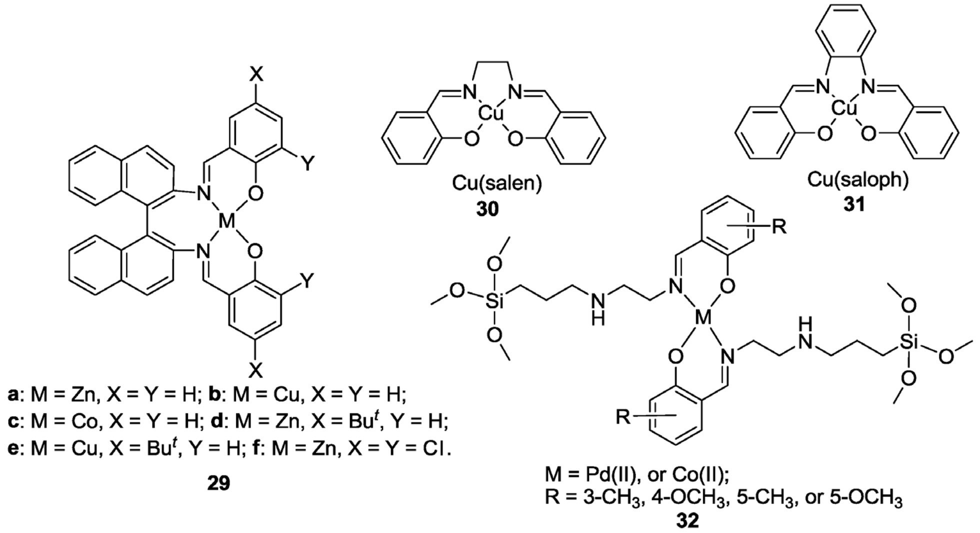


Fig. 6 Examples of typical metal salen and Schiff-base chlorine-free structures under recent investigation for catalytic activity.

and epoxides (e.g., 1,2-epoxybutane, propylene oxide, styrene oxide, and epichlorohydrin) (Fig. 6) [37]. The Pd(II) and Co(II) complexes bearing 5-methyl substituent on the aryl ring ([M(L$_3$)$_2$]) were more active than other complexes used. Under 1.6 MPa of CO$_2$ and 100 °C for 2 h, the [Pd(L$_3$)$_2$] catalyst produced SC with an 82 % yield and 99 % selectivity. Moreover, this catalyst could be reused more than eight times with only a minimal loss of activity.

Metal nitrogen-containing macrocycles catalysts

Several biomimetic Cu complexes bearing porphyrin (**33**), phthalocyanine (**34**), or cyclen ligands (**35–36**) had been utilized as chlorine-free catalysts for the green synthesis of CCs from CO$_2$ and epoxides (Fig. 7) [36]. Some salen complexes (**30–31**), phenanthroline (phen) (**37**), and bipyridine (bipy) complexes (**38**) based on Cu were also synthesized for comparison. It was found that the catalytic activity of such catalyst depended on the biomimetic ligand introduced. In the synthesis of chloropropylene carbonate under 0.7 MPa of CO$_2$ at 120 °C for 4 h, the activities of these catalysts decreased in an order of phthalocyanine (Pc) > tetraphenyl porphyrin (TPP) > phenanthroline (phen) > saloph > salen > cyclen > bipyridine. In the PC preparation, however, the catalytic activity decreased according to the following order: cyclen > phen > saloph > bipy > salen. The catalysts bearing the unsaturated ligands such as Pc and TPP were more efficient than those containing the saturated ligands. Moreover, a remarkable increase in activity was observed if the metal center Cu(II) ions of these catalysts were replaced by the Mn(III) ions.

Recently, a cobalt tetraamidomacrocyclic complex (**39**) was reported as an efficient catalyst for the production of CCs from CO$_2$ with various aliphatic and aromatic epoxides without any solvent even in the low CO$_2$ pressure of about 0.7 MPa [38]. A strong basic cocatalyst such as DMAP was required to remarkably enhance the reaction activity, affording PC with 100 % yield under 2 MPa of CO$_2$ at 120 °C for 3 h.

