



CO₂ Capture and *in situ* Catalytic Transformation

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The escalating rate of fossil fuel combustion contributes to excessive CO₂ emission and the resulting global climate change has drawn considerable attention. Therefore, tremendous efforts have been devoted to mitigate the CO₂ accumulation in the atmosphere. Carbon capture and storage (CCS) strategy has been regarded as one of the promising options for controlling CO₂ build-up. However, desorption and compression of CO₂ need extra energy input. To circumvent this energy issue, carbon capture and utilization (CCU) strategy has been proposed whereby CO₂ can be captured and *in situ* activated simultaneously to participate in the subsequent conversion under mild conditions, offering valuable compounds. As an alternative to CCS, the CCU has attracted much concern. Although various absorbents have been developed for the CCU strategy, the direct, *in situ* chemical conversion of the captured CO₂ into valuable chemicals remains in its infancies compared with the gaseous CO₂ conversion. This review summarizes the recent progress on CO₂ capture and *in situ* catalytic transformation. The contents are introduced according to the absorbent types, in which different reaction type is involved and the transformation mechanism of the captured CO₂ and the role of the absorbent in the conversion are especially elucidated. We hope this review can shed light on the transformation of the captured CO₂ and arouse broad concern on the CCU strategy.

Keywords: CO₂ capture, activation, conversion, *in situ* catalysis, green chemistry

INTRODUCTION

The demand for energy of the rapid industrialization results in large-scale combustion of fossil fuel, which causes excessive emissions of carbon dioxide. As the detrimental environmental impacts of CO₂ have drawn considerable attention, various strategies have been developed to mitigate CO₂ accumulation in the atmosphere, among which carbon capture and storage/sequestration (CCS) is considered as a promising CO₂ reducing option (Alexander et al., 2015). Nowadays, a plethora of CO₂ absorbents have been developed to facilitate CO₂ capture and desorption. Nevertheless, the extensive energy needed in the absorbent regeneration and CO₂ separation is not conducive to the implementation of CCS strategy.

In contrast to carbon sequestration, converting CO₂ into valuable chemicals could be a sustainable option, which has been proposed by Ciamician as early as 1912 (Ciamician, 1912). In recent decades, CO₂ conversion has attracted considerable concern and been intensively investigated (Rahman et al., 2017). However, in most processes for CO₂ conversion, pure or high pressure CO₂ is needed, implying that the CO₂ from the atmosphere or industrial exhaust cannot be used as C₁ source directly and thus the energy issue in CO₂ capture and separation still remains.

To address the energy penalties associated with CCS strategy and realize the direct fixation of CO₂ from the atmosphere or industrial exhaust, the CO₂ capture and utilization (CCU) strategy, whereby the captured CO₂ is used as a non-toxic, abundant, and sustainable feedstock to produce valuable organic compounds via chemical, electrochemical or photochemical reactions, was proposed and now is flourishing (**Scheme 1**). By now, both organic compounds and functional materials containing the bridging-carbonato metal complexes can be obtained from atmospheric CO₂ using the CCU strategy (Yang et al., 2011; Liu et al., 2012; Massoud et al., 2015). Although realizing the attractive prospect of the CO₂ capture and *in situ* conversion in the industry scale remains a challenge (Zhang and Lim, 2015), the emergence of efficient absorbents and the development of CO₂ transformation will cast light on it. In continuation of our work on the conversion of the captured CO₂ into value-added organic chemicals, this review summarized the recent progress on CO₂ capture and *in situ* conversion into organic products.

To realize the carbon capture and *in situ* conversion strategy, effective absorbents are always necessary. Ideally, the absorbents for CCU strategy should not only capture CO₂, but also activate CO₂ and even the substrate. Thus, the chemical transformation can proceed under mild conditions. Up to now, organic and inorganic bases, *N*-heterocyclic carbenes (NHCs) and *N*-heterocyclic olefins (NHOs), ionic liquids (ILs) and frustrated Lewis pairs (FLPs) have already been applied to CO₂ capture and *in situ* conversion. A plethora of valuable organic chemicals have been obtained through the CCU strategy as shown in **Scheme 2**.

