

HCAII-inspired Catalysts for Making Carbon Dioxide-based Copolymers: The Role of Metal-hydroxide Bond

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Abstract The general characteristics of the active center of the catalysts (including zinc-cobalt(III) double metal cyanide complex [Zn-Co(III) DMCC]) for the copolymerization reaction of carbon dioxide (CO₂) with epoxide are summarized. By comparing the active center, catalytic performance of the Zn-Co(III) DMCC (and other catalysts) with HCAII enzyme in the organism for activating CO₂ (COS and CS₂), we proposed that the metal-hydroxide bond (M-OH), which is the real catalytic center of human carbonic anhydrase II (HCAII), is also the catalytic (initiating) center for the copolymerization. It accelerates the copolymerization and forms a closed catalytic cycle through the chain transfer reaction to water (and thus strictly meets the definition of the catalyst). In addition, the metal-hydroxide bond catalysis could well explain the oxygen/sulfur exchange reaction (O/S ER) in metal (Zn, Cr)-catalyzed copolymerization of COS (and CS₂) with epoxides. Therefore, it is very promising to learn from HCAII enzyme to develop biomimetic catalyst for highly active CO₂/epoxide copolymerization in a well-controlled manner under mild conditions.

Keywords Carbon dioxide; Carbonic anhydrase (CA); Copolymerization; Metal-hydroxide bond

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INTRODUCTION

Carbon dioxide (CO₂) is the most important part of the carbon cycle in the natural environment. The CO₂ concentration in the atmosphere increased sharply due to the explosive growth of the industrial activities in recent 100 years. It no doubt causes climate change, global temperature rise, ocean acidification and glacial melting^[1–3]. The environmental disaster events will increase if we do not take any actions. The utilization of CO₂, and reduction of CO₂ emission are of great importance and urgency to the future of the human beings. The chemical fixation of CO₂ into useful materials has been a meaningful and pragmatic subject in both chemistry and environment science^[4–7], since CO₂ is a naturally abundant, nontoxic, nonflammable and low-cost one-carbon (C1) building block.

CO₂, as a symmetrical heterocumulene, inherently comprises both electron donating and electron accepting sites. The conversion of CO₂ into small organic compounds^[8–12] and polymers^[1, 13–21] has been studied by intensive works. It is still challenging to activate CO₂ for polymerization because CO₂ is thermodynamically stable and/or kinetically inert in such chemical transformations^[19, 20]. Energy-rich substrates such as epoxides are often used to couple with CO₂ to produce

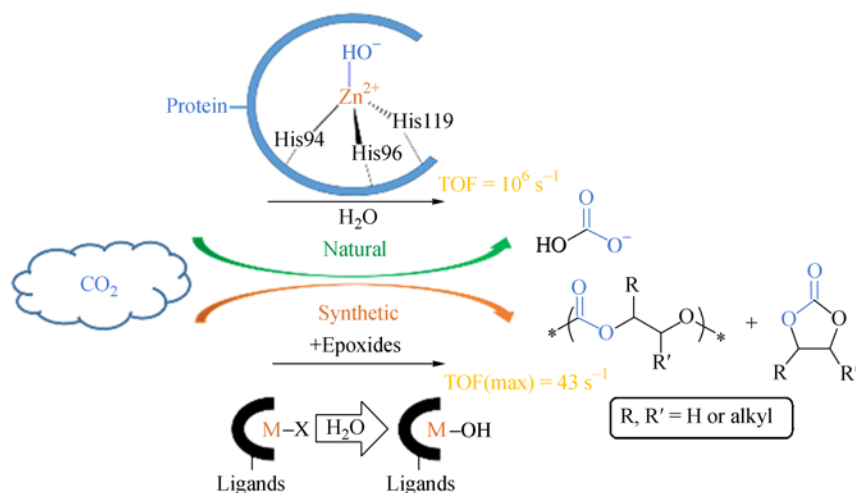
polycarbonates *via* the catalysis of the metallic catalysts, which has made a huge success over the past decades^[1, 14–17, 22]. Compared with the ring-opening polymerization of propylene oxide (PO) for making polyols, a widely used oligomer for making polyurethanes, if 20 wt% CO₂ was incorporated into the PO-based polyols to form poly(ether-co-carbonate), 11%–19% carbon emission could be reduced based on the estimation of the pilot production^[23]. Therefore, the CO₂/epoxide copolymerization reaction is indeed a low-carbon route for preparing new polymers.

To date, the most active catalyst was reported with a maximum turnover frequency (TOF) of 155000 h^{−1} (*ca.* 43 s^{−1}) for the copolymerization of CO₂ with an epoxide, cyclohexene oxide (CHO)^[24]. In contrast, a widely existing zinc enzyme in nature, human carbonic anhydrase II (HCAII), can reversibly convert CO₂ to HCO₃[−] in its atmospheric concentration with a TOF of 10⁶ s^{−1} in aqueous solution (pH = 9) at 25 °C, *i.e.*, CO₂ hydration^[25], as shown in Scheme 1. Hopefully, there is lots of scope to improve the catalyst activity for CO₂/epoxide copolymerization. On the other hand, the catalytic activity for CO₂/epoxide copolymerization is still about 1–2 orders of magnitude lower than either Ziegler-Natta catalyst or metallocene catalyst for olefin polymerization, which has been widely used in large-scale production^[26]. Hence, it is still a big challenge to design new catalysts with satisfied catalytic activity for CO₂/epoxide copolymerization with a commercial value.