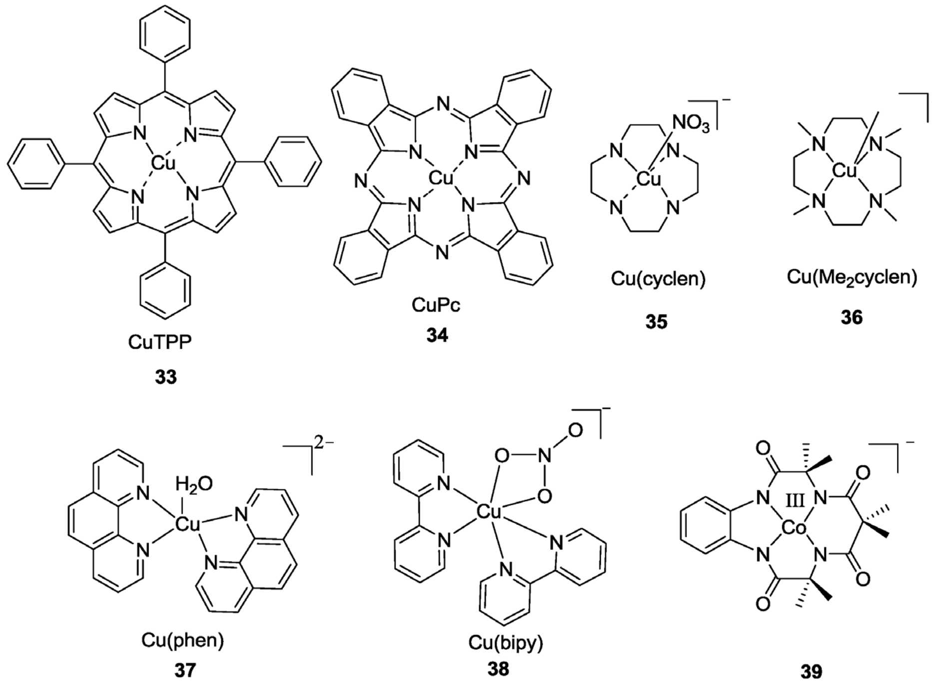


Fig. 7 Examples of typical metal nitrogen-containing macrocycles chlorine-free structures under recent investigation for catalytic activity.

Heterogeneous supported catalysts

Heterogeneous supported catalysts attracted much attention from the industrial view because they could be easily separated at the end of a reaction by filtration and recycled seven times without loss of activity and selectivity, which made them environmentally friendly and markedly superior to the small molecular catalysts.

In the presence of DMAP, the titanosilicate molecular sieves (TS-1 and TiMCM-41) were identified as both efficient and reusable catalysts for the synthesis of CCs from CO_2 with epoxides such as epichlorohydrin and propylene oxide without any solvent [39]. Under 6.8 MPa of CO_2 and 120 °C for 4 h, the TS-1/DMAP system gave 90 % yield of EC with 98 % selectivity and 78 % yield of PC with 88 % selectivity. In contrast, these catalysts exhibited lower activities if larger styrene oxide was used as reactant.

Ti-SBA-15-*pr*-Ade, an organofunctionalized mesoporous titanosilicate adenine-modified Ti-SBA-15 solid, could serve as a highly efficient and single-component catalyst for the coupling reaction of CO_2 with epoxides such as propylene oxide, styrene oxide, and epichlorohydrin without any cocatalyst and solvent [40]. A 94 % yield of SC with 95 % selectivity was obtained by Ti-SBA-15-pr-Ade under 0.7 MPa of CO_2 and 120 °C for 8 h. Moreover, the catalytic activity was further enhanced by increasing the surface concentrations of CO_2 and epoxides. It was suggested that both acidic and basic sites were essential for the insertion of CO_2 into epoxides, and the activation of CO_2 at basic nitrogen groups of adenine was of greater importance to determine the rate of reaction. This catalyst could be reused in several recycle processes.

The green synthesis of PC from CO_2 and propylene oxide was also achieved by a sodium oxide (NaOx) impregnated Engelhard titanosilicate-10 (ETS-10) molecular without any solvent [41]. At 3 MPa of CO_2 and 150 °C for 24 h, a 50 % yield enhancement compared to the unmodified ETS-10 was gained at a loading of 2.0 excess NaOx per unit cell for the dry supported catalyst. Moreover, an increasing activity could be observed after rehydrating the modified ETS-10 overnight in a high humidity chamber. The hydration of this catalyst by waters might create more –OH groups in the surface, which enhanced the Brønsted acidity of the ETS-10 and further increased the yield of PC.