INORGANIC/ORGANIC BASES

Due to the electrophilicity of carbon atom in CO₂, the organic and inorganic bases containing strong nucleophilic atom have been widely used in CO₂ trapping, where the base can interact with CO₂ directly or function as a proton acceptor. The resulting CO₂ capture products i.e., CO₂ adducts have been employed for subsequent synthesis of various valuable chemicals.

Considering the transformations of the captured CO₂ derived from primary and secondary amines and amino alcohols to isocyanates, carbamates, ureas, and oxazolidinones have been concerned by several excellent review papers (Hampe and Rudkevich, 2003; Chaturvedi and Ray, 2006; Yang et al., 2012; Tamura et al., 2014; Wang et al., 2017a,b), here we focus on the transcarboxylation effect and other transformations of the captured CO₂, namely CO₂ derivatives.

Synthesis of Carbamates and Ureas

In the synthesis of carbamates, the aprotic organic bases can function as CO₂ absorbents and transcarboxylation agents. The initial attempt was made by Rossi group, in which CO₂ is trapped by a methanol solution of commercially available tetraethylammonium hydroxide. The resulting tetraethylammonium hydrogen carbonate can be used as a surrogate of CO₂ in the synthesis of carbamate. Meanwhile, the presence of tetraethylammonium ion as counterion increases the nucleophilicity of carbamate anion (Inesi et al., 1998).

Soon after, Franco group has successfully identified the DBU-CO₂ complex via reacting CO₂ with DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) in anhydrous acetonitrile, implying that DBU can be used as CO₂ trap reagent (Pérez et al., 2002). Moreover, the resulting reactive DBU-CO₂ adduct can be utilized as transcarboxylating reagent for synthesis of *N*-alkyl carbamates. Later, the same group revealed the activation capacity of CO₂ by other bicyclic amidines and observed the inverse relation between the thermal stability and the transcarboxylating activity for the amidine-CO₂ adducts (**Scheme 3**) (Pérez et al., 2004), which is the first time to investigate the activation ability of organic bases to CO₂.

The combination of organic base and alcohol is an efficient CO₂ capture system and the absorbed CO₂ can be *in situ* transformed. The prototypical example is the polyethylene glycol (PEG)/superbase system developed by our group in 2011 (Yang et al., 2011). In the capture step, the superbase is used as a proton acceptor and almost equimolar CO₂ per mole superbase can be absorbed (**Scheme 4**). The resulting liquid amidinium carbonate can directly react with *n*-butylamine at 110°C to afford dibutyl urea in almost quantitative yield (96%) without any other additives. This protocol can be used in the synthesis of other symmetrical urea derivatives.