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Scheme 1 Illustration of natural CO₂ hydration by HCAII and CO₂/epoxide copolymerization by metal complexes (M is metal ion, and X is anion)

In this article, we present a comparative review on the catalytic center, catalytic mechanism of zinc-cobalt(III) double metal cyanide complex [Zn-Co(III) DMCC] (and most of the highly active catalysts) for CO₂/epoxide copolymerization with HCAII for CO₂ hydration. It is proposed that the metal-hydroxide bond, which is the real catalytic center of HCAII, is also the catalytic (initiating) center for the copolymerization. The result of the COS (CS₂)/epoxide copolymerization *via* metal catalysts strongly supported the metal-OH catalysis. Furthermore, organic Lewis acid-base catalysis for C1/epoxide copolymerization is presented. This study may be helpful to the design of new catalysts for CO₂/epoxide copolymerization.

HCAII-INSPIRED CATALYSTS

Metal Catalysts for CO₂/Epoxide Copolymerization

In 1969, Inoue and co-workers reported a landmark discovery of the diethyl zinc (ZnEt₂)/H₂O system for CO₂/PO copolymerization^[13]. Since then, much progress has been made in developing various metal complex catalysts for the copolymerization of CO₂ with various epoxides^[1, 14–17]. The catalysts for the copolymerization of CO₂ with epoxides can be classified into two major categories. One is the heterogeneous catalysts including ZnEt₂/protic compounds^[13, 27–29], zinc dicarboxylates^[30–33], rare earth metals (including Y and La) in combination with other metals (*e.g.* zinc)^[34, 35], and double metal cyanide complexes (DMCCs)^[36, 37], *etc.* Mostly, they are zinc-based catalysts. The others are the homogeneous metal catalysts that have been intensively explored, for example, aluminium tetraphenylporphyrin (tpp) complex^[38], zinc bis-phenoxide complex^[39], β -diiminate (BDI) zinc complexes^[40], bimetallic anilido-alimine zinc complexes^[41], salen (salicylalimine) Co (Cr or Al) complexes^[42–45], *etc.* The preparation, catalytic performance and mechanism of these metal catalysts were investigated in detail.

Among all reported catalysts, heterogeneous Zn-Co(III) DMCC has been developed to be a promising class of effective catalyst for C1 (CO₂, COS and CS₂)/epoxide

copolymerization^[46–51]. The traditional preparation of Zn-Co(III) DMCC was usually operated at room temperature *via* precipitation reaction of excess ZnCl₂ and K₃Co(CN)₆ in water/*tert*-butanol (*t*-BuOH) mixed solution^[52]. By using a hydrothermal method, our group prepared nano-sized hybrid SiO₂/Zn-Co(III) DMCC (and Zn-Co(III) DMCC) with nanolamellar morphology with nano-sized pores (Fig. 1a). It presented high surface area of > 500 m²/g determined from N₂ adsorption-desorption isotherm^[53] and can accommodate more catalytic sites on the surface of the catalyst. Thus, such nano-sized Zn-Co(III) DMCC presented improved catalytic activity for CO₂/epoxide copolymerization. Meanwhile, the nano-sized catalysts were thermally stable, non-sensitive to air and moisture, and thus satisfied large-scale production of CO₂-based copolymers.

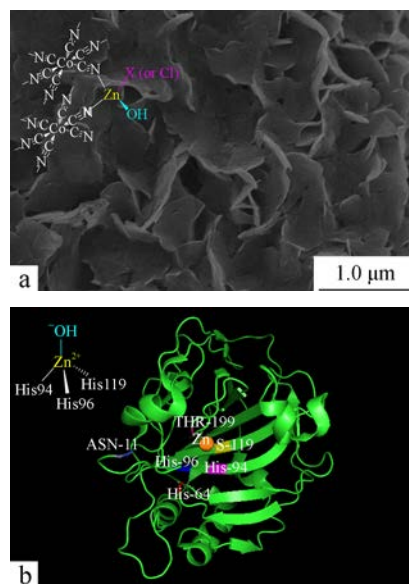
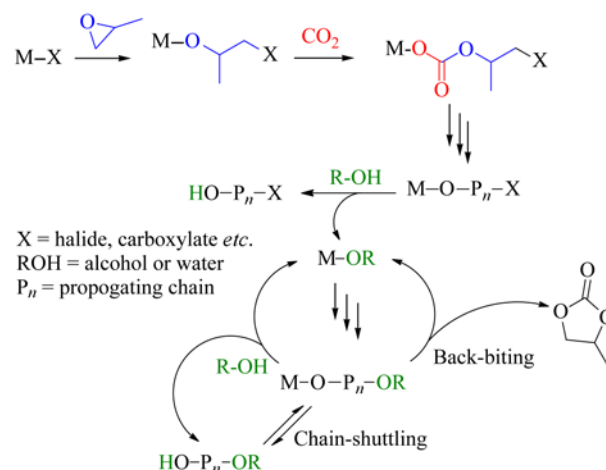