In 2007, Jones et al. reported that a new immobilized DMAP analog supported on mesoporous SBA-15 could promote the cycloaddition of CO_2 with propylene oxide to produce PC with 81 % yield at 3.6 MPa of CO_2 and 120 °C for 4 h [42]. After reaction, the catalyst could be easily separated by filtration. Meanwhile, work by Bhanage et al. showed that silica-supported polyvinyl pyridine (PVP) was a highly effective base catalyst for the synthesis of CCs from CO_2 and epoxides such as propylene oxide, styrene oxide, and epichlorohydrin [43]. At 5.5 MPa of CO_2 and 150 °C for 6 h, the typical optimized PVP/SiO_2 catalyst gave 91 % yield of PC by using toluene as solvent. This catalyst was found to be recyclable over four recycles without any loss in activity.

Recently, Park et al. successfully synthesized the melamine tri-silsesquioxane bridged periodic mesoporous organosilica (PMO) and investigated its catalytic property in the coupling of CO_2 and propylene oxide using DMF as solvent [44]. The catalyst exhibited good yield and selectivity under 5.4 MPa of CO_2 and 100 °C for 10 h. The combination of secondary amine and tertiary amine in a certain position was proposed to be more efficient in activating CO_2 compared with single-type amine species. More recently, Lu et al. reported that N-heterocyclic carbine (NHC) functionalized NHC-CO_2 adduct (MCM-41-IPr-CO_2) (**40**) was also active for the synthesis of CC, which completely converted propylene oxide to PC with 100 % yield and excellent regioselectivity under 2.0 MPa of CO_2 and 120 °C for 48 h (Fig. 8) [45]. This catalyst could be recovered easily through a simple filtration process and reused several times without obvious loss in activity. A mechanism was proposed about the catalytic process. Firstly, the zwitterionic moiety IPr-CO_2 on MCM-41 attacks the strained three-membered heterocyclic rings to form the newzwitterion. Then the nucleophilic attacks of the formed oxy anions toward the carbon atom of carbonyl group produced CC by intramolecular cyclic elimination. Finally, the produced MCM-41-IPr quickly reacted with CO_2 to regenerate MCM-41-IPr-CO_2 adduct.

In 2005, He et al. reported that a type of polystyryl-supported catalysts containing an amino group displayed good activities and reusable properties for the synthesis of PC from CO_2 and propylene oxide under scCO_2 conditions [46]. At 100 °C and 8 MPa of CO_2 for 24 h, the insoluble ion-exchange resins (D380, trade name) containing primary amine (NH_2) afforded PC with 82 % yield and 99 % selectivity. The catalytic activity depended on the functional group and decreased in the following order: tertiary amine [$N(CH_3)_2$] > secondary amine ($NHCH_3$) > primary amine (NH_2). The catalyst could be easily recovered and reused over 5 times without significant loss in activity.

A polymer-supported nanogold was reported to serve as an effective catalyst for the green synthesis of CCs from CO_2 and epichlorohydrin [47]. At 3 MPa of CO_2 and 150 °C for 15 h, 94 % yield of EC was obtained. It was suggested that the unique activity of this catalytic system accounts for the synergy between nanogold species and the peculiar microenvironment of the polymer surface.

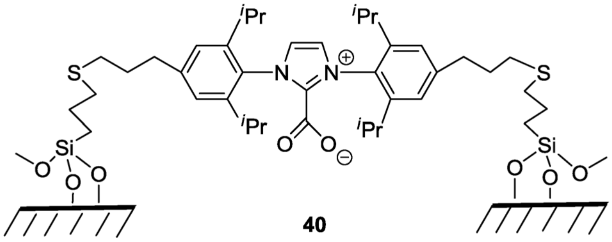


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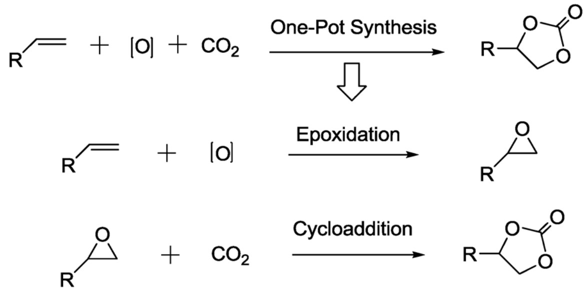
Fig. 8 Example of typical heterogeneous supported chlorine-free structures under recent investigation for catalytic activity.