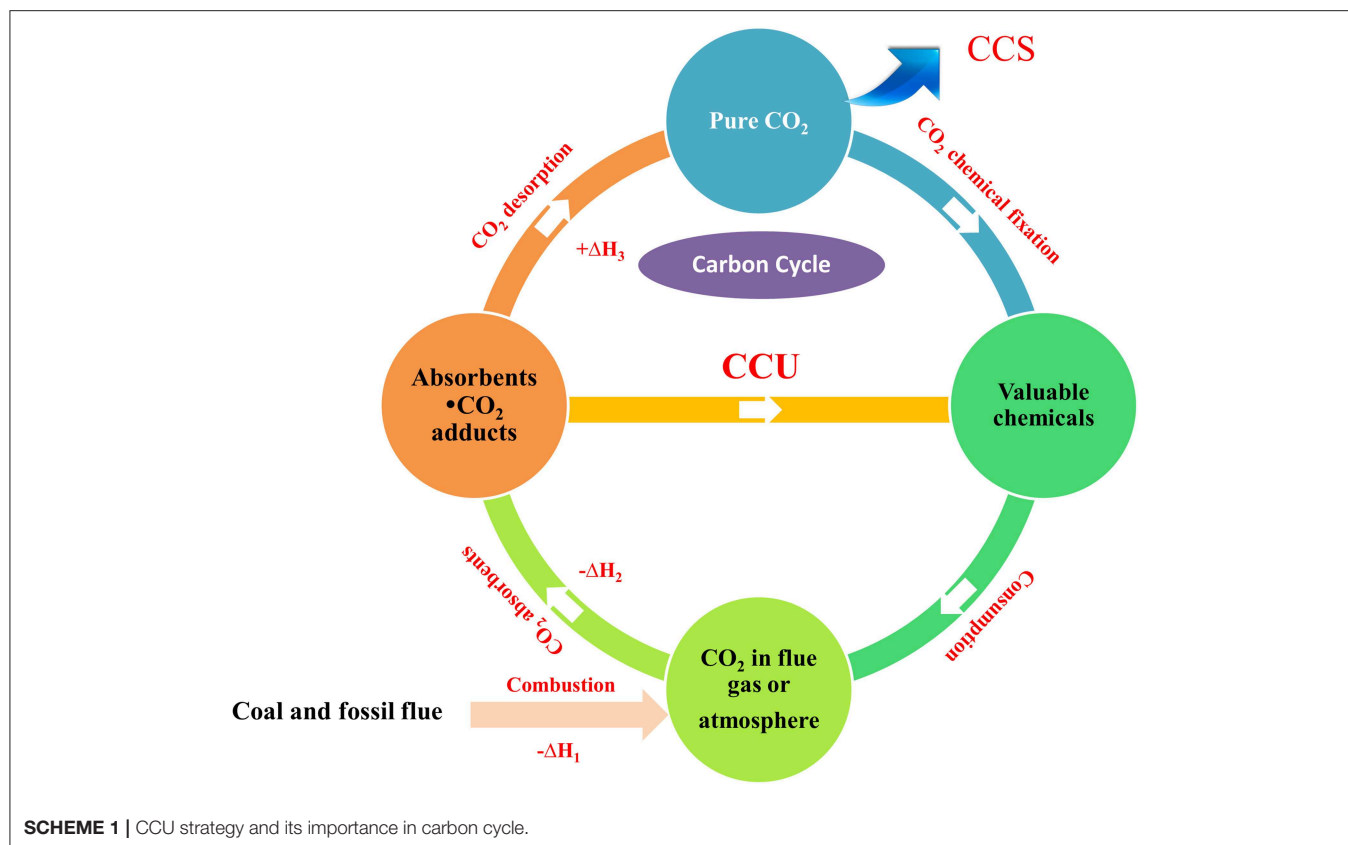
In the above examples, the captured CO₂ in the transcarboxylating agents can be regarded as the activated CO₂ because the linear structure of CO₂ is converted to bent structure, which is more liable to nucleophilic attack.

Synthesis of Oxazolidinones

The “CO₂ absorption and subsequent transcarboxylation” triggers the research on CO₂ capture and *in situ* transformation. Several years later, M. Yoshida and coworkers use DBU to enrich and activate CO₂ in air and perform the first example of directly transforming atmospheric CO₂ into the substituted 5-vinylideneoxazolidin-2-ones using propargylic substrate 4-(benzylamino)-2-butynyl carbonates or benzoates as a substrate (**Scheme 4**) (Yoshida et al., 2008). In their follow-up work, they further improve the reaction efficiency by utilizing AgNO₃ as catalyst and propargylic amines as substrates (**Scheme 4**) (Yoshida et al., 2012).

Inspired by these works, our group designs a series of novel CO₂ capture and activation systems. For example, by employing ammonium iodide as catalyst, the cycloaddition reaction of various aziridines with the captured CO₂ by NH₂PEG₁₅₀NH₂ gives rise to oxazolidinones at 40°C in >94% yield and selectivity (**Scheme 4**) (Yang et al., 2011).