Fig. 1 (a) Typical nanolamellar structure and the proposed ground state of the active site of the Zn-Co(III) DMCC catalyst (X is complexing agent and often *t*-BuOH); (b) Protein fold and the active site of HCAII

Being different from the similar catalysts reported early^[31, 54, 55], Zn-Co(III) DMCC prepared from hydrothermal method has certain composition ratio of the elements, rather than non-stoichiometric. The molar ratio of $\text{Zn}^{2+}:\text{Co}^{3+}:\text{CN}^-$ in the catalyst was 2:1:6 even excess ZnCl_2 was applied to the synthesis. The formula of Zn-Co(III) DMCC was thus supposed to be $\text{Zn}_2[\text{Co}(\text{CN})_6](\text{OH})_a\text{Cl}_b\cdot y\text{CA}\cdot z\text{H}_2\text{O}$ ($a + b = 1$, CA is complexing agent) (Fig. 1a) based on the elemental analysis and Fourier transform infrared (FTIR) spectroscopy of the catalyst at different temperatures^[47]. Herein, two CN^- groups are shared by Zn^{2+} and Co^{3+} ions. The proposed active center contains one negative charge in one tetrahedral Zn^{2+} , which meets the electroneutrality principle due to the existence of OH^- (and Cl^-). Such zinc-hydroxide ($\text{Zn}-\text{OH}$) bond is similar to that of the active site of HCAII (Fig. 1b), which will be discussed in the next section. In addition, the $\text{Zn}-\text{OH}$ bond of Zn-Co(III) DMCC can also be regarded as a Lewis acid-base pair with nucleophilicity that is influenced by the Co-CN-Zn bridge bond (Fig. 1a)^[56].

Mechanistic study on Zn-Co(III) DMCC catalysis for CO_2 /epoxide copolymerization also confirmed the existence of $\text{Zn}-\text{OH}$ bond^[47, 57], which is able to activate the epoxide and CO_2 collaboratively^[47]. All reported CO_2 /epoxide copolymers via Zn-Co(III) DMCC catalysis had two $-\text{OH}$ end groups, which were clearly revealed by the electrospray ionization mass spectroscopy (ESI-MS). Considering CO_2 /PO copolymerization as an instance (Scheme 2), one $-\text{OH}$ end group can only come from the initiation of $\text{Zn}-\text{OH}$ bond of the catalyst, and the other is produced by the chain transfer process of the propagating chain to water (or free copolymer with $-\text{OH}$ end groups, or other impurities with active protons) in the reaction system, and thus it is an immortal polymerization. Therefore, a closed catalytic cycle for regenerating $\text{Zn}-\text{OH}$ bond is achieved, and Zn-Co(III) DMCC is a real catalyst for CO_2 /epoxide copolymerization, which can be revived and recycled rather than only an initiator^[58]. Note that, although Zn-Co(III) DMCC contained chlorine (Cl), not any Cl-capped copolymers were observed in the above copolymerization systems, indicating that $\text{Zn}-\text{Cl}$ bond initiation could be minimized, even if occurred. Concurrently, our previous work revealed that $\text{Zn}_2[\text{Co}(\text{CN})_6]\text{OH}$ ^[59] and $\text{Zn}_2[\text{Co}(\text{CN})_6]\text{Cl}$ had no catalytic activity towards CO_2 /epoxide copolymerization. Therefore, the role of Cl in the proposed structure of $\text{Zn}_2[\text{Co}(\text{CN})_6](\text{OH})_a\text{Cl}_b$ ($a + b = 1$)^[60] still needs further exploration.

The chain initiation, growth and transfer reaction for Zn-Co(III) DMCC-catalyzed CO_2 /PO copolymerization could be generally depicted in Scheme 2^[47]. Clearly, the control of the molecular weights, and the chain microstructure especially the end groups of the final copolymer are closely related to the water content in the reaction system. However, it is difficult to completely remove water from CO_2 /epoxide reaction system, and thus the effect of trace water on the catalysis should be carefully considered. Furthermore, the notable feature of the chain growth of the CO_2 /epoxide copolymerization is directly related to the formation of new carbon-oxygen bond between CO_2 and



Scheme 2 The general chain initiation, chain growth and termination (chain transfer) for the CO_2 /PO copolymerization via metal catalysis (X is anion, such as OH^- , Cl^- and others listed in Table 1. When ROH is water, the catalytic cycle is achieved with regenerating $\text{M}-\text{OH}$ bond.)

epoxide by sequential ring-opening reaction of epoxide and breaking of one $\text{C}=\text{O}$ double bond of CO_2 . The alternated formation of new carbon-oxygen bond by the metal catalysts often undergoes a coordination-insertion pathway, as illustrated in Scheme 2, which determines the selectivity of the copolymerization^[14].