CHLORINE-FREE CATALYSTS FOR SYNTHESIS OF CCs FROM CO_2 AND OLEFINS

The direct synthesis of CCs from CO_2 and olefins, which can be regarded as an oxidative carboxylation process in combination of two sequential reactions of epoxidation of olefins and subsequent cycloaddition of CO_2 to epoxides formed in one pot, is a more economically viable process because of low-priced and easily available raw material olefin compared with epoxide and the avoidance of separation of epoxide after its synthesis in the first step (Scheme 2). Although the oxidative carboxylation of olefin has been known for a long time since 1962 [48], however, only a few reports are known thus far about such a useful process in contrast to extensive studies on the cycloaddition of CO_2 and epoxides [49]. Moreover, most of them were based on quaternary ammonium halides (special TBAB) with or without organic base cocatalyst (such as DBU) using *tert*-butyl hydroperoxide (TBHP) or H_2O_2 as oxidant [50]. Therefore, the search for a green and highly efficient catalyst for direct synthesis of CCs from olefins and CO_2 is still of great importance from the industrial point of view.

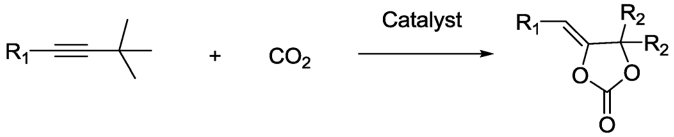


Scheme 2 Synthesis of monosubstituted CCs via cycloaddition of CO_2 with olefins.

In 2000, Aresta et al. reported that transition-metal complexes or metal oxides could catalyze oxidative carboxylation of CO_2 and olefins to form CCs [51]. In comparison, rhodium catalysts showed a lower activity owing to their short life under homogeneous-phase oxidative carboxylation conditions. Moreover, low temperature was required in order to limit the decomposition of catalyst and favor to the oxidation of olefins. By use of Nb_2O_5 as catalyst, 27 % of styrene was converted under 0.5 MPa of O_2, 4.5 MPa of CO_2, and 120 °C for 5 h, affording SC with 17 % selectivity. If V_2O_5 was used as catalyst, the conversion of styrene was increased to 34 % and the selectivity of the resulting SC dropped to 7 % under the same conditions. It was suggested that the reaction process might undergo a radical mechanism started by the heterogeneous catalyst in the oxidation process.

CHLORINE-FREE CATALYSTS FOR SYNTHESIS OF CCs FROM CO_2 AND PROPARGYLIC ALCOHOLS

A green, direct, one-pot synthesis of CC could also be achieved by the one-pot carboxylative cyclization reaction of CO_2 with propargylic alcohols, which affords a particularly simple and environmentally friendly synthetic process (Scheme 3).

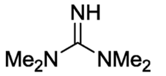


Scheme 3 Synthesis of monosubstituted CCs via carboxylative cycloaddition of CO_2 with propargylic alcohols.

In 1999, Inoue et al. found that the K_2CO_3/crown ether system was an effective catalyst for the preparation of α-alkylidene CC from CO_2 and propargylic alcohol [52]. Under 0.5 MPa of CO_2 and 80 °C for 5 h, the K_2CO_3/dibenzo-18-crown-6-ether system gave a 78 % yield of α-alkylidene CC using *N*,*N*-dimethyl-acetamide (DMAc) as solvent. The catalytic activity was dependent on the pressure of CO_2 and the kind of cation used.

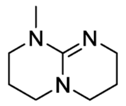
A silver acetate (AgOAc)/DBU catalytic system was developed by Yamada in 2007 for the incorporation of CO_2 with various propargylic alcohols under mild conditions [53]. Under 1.0 MPa of CO_2 and at room temperature, the yields of the resulting CCs ranged from 76 to 96 %. Simultaneously, Ikariya et al. reported that $P(n\text{-}C_4H_9)_3$ showed excellent regio- and stereoselectivity for the carboxylative cyclization of CO_2 and α-alkylidene alcohols under $scCO_2$ conditions [54]. Under 10 MPa of CO_2 and 100 °C for 15 h, the reaction of CO_2 with an internal alkynol 2-methyl-4-phenyl-3-propyn-2-ol gave 88 % yield of 4-benzylidene-5,5-dimethyl-1,3-dioxolan-2-one. It was found that the CO_2 pressure and various electron-withdrawing aromatic groups of the substrates strongly influenced the carboxylative cyclization process.