Soon after, we report the first example of steric-hindrance-controlled CO₂ absorption, where the sodium *N*-alkylglycinates and *N*-alkylalaninates dissolved in PEG₁₅₀ are used to capture CO₂, generating the carbamic acid rather than the ammonium carbamate (Liu et al., 2012). *N*-isopropylglycinate is found to be the best absorbent for the rapid and reversible capture of almost equimolar CO₂. Crucially, the captured CO₂ can be activated simultaneously and the resulting carbamic acid can react with either aziridine or propargyl amine to afford oxazolidinones in the presence of NH₄I and AgOAc as a catalyst, respectively (**Scheme 4**).



Motivated by these results, we further develop potassium phthalimide as absorbent to realize equimolar CO_2 capture in PEG_{150} . Moreover, the obtained product can be used as *in situ* transcarboxylating reagent to synthesize oxazolidinone derivatives (**Scheme 4**) (Zhang et al., 2014).

Recently, Hu group subtly designs a CCU example (Yu et al., 2016), in which carbamate salts generated from CO_2 and primary amines are used as substrates. The captured CO_2 not only acts as a reactant but also acts as a protecting reagent for the amine to avoid poisoning of the copper catalyst. By using 5 mol% of CuI as catalyst, carbamate salts can react with aromatic aldehydes and aromatic terminal alkynes, affording the important oxazolidin-2-ones (**Scheme 4**).

Synthesis of β -Oxopropylcarbamates

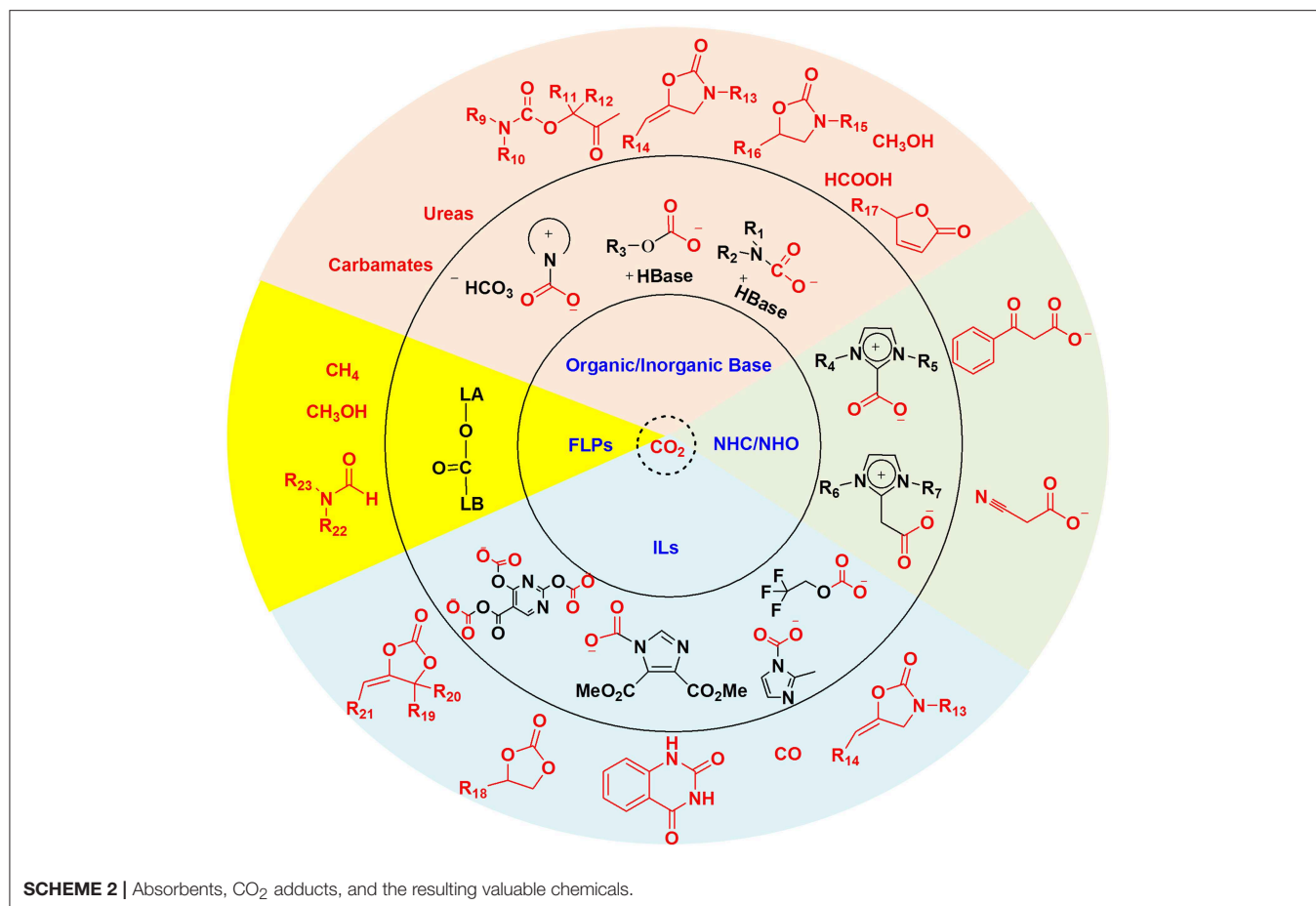
Based on these inspiring results, our group uses ammonium carbamates as surrogates of carbon dioxide and secondary amines in the three-component synthesis of β -oxopropylcarbamates from propargylic alcohols, secondary amines, and CO_2 . Catalyzed by silver (I) catalyst, ammonium carbamates can react with propargylic alcohols to generate β -oxopropylcarbamates under atmospheric pressure (**Scheme 5**) (Song et al., 2015). In this example, the substitution of pure CO_2 with the captured CO_2 can facilitate the reaction running at atmospheric pressures with a broad substrate and reaction application scope. Furthermore, the solid ammonium