Another kind of heterogeneous catalyst, zinc carboxylate has been subjected to the most intensive studies because it could catalyze CO_2 /PO copolymerization to afford high molecular weight copolymer. Various zinc compounds (e.g. ZnO , $\text{Zn}(\text{OH})_2$, $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{ClO}_4)_2$, ZnEt_2) and carboxylates (e.g. glutaric acid, anhydride, methyl ester, glutaronitrile)^[29–33] were used to prepare zinc carboxylates. Thereof, the product of ZnO and glutaric acid (GA), was optimized to be the best zinc carboxylate catalyst for CO_2 /epoxide copolymerization. An early study on the ZnGA-catalyzed PO/ CO_2 copolymerization disclosed that the resultant copolymer had two $-\text{OH}$ end groups, identified by MALDI TOF-MS^[61]. It is inferred that ZnGA contained $\text{Zn}-\text{OH}$ bond was the catalytic species, similar to Zn-Co(III) DMCC catalyst.

Homogeneous catalysts are particularly popular in CO_2 /epoxide copolymerization. They have generally octahedral (seldom, tetrahedral) coordination structures with multi-dentate metal complexes with N_4 -, O_2 -, N_2 - and N_2O_2 -chelating ligands (L_n) and anion (X^-). A pristine catalyst (or precatalyst) is often denoted as a simplified formula of $(\text{L}_n)\text{M}-\text{X}$, where L_n is an ancillary ligand that is mono-, di-, or trianionic ($n = 1-3$), and X^- is an anion with nucleophilic ability^[14, 62], as summarized in Table 1. The effect of the ligand backbone, metal ions, anions and cocatalysts on the copolymerization has been investigated in detail in intensive of previous works^[1, 15, 17, 43, 44, 63–69]. Totally, X^- is coordinated with the metal ion and can often attack the binding monomers (usually epoxide) for initiating the copolymerization; the resultant products reasonably contain polymers with one $-\text{X}$ end group and one $-\text{OH}$ end group

Table 1 Summary of typical homogeneous metal catalysts for CO₂/epoxide copolymerization (only metal ions, anions X and cocatalysts are presented)

Metal	X	Cocatalysts
Mg	Br, OAc, O ₂ CCF ₃	[PPN]X (X = F, Cl, Br, I, OAc, N ₃ , HCO ₃ , DNP), <i>n</i> -Bu ₄ NX (X = F, Cl, Br, I), Et ₃ N, EtPh ₃ PBr,
Al	Me, Cl, OR, O ₂ CR (R = alkyl)	4-(dimethylamino)pyridine (DMAP),
Ti	Cl	4-(pyrrolidin-1-yl)pyridine (4-PYP), 1-methylimidazole (MeIm), 18-diazabicyclo[5.4.0]undec-7-ene (DBU),
Cr	Cl, OR, N ₃ , NO ₃	7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD),
Co	I, Br, Cl, OR, 2,4-dinitrophenolate (DNP), N ₃ , OAc, O ₂ CCl ₃ , O ₂ CCF ₃ , <i>p</i> -NO ₂ C ₆ H ₄ CO ₂ , C ₆ F ₅ CO ₂ , NO ₃ , OTs, ClO ₄ , BF ₄ , PF ₆	1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)
Zn	OAc, O ₂ CCF ₃	

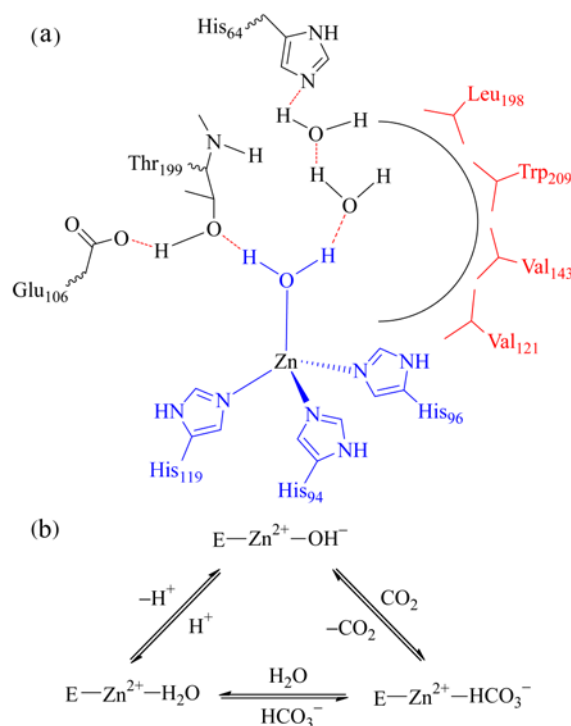
(Scheme 2). It should be noted that, for CO₂/epoxide copolymerization with an immortal style, *i.e.*, the rate of the chain transfer reaction is much faster than that of the chain growth. The chain transferring to trace water in the reaction system will generally lead to the formation of copolymers with two —OH end groups. That is, metal —OH species was *in situ* generated and initiated the copolymerization inevitably. Indeed, most of the previous publications disclosed bimodal GPC curves even the resultant copolymers had narrow molecular weight distributions, one of which was a copolymer with two —OH end groups^[42, 70–74]. However, in the preparation of these organic metal complexes, when X[−] was replaced by OH[−], the resultant metal hydroxide compounds were often to form dimer or solid aggregates that did not dissolve in most of the organic systems and thus no catalytic activity for CO₂/epoxide copolymerization. An exception is a (salen)Cr-OH complex reported by Klaus *et al.* and Salmeia *et al.*, which could catalyze the CO₂/PO copolymerization in a moderate (low) activity^[74, 75].