In 2008, Sun et al. first reported a series of organic bases such as TBD, DBU, and NEt_3 as effective catalysts for the preparation of PC from CO_2 and propylene glycol in the presence of acetonitrile (CH_3CN) [55]. Under 1.0 MPa of CO_2 and 175 °C for 15 h, the TBD/CH_3CN system afforded 15 % yield of PC with 100 % selectivity. In the reaction, CH_3CN acted not only as the solvent but also the dehydrating reagent to remove the resulting water from the reaction. Interestingly, it was found that the selectivity could be significantly enhanced if ammonium carbonate was added into the reaction system. Recently, an organic base guanidine derivative TBD, DBU, 1,1,3,3-tetramethylguanidine (TMG) (**41**), and 1,3,4,6,7,8-hexaydro-1-methyl-2*H*-pyrimido[1,2-a]pyrimidine (MTBD) (**42**) was reported to serve as effective catalyst for the reaction of CO_2 and propargyl alcohols using either $scCO_2$ as solvent and reagent or gaseous CO_2 in MeCN as the solvent (Fig. 9) [56]. MTBD exhibited the highest activity under $scCO_2$ at 100 °C for 24 h, affording 84 % yield.



TMG

41



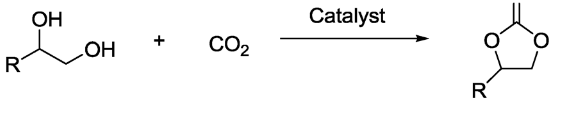
MTBD

42

Fig. 9 Examples of typical chlorine-free structures via cycloaddition of CO_2 with propargylic alcohol under recent investigation for catalytic activity.

CHLORINE-FREE CATALYSTS FOR SYNTHESIS OF CCs FROM CO_2 AND 1,2-DIOLS

The carboxylation of CO_2 and 1,2-diols had received much attention since it is the simplest route for the one-step synthesis of CCs (Scheme 4). Until now, there are some chlorine-free catalysts reported in the literature for this reaction.



Scheme 4 Synthesis of monosubstituted CCs via carboxylative cycloaddition of CO_2 with 1,2-diols.

Work reported by Tomishige in 2004 demonstrated that ceria-based complexes (e.g., CeO_2–ZrO_2) could promote the carboxylation of CO_2 and 1,2-diols, such as ethylene glycol and propylene glycol, to produce the corresponding CCs with good yields [57]. It indicated that the catalytic activity was much dependent on the composition and calcination temperature of the CeO_2–ZrO_2 solid solution. He et al. also reported that a magnesium oxides/metal oxides system (MgO–Al_2O_3), in the absence of any solvents or additives, was also effective for the synthesis of CCs from CO_2 and 1,2-diols (such as glycol, phenyl glycol, and methanol) under 15 MPa of CO_2 and 180 °C for 12 h, producing the corresponding CCs with 100 % selectivity [58].

In the presence of CH_3CN, metal acetates exhibited good activities for the synthesis of CCs from CO_2 and 1,2-diols [59]. Among them, anhydrous zinc acetate $Zn(OAc)_2$ was the best catalyst when 1,2-propylene glycol was used as reactant. Under the optimum conditions of 10 MPa of CO_2 and 170 °C for 12 h, the conversion of 1,2-propylene glycol could reach about 39 %, affording 24 % yield of 1,2-propylene carbonate. CH_3CN, which served as not only the solvent but also the dehydrating reagent, played a crucial role to remove the water formed in the reaction process and further improve the yield of CCs.

In 2005, organometallic stannum complexes such as dibutyltin oxide (Bu_2SnO) or dibutyltin dimethoxide [$Bu_2Sn(OMe)_2$] were investigated by He to serve as effective catalysts for the synthesis of PC from CO_2 and propylene glycol [60]. When ketal was used as a dehydrating agent and DMF was used as a cosolvent, the catalytic activity could be further enhanced. Under 20 MPa of CO_2 and 180 °C for 12 h, both Bu_2SnO and $Bu_2Sn(OMe)_2$ showed similar activities for the carboxylation of CO_2 and propylene glycol by use of DMF as solvent. Bu_2SnO was also active for the preparation of the corresponding CCs from CO_2 and glycerol, propanediol, and ethylene glycol in the presence of methanol [61]. For example, it afforded 35 % yield of 1,2-glycerol carbonate under 3.5 MPa of CO_2 and 80 °C for 4 h. In order to achieve a higher yield of CCs, it was necessary to remove the water formed during the reaction from the system. The intermediates were identified by ^{13}C NMR, IR, and mass spectroscopy.