carbamates are easier to handle and quantify than the volatile amines and gaseous CO_2 .

The transcarboxylation is an important transformation strategy for the CO_2 adducts to valuable chemicals. However, for the CO_2 adducts formed by base and CO_2 , the transcarboxylation is still limited to the substrates including amines, propargylamines and aziridines. Therefore, novel CO_2 absorbents and extended substrates are expected to facilitate the application of CO_2 adducts as transcarboxylation reagent in CCU strategy. Besides transcarboxylation, the integral transformation of CO_2 capture products is another attractive option in CCU strategy, wherein the ammonium carbamates derived from CO_2 and amines is a promising raw material. Nevertheless, the integral transformation of ammonium carbamates to valuable chemicals remains sporadic and underexplored. Hopefully, more conversion protocols of ammonium carbamates can be designed based on the reactivity of amine and CO_2 .

CO_2 Capture and *in situ* Hydrogenation

CO_2 hydrogenation is widely investigated in the CCU strategy because the basic absorbent can react with the resulting formic acid to form formate, thus overcomes the thermodynamic limitation in the hydrogenation of CO_2 . In the researches on CO_2 capture and *in situ* hydrogenation, both metal-based homogeneous catalysts (containing Rh-, Ru-, and Fe-based catalysts) and heterogeneous catalysts have been investigated.