Zn—OH Bond of HCAII for CO₂ Hydration

As mentioned above, we have demonstrated that metal—OH bond of all metal catalysts could be the real catalytic center for immortal CO₂/epoxide copolymerization due to the chain transfer reaction to water. Concurrently, carbonic anhydride (CA) zinc enzyme, which presents high catalytic activity towards the reversible CO₂ hydration, *i.e.*, CO₂/HCO₃[−] interconversion^[25], belongs to a superfamily of metalloenzymes in all living beings. CA dominates a number of important biological processes, including CO₂/HCO₃[−] exchange during the animal respiration and plant photosynthesis process^[76], which are the result of the natural selection. Undoubtedly, CA is a universal enzyme of the carbon-based life. It basically contained one Zn—OH bond in a tetrahedral coordination^[76] (Fig. 1b).

HCAII is the most active among all currently known hundreds of CAs (TOF: 10⁶ s^{−1} for CO₂ hydration)^[25]. It can be said that the rate of HCAII catalysis for CO₂ hydration is only limited by the rate of ion diffusion^[77], which is closely related to its dynamic molecular structure. The crystallographic studies show that the active site of HCAII is a cavity of tetrahedral geometry formed by three amino acid residues and one deprotonated water^[78]. The polypeptide chain of HCAII is composed of more than 260 amino acids and forms an ellipsoid^[79–81] with the dimensions of 55 Å × 42 Å × 39 Å and has a molecular weight of 3.0 × 10⁴ Da. The zinc ion is coordinated to three imidazole groups from His-94, His-96, and His-119 with an additional water molecule, completing a

nearly symmetrical, tetrahedral coordination geometry (Scheme 3a). The arrangement of the amino acids leads to a hydrophilic and a hydrophobic surrounding in the cavity. The hydrophilic region contains His64 and additional water molecules and is responsible for the migration of the proton from the zinc-bound water to the external medium. The hydrophobic site is thought to provide binding pockets for fast CO₂ transport to and from the blood stream^[81]. Such hydrophilic-hydrophobic structure drives the activation of CO₂ very efficiently. Totally, Zn—OH nucleophilic species with a unique adaptable architecture and hydrophilic-hydrophobic environment allows HCAII to act as the most effective catalysts known in nature^[78].

**Scheme 3** (a) The active zinc site of HCAII and the local environment around the site; (b) The catalytic pathways of HCAII for CO₂ hydration

The catalysis of HCAII for CO₂ hydration is presented by two steps^[82]. The first stage involves the conversion of CO₂ into HCO₃[−]. Zn—OH in the active site of the enzyme is a strong nucleophile, which attacks a CO₂ molecule, leading to the formation of HCO₃[−] associated with Zn²⁺ (Scheme 3b). Then, HCO₃[−] is replaced with one water molecule and

released into solution. This generates an inactive acid form of the enzyme, with water coordinated to Zn^{2+} . The second stage regenerates the active basic form of the enzyme by ionization of one water molecule associated with zinc ion, and a proton is released from the active site. In some cases, this step is promoted by individual amino acid residues located near the active center of the enzyme (His64 shuttle)^[83]. Removal of a proton from the acid form of $\text{Zn-H}_2\text{O}$ and the recovery of Zn-OH species of the enzyme is the rate-limiting step of the catalytic process.

By comparing the proposed Zn-OH catalysis for either CO_2 /epoxide copolymerization or CO_2 hydration, Zn-OH bond, combined with acid and base together, can activate CO_2 collaboratively. Of importance, water is a key molecule for constituting a closed catalytic cycle. In CO_2 /epoxide copolymerization, *i.e.*, the regeneration of Zn-OH bond, it is directly related to the high catalytic activity, because the regeneration of Zn-OH bond ensured that one zinc center could form many polymer chains. Moreover, zinc ion in CA could be replaced by other metal ions without the loss of the catalytic activity. For example, in ξ -CAs, Zn^{2+} is interchangeable with Cd^{2+} ^[84]. γ -CAs may use Fe^{2+} under anaerobic conditions^[85] and retain the activity with Co^{2+} ^[86]. Co^{2+} may also substitute Zn^{2+} in many α -CAs without a significant loss of the catalytic activity^[78]. Clearly, this provides us with a clue to tune CA-like catalysts for CO_2 copolymerization. In fact, Cd, Fe, and Co had been used as the metals for CO_2 /epoxide copolymerization^[44, 87, 88].