CONCLUSION

As described above, some progress in the green synthesis of CCs from CO_2 catalyzed by chlorine-free catalysts have been achieved in the past three decades. Changing synthetic routes, organic catalyst structures, metal, or the ancillary ligands of metal-based complexes is obviously an important strategy for the modification of the catalytic performance. In the classical and industrial way for the preparation of CCs from CO_2 and epoxides, chlorine-free organic catalysts have demonstrated to be greener for the cycloaddition of CO_2 with various epoxides under mild conditions. However, the relatively low catalytic activity limited their wide applications in industry. Chlorine-free POMs with α-Keggin-type structures also represented a type of economically attractive catalysts for such cycloaddition, nevertheless, highly efficient POMs based on other structures are still very limited. Chlorine-free metal-based catalysts are the most extensively investigated catalytic systems for the green synthesis of CCs from CO_2 and epoxides, and a large number of metal complexes bearing various ancillary ligands have been examined. The subtle interplay between the Lewis base site and Lewis acid site of the ancillary ligands in such metal-based complexes could result in a significantly increasing activity in some cases.

It should also be pointed out that in comparison with the rather successful synthesis of CCs from CO_2 and epoxide, the green synthesis of CCs from CO_2 with other reactants such as olefin, propargylic alcohol, and 1,2-diol achieved only limited success, which usually yielded the CCs with low activity and selectivity. Therefore, future challenges in this area will include the development of more effective chlorine-free catalysts that can efficiently promote the green synthesis of CCs from CO_2 via not only an environmentally benign process but also an economical process in a reusable fashion, to produce diverse CCs with low price using widespread raw material. Undoubtedly, the synthesis of new chlorine-free complexes with various sophisticatedly controlled organic ligand and/or various metal centers will continue to play an important role in these endeavors.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Fund Council of China (20974014, 20731002, 10876002), the 111 Project (B07012), the Program of Cooperation of the Beijing Education Commission (20091739006), the Excellent Young Scholars Research Fund of the Beijing Institute of Technology (No. 22050205), and the Basic Research Fund of Beijing Institute of Technology (20091742015).

REFERENCES

1. (a) I. Omae. *Catal. Today* **115**, 33 (2006); (b) C. Song. *Catal. Today* **115**, 2 (2006); (c) T. Sakakura, J. Choi, H. Yasuda. *Chem. Rev.* **107**, 2365 (2007); (d) D. J. Darensbourg, M. W. Holtcamp. *Coord. Chem. Rev.* **153**, 155 (1996); (e) M. Shi, Y. Shen. *Curr. Org. Chem.* **7**, 737 (2003); (f) M. Aresta, A. Dibenedetto. *Dalton Trans.* 2975 (2007); (g) M. Mikkelsen, M. Jørgensen, F. C. Krebs. *Energy Environ. Sci.* **3**, 43 (2010).
2. (a) A. A. G. Shaikh, S. Sivaram. *Chem. Rev.* **96**, 951 (1996); (b) J. H. Clements. *Ind. Eng. Chem. Res.* **42**, 663 (2003); (c) B. Schäffner, F. Schaffner, S. P. Verevkin, A. Börner. *Chem. Rev.* **110**, 4554 (2010).
3. (a) D. J. Darensbourg, M. W. Holtcamp. *Coord. Chem. Rev.* **153**, 155 (1996); (b) G. W. Coates, D. R. Moore. *Angew. Chem., Int. Ed.* **43**, 6618 (2004); (c) J. M. Sun, S. Fujita, M. Arai. *J. Organomet. Chem.* **690**, 3490 (2005).
4. (a) M. Aresta, E. Quaranta. *J. Mol. Catal.* **41**, 355 (1987); (b) M. Aresta, A. Dibenedetto, I. Tommasi. *Appl. Organomet. Chem.* **14**, 799 (2000); (c) J. Sun, S.-I. Fujita, F. Zhao, M. Hasegawa, M. Arai. *J. Catal.* **230**, 398 (2005).
5. H. F. Jiang, A. Z. Wang, H. L. Liu, C. R. Qi. *Eur. J. Org. Chem.* 2309 (2008).
6. Q. Li, W. Zhang, N. Zhao, W. Wei, Y. Sun. *Catal. Today* **115**, 111 (2006).
7. (a) T. Sakakura, K. Kohno. *Chem. Commun.* 1312 (2009); (b) M. North, R. Pasquale, C. Young. *Green Chem.* **12**, 1514 (2010).
8. Y. Shen, W. Duan, M. Shi. *Adv. Synth. Catal*. **345**, 337 (2003).
9. R. Srivastava, T. H. Bennur, D. Srinivas. *J. Mol. Catal., A* **226**, 199 (2005).
10. H. Kawanami, Y. Ikushima. *Chem. Commun*. 2089 (2000).
11. J. Jiang, R. Hua. *Synth. Commun.* **36**, 3141 (2006).
12. R. A. Shiels, C. W. Jones. *J. Mol. Catal., A* **261**, 160 (2007).
13. K. M. K. Yu, I. Curcic, J. Gabriel, H. Morganstewart, S. C. Tsang. *J. Phys. Chem. A* **114**, 3863 (2010).
14. Y. Tsutsumi, K. Yamakawa, M. Yoshida, T. Ema, T. Sakai. *Org. Lett*. **12**, 5728 (2010).
15. H. Zhou, W. Zhang, C. Liu, J. Qu, X. Lu. *J. Org. Chem*. **73**, 8039 (2008).
16. T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima. *Chem. Commun*. 1129 (1997).
17. K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda. *J. Am. Chem. Soc*. **121**, 4526 (1999).
18. M. Tu, R. J. Davis. *J. Catal.* **199**, 85 (2001).
19. W. Dai, S. Yin, R. Guo, S. Luo, X. Du, C. Au. *Catal. Lett*. **136**, 35 (2010).
20. H. Yasuda, L. He, T. Takahashi, T. Sakakura. *Appl. Catal., A* **298**, 177 (2006).
21. M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore. *J. Mol. Catal., A* 245 (2003).