Hydrogenation Using Rh-Based Catalysts

The first example of CO₂ capture and *in situ* hydrogenation is reported by our group in 2013, in which polyethyleneimine 600 (PEI₆₀₀) or the combination of PEI₆₀₀ and ethylene glycol is developed to absorb gaseous CO₂, affording the PEI-CO₂ or ethylene glycol-CO₂ adducts. With RhCl₃·3H₂O/CyPPh₂ as catalyst, the captured CO₂ can be *in situ* transformed to formate (**Scheme 6**) (Li et al., 2013). Furthermore, direct hydrogenation of ammonium carbamate derived from CO₂, e.g., DETA⁺CO₂⁻ (DETA = diethylenetriamine), ammonium carbonates such as [DBNH] [OCO₂(C₂H₄O)₃H], [DBNH] [OCO₂CH₂OH] (DBN=1,5-diaza bicycle[4.3.0]non-5-ene), is also successfully performed facilitated by this Rh-based catalyst. Notably, a higher reaction rate and better results can be achieved when using the captured CO₂ in the form of ammonium carbonates as feedstock than using equivalent free gaseous CO₂ or ammonium carbamate, implying CO₂ activation upon capture with DBN/PEI and glycol.

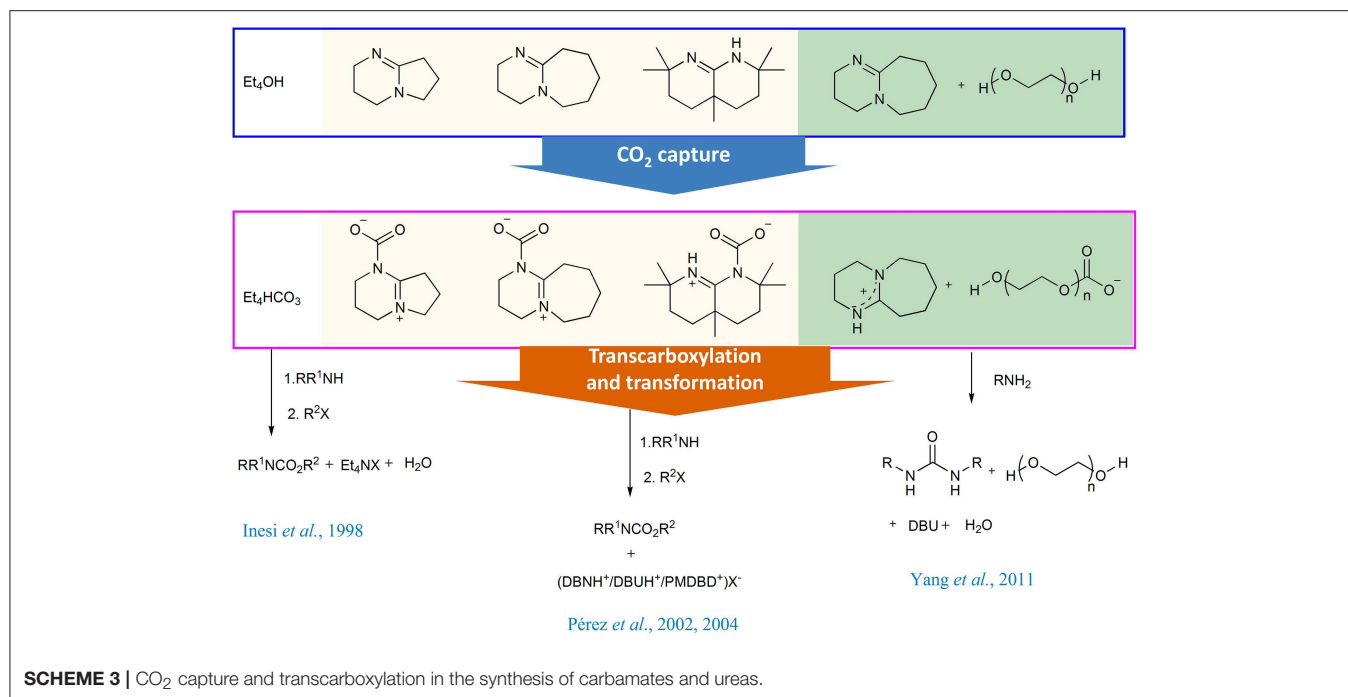
After that, we further design a tunable ethoxyl-functionalized amidine to absorb CO₂ in order to avoid the use of volatile proton donor (Li et al., 2014). As an activated form of CO₂, the captured CO₂ in the