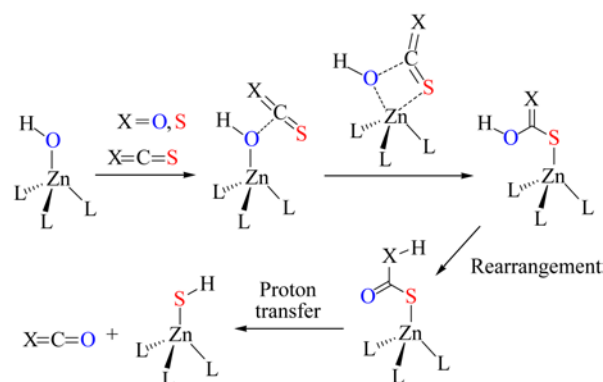
Furthermore, our recent study on the copolymerization of COS (CS_2) with epoxides also disclosed the similarity of the abovementioned catalysts and HCAII. The catalysts for COS (CS_2)/epoxide copolymerization could react with COS (CS_2) in the presence of water to form CO_2 (COS), which is very similar to the result of the reaction of HCAII with COS (CS_2) in water, which is discussed as follows.

Correlation of Copolymerization Catalyst and HCAII: Oxygen/Sulfur Scrambling

HCAII analogues were synthesized and investigated by considerable amounts of literatures for mimicking HCAII^[89–91]. These compounds often contain one zinc ions coordinated with three amine molecules and one $-\text{OH}$ anion, *i.e.*, $\text{L}_3\text{Zn-OH}$, as shown in Scheme 4, which can quantitatively convert carbon disulfide (CS_2) to carbonyl sulfide (COS), and COS to CO_2 , respectively. Thereof, the conversion of COS to CO_2 via CA catalysis is indeed a universal reaction in nature. It is proposed to undergo the pathway disclosed in Scheme 4, in which, OH^- acts as a nucleophile and attacks COS; through a four-membered ring transition state, then *via* rearrangement and proton transfer step (in real HCA catalyst, water assists the proton

transfer^[89]), a CO_2 molecule was produced along with a $\text{L}_3\text{Zn-SH}$.

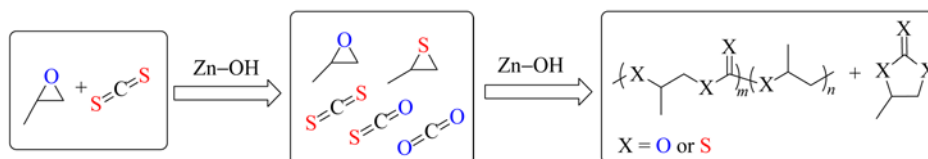
CS_2 and COS, as sulfur-containing C1 monomers, have been investigated to couple with various epoxides to form poly(thiocarbonate)s. For CS_2 /PO (CHO) copolymerization catalyzed by Zn-Co(III) DMCC^[92, 93] or CS_2 /oxetane (or CHO) copolymerization^[94–96] catalyzed by (salen)CrCl complexes, an oxygen/sulfur scrambling was observed in both the polymeric and cyclic products. Considering CS_2 /PO copolymerization catalyzed by Zn-Co(III) DMCC as an example, the afforded polymer displayed mixed thiocarbonate and carbonate units, instead of the expected dithiocarbonate ($-\text{O}(\text{C}=\text{S})\text{S}-$) unit. Moreover, the ether and thioether units were also produced (Scheme 5). Such complexity resulted from the randomly crossed coupling reactions of CS_2 , PO and intermediates COS, CO_2 , and propylene sulfide (PS) that were generated by oxygen/sulfur exchange reaction (O/S ER). Apparently, the sulfur atom of CS_2 was replaced by the oxygen of PO in the copolymerization process. We proposed that Zn-OH bond of Zn-Co(III) DMCC could react with CS_2 even in the presence of trace water in a similar pathway of HCAII, as disclosed in Scheme 5. Although the real O/S ER process is still unclear, we have proven that such O/S ER process was closely related to the water content in the copolymerization system and reaction temperature^[48, 97]. Compared with the conversion of HCAII for CS_2 (COS) in Scheme 4, it is reasonable that the Zn-OH bond does exist and catalyze the copolymerization reaction. Therefore, to a great extent, these Zn-OH species, which can convert CS_2 (COS) into COS (CO_2) quantitatively, are a mimic of HCAII enzyme^[98].