22. (a) C. L. Hill, C. M. Prosser-McCartha. *Coord. Chem. Rev.* **143**, 407 (1995); (b) T. Okuhara, N. Mizuno, M. Misono. *Adv. Catal.* **41**, 113 (1996); (c) I. V. Kozhevnikov. *Chem. Rev.* **98**, 171 (1998); (d) N. Mizuno, M. Misono. *Chem. Rev.* **98**, 199 (1998).
23. (a) S. H. Szczepankiewicz, C. M. Ippolito, B. P. Santora, T. J. Van de Ven, G. A. Ippolito, L. Fronckowiak, F. Wiatrowski, T. Power, M. Kozik. *Inorg. Chem.* **37**, 4344 (1998); (b) M. Sankar, N. H. Tarte, P. Manikandan. *Appl. Catal., A* **276**, 217 (2004); (c) C. G. Wang, C. J. Jiang, C. W. Hu. *Chem. J. Chin. Univ. (in Chinese)* **25**, 1325 (2004); (d) D. W. Sun, H. J. Zhai. *Catal. Commun.* **8**, 1027 (2007).
24. M. Sankar, N. H. Tarte, P. Manikandan. *Appl. Catal., A* **276**, 217 (2004).
25. H. Yasuda , L. He, T. Sakakura, C. Hu. *J. Catal.* **233**, 119 (2005).
26. C. G. Wang, C. J. Jiang, C. W. Hu. *Chem. J. Chin. Univ.* **25**, 1325 (2004).
27. F. Chen, T. Dong, Y. Chi, Y. Xu, C. Hu. *Catal. Lett.* **139**, 38 (2010).
28. F. Chen, T. Dong, X. Li, T. Xu, C. Hu. *Chin. Chem. Lett.* **22**, 871 (2011).
29. G. Rokicki, W. Kuran, B. Pogorzelska-Marciniak. *Monatsh. Chem.* **115**, 205 (1984).
30. T. A. Zevaco, A. Janssen, E. Dinjus. *Arkivoc* **3**, 151 (2007).
31. (a) S. A. Lermontov, T. N. Velikokhat'ko, V. O. Zavel'skii. *Russ. J. Gen. Chem.* **72**, 1492 (2002); (b) S. A. Lermontov, T. N. Velikokhat'ko, V. O. Zavel'skii. *Russ. Chem. Bull. Int. Ed.* **51**, 836 (2002).
32. K. Mori, Y. Mitani, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda. *Chem. Commun.* 3331 (2005).
33. (a) F. Torres, E. Sola, A. Elduque, A. R. Martinez, F. J. Lohoz, L. A. Oro. *Chem.—Eur. J.* **6**, 2120 (2000); (b) Y. Ohki, H. Suzuki. *Angew. Chem., Int. Ed.* **112**, 3605 (2000).
34. (a) K. C. Gupta, A. K. Sutar. *Coord. Chem. Rev.* 252 (2008); (b) A. Decortes, A. M. Castilla, A. W. Kleij. *Angew. Chem., Int. Ed.* **49**, 9822 (2010).
35. Y. Shen, W. Duan, M. Shi. *J. Org. Chem.* **68**, 1559 (2003).
36. R. Srivastava, T. H. Bennur, D. Srinivas. *J. Mol. Catal., A* **226**, 199 (2005).
37. M. Ulusoy, A. Kilic, M. Durgun, Z. Tasci, B. Cetinkaya. *J. Organomet. Chem.* **696**, 1372 (2011).
38. A. Ghosh, P. Ramidi, S. Pulla, S. Z. Sullivan, S. L. Collom, Y. Gartia, P. Munshi, A. S. Biris, B. C. Noll, B. C. Berry. *Catal. Lett.* **137**, 1 (2010).