Scheme 4 Mechanism of fixing COS by the CA compound $[\text{L}_3\text{Zn-OH}]^+$, with L as histidine (CA center structure), or ligand (generally, amine)

Beyond Metal—OH: Lewis Acid-base Catalysis for CO_2 Copolymerization

It has been established that ligand-stabilized metal catalysts



Scheme 5 O/S ER in CS_2 /PO copolymerization *via* Zn-Co(III) DMCC catalysis

for CO₂/epoxide copolymerization process involving CO₂, COS, or CS₂ proceed via a coordination-insertion mechanism, as shown in Scheme 2, where the metal complex acts as a Lewis acid center to activate the epoxide^[14, 63, 66]. In addition, quaternary ammonium salts and organic bases usually serve as Lewis bases, which are necessary for improving the catalytic activity of these metal catalysts^[65, 99, 100]. The catalytic activity and selectivity of these metal Lewis acid/organic base systems for copolymerization can be subtly tailored by tuning their ligand structures, which has been investigated in detail by considerable amounts of works. The proposed metal—OH bond, whatever original or *in situ* generated during CO₂/epoxide copolymerization, could be regarded as a combination of a metal Lewis acid and base. Under the concept of the Lewis acid-base catalysis, metal Lewis acid could be replaced by organic Lewis acid for the copolymerization, i.e., a metal-free Lewis acid-base pair catalysis could be built.

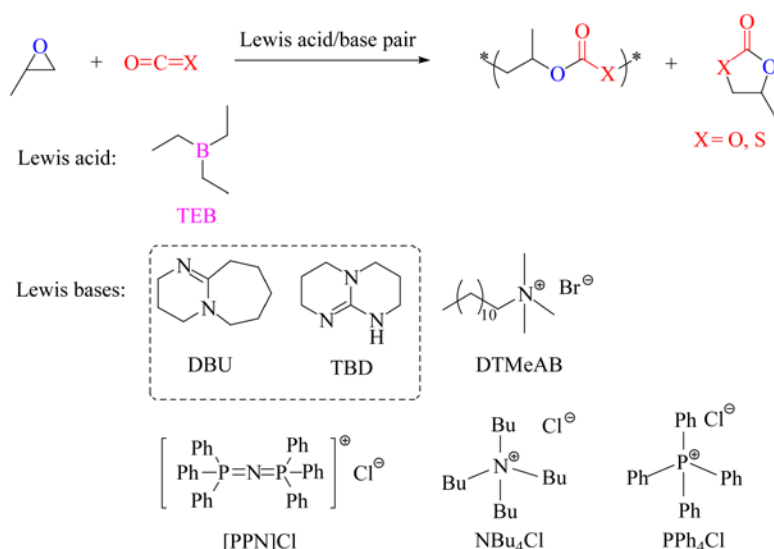
Very recently, Gnanou, Feng and coworkers presented a remarkable study, demonstrating that the copolymerization of CO₂ with PO or cyclohexane oxide (CHO) was mediated successfully by onium halides or alkoxides and triethylborane (TEB)^[101]. TEB acted as a Lewis acid, while onium halide was Lewis base. We have developed a fully alternating and perfectly regioselective COS/epoxide copolymerization process catalyzed by using the Lewis pairs of TEB with various Lewis bases, including amidine, quinidine, quaternary onium salts, to provide colorless and highly transparent well-defined poly(monothiocarbonate)s (Scheme 6). Like the metal-catalyzed process, the Lewis pair binds the epoxide followed by ring-opening reaction with subsequent alternating insertion of COS and epoxide leading to copolymer formation. However, the organic Lewis pair catalytic process might be more anionic. In both newly reported metal-free catalysis for C1 copolymerization, the acidity of the Lewis acid, the nucleophilicity of the Lewis

base, together with the steric effects of the Lewis pair are the deciding factors for effective catalysis. The discovery of Lewis acid-base pairs for CO₂ (COS) copolymerization reaction provides a new powerful tool to make C1-based copolymer without using metal complexes.

Structure Control of CO₂-based Copolymers

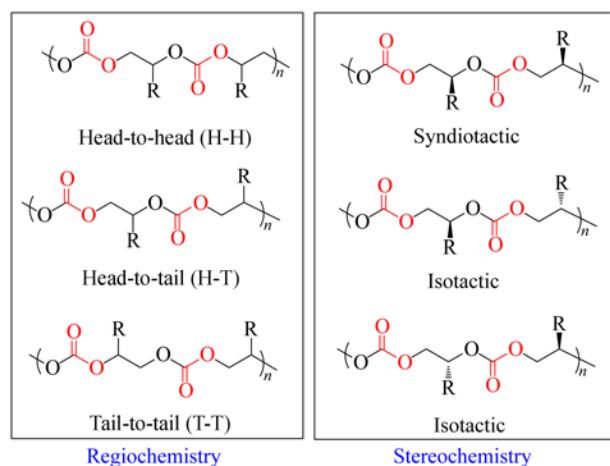
The most important task in copolymerization is to precisely control the microstructure of the copolymer. The metal—OH catalysis is powerful to the synthesis of CO₂-based polycarbonate polyols without contamination of other anion-capped groups. For Zn-Co(III) DMCC catalyzed-CO₂/PO copolymerization, the Zn—OH bond was observed to well regulate the end group of the final copolymer, since water was an efficient chain transfer agent. Based on this observation, some organic compounds with at least two —OH groups (alcohols, carboxyl acid and phenol) were employed as the chain transfer agents for synthesizing polycarbonate polyols. In fact, for homogeneous catalysts such as (salen)CoCl and (salen)CrCl complexes, the use of excess chain transfer agents with at least two —OH groups could also provide polycarbonate polyols, and the Cl-capped polycarbonates could be minimized.

The copolymerization of the mono-substituted epoxides with CO₂ results in different regiochemistry, which was indicated by the diad structure in the copolymer (Scheme 7), including head to tail (H-T), head to head (H-H) and tail to tail (T-T). H-T diad is produced by successive epoxide ring-opening at either the methylene (CH₂) or methine (CH) C—O bond, while the H-H or T-T diads were formed by alternating ring-opening at the CH₂ site of one epoxide and the CH site of the next epoxide^[15]. The regioselective CO₂/epoxide copolymerization has been achieved by using Zn-Co(III) DMCC solely^[60, 102]. Being different from some homogeneous catalysts accompanied by cocatalysts^[44, 65, 103], the carbonate anion (—OOCO[−]) was the only nucleophilic



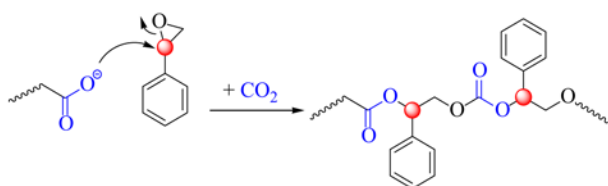
Scheme 6 TEB/Lewis base pairs for the COX (X = O, S)/epoxide copolymerization

DBU: 1,5-diazabicyclo[5.4.0]undec-5-ene, TBD: 1,5,7-triazabicyclododecene, [PPN]Cl: bis(triphenyl phosphine) iminium chloride, DTMeAB: dodecyl trimethylammonium bromide, NBu₄Cl: tetrabutylammonium chloride, PPh₄Cl: tetraphenyl phosphonium chloride. DBU and TBD were only reported for COS/PO copolymerization



Scheme 7 Regiochemistry and stereochemistry of polycarbonates

species to attack the methylene or methine sites of epoxide for ring-opening, without assistance of cocatalysts such as organic base or quaternary ammonium salts. For CO₂/styrene oxide copolymerization, the electron induction effect of the electron-withdrawing phenyl group dominated the regioselective copolymerization (Scheme 8)^[102]. When referring the result by Hirano *et al.*^[104], in which ZnEt₂/water system was employed in the copolymerization of CO₂ with styrene oxide, the ring-opening of styrene oxide predominantly occurred at methine carbon (96%), similar to the result from Zn-Co(III) DMCC catalysis. Therefore, it is believed that ZnEt₂/water system has Zn—OH bond.



Scheme 8 Proposed mechanism for regioselective CO₂/styrene oxide copolymerization via Zn-Co(III) DMCC catalysis (Red dot in the backbone represents the site that was proposed to be attacked by the carbonate anion.)

Note that, for the copolymerization of CO₂ with mono-substituted epoxide, highly regioselective ring-opening of the epoxide is a prerequisite for highly stereoregular copolymers^[15]. For an immortal CO₂/epoxide copolymerization reaction, the regeneration of metal—OH bond plus the chain transfer reaction to —OH end group of the produced macromolecules will cause low regioregularity of the final copolymer, and of course low stereochemistry.

CONCLUSIONS AND OUTLOOK

In summary, we presented the results of the comparative study on the catalysts for CO₂/epoxide copolymerization and HCAII for CO₂ hydration. The catalytic copolymerization of CO₂ with epoxide, not only fixes CO₂ and thus reduces the carbon emission, but also affords useful polymeric materials. In nature, CA enzyme, as a protein metal catalyst, does the same thing all the time and is definitely far beyond our ability.

Because of its speed and ability to activate C1 compounds, it is an ideal model for designing biomimetic catalyst^[105] for C1/epoxide copolymerization^[98, 106]. We correlated the functions of the Zn—OH bond in Zn-Co(III) DMCC for copolymerization and in HCAII for the CO₂ hydration. It is proposed that the Zn—OH bond (original or *in situ* generated) is the real catalytic center that accelerates the copolymerization. A closed catalytic cycle through the chain transfer reaction to water regenerates Zn—OH bond, which will initiate another copolymerization and produce a new chain. Furthermore, the Lewis acid-base character of Zn—OH bond guided us to discover organic Lewis pairs for successful copolymerization of COS with epoxides. In contrast, the current catalysts for CO₂/epoxide copolymerization are clearly inferior to the ability of the HCAII, indicating a huge blank area for designing new catalysts with better performance. The tetrahedral Zn-OH coordination, the ligand-zinc affinity, the dynamic protein fold and active site architecture are the lessons for designing new catalysts. It is very promising to develop biomimetic HCAII catalysts for making CO₂-based polymers.

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