39. R. Srivastava, D. Srinivas, P. Ratnasamy. *Catal. Lett.* **91**, 1 (2003).
40. R. Srivastava, D. Srinivas, P. Ratnasamy. *J. Catal.* **233**, 1 (2005).
41. E. J. Doskocil. *J. Phys. Chem. B* **109**, 2315 (2005).
42. R. A. Shiels, C. W. Jones. *J. Mol. Catal., A* **261**, 160 (2007).
43. S. R. Jagtap, V. P. Raje, S. D. Samant, B. M. Bhanage. *J. Mol. Catal., A* **266**, 69 (2007).
44. E. A. Prasetyanto, M. B. Ansari, B. H. Min, S. E. Park. *Catal. Today* **158**, 252 (2010).
45. H. Zhou, Y. Wang, W. Zhang, J. Qu, X. Lu. *Green Chem.* **13**, 644 (2011).
46. Y. Du, F. Cai, D.-L. Kong, L. He. *Green Chem.* **7**, 518 (2005).
47. F. Shi, Q. Zhang, Y. Ma, Y. He, Y. Deng. *J. Am. Chem. Soc.* **127**, 4182 (2005).
48. J. A. Verdol. U.S. Patent 3025305 (1962).
49. (a) J. L. Wang, J. Q. Wang, L. N. He, X. Y. Dou, F. Wu. *Green Chem.* **10**, 1218 (2008); (b) D. Xiang, X. F. Liu, J. S. Sun, F. S. Xiao, J. M. Sun. *Catal. Today* **148**, 383 (2009); (c) J. Zhang, Y. M. Liu, N. N. Li, H. H. Wu, X. H. Li, W. Xie, Z. L. Zhao, P. Wu, M. Y. He. *Chin. J. Catal.* **29**, 589 (2008).
50. (a) J. M. Sun, S. I. Fujita, B. Bhanage, M. Arai. *Catal. Commun.* **5**, 83 (2004); (b) J. M. Sun, S. I. Fujita, B. Bhanage, M. Arai. *Catal. Today* **93–95**, 383 (2004); (c) F. Chen, T. Dong, T. Xu, X. Li, C. Hu. *Green Chem.* **13**, 2518 (2011).
51. M. Aresta, A. Dibenedetto, I. Tommasi. *Appl. Organomet. Chem.* **14**, 799 (2000).
52. K. Uemura, T. Kawaguchi, H. Takayama, A. Nakamura, Y. Inoue. *J. Mol. Catal., A* **139**, 1 (1999).
53. W. Yamada, Y. Sugawara, H. Cheng, T. Ikeno, T. Yamada. *Eur. J. Org. Chem.* 2604 (2007).
54. Y. Kayaki, M. Yamamoto, T. Ikariya. *J. Org. Chem.* **72**, 647 (2007).
55. S. Huang, J. Ma, J. Li, N. Zhao, W. Wei, Y. Sun. *Catal. Commun.* **9**, 276 (2008).

56. N. Ca, B. Gabriele, G. Ruffolo, L. Veltri, T. Zanetta, M. Costa. *Adv. Synth. Catal*. **353**, 133 (2011).
57. K. Tomishige, H. Yasuda, Y. Yoshida, M. Nurunnabi, B. Li, K. Kunimori. *Green Chem*. **6**, 206 (2004).
58. Y. Du, L. He, D. Kong. *Catal. Commun.* **9**, 1754 (2008).
59. S. Huang, S. Liu, J. Li, N. Zhao, W. Wei, Y. Sun. *J. Fuel Chem. Technol*. **35**, 701 (2007).
60. Y. Du, D. Kong, H. Wang, F. Cai, J. Tian, J. Wang, L. He. *J. Mol. Catal., A* **241**, 233 (2005).
61. J. Georgea, Y. Patel, S. Pillai, P. Munshic. *J. Mol. Catal., A* **304**, 1 (2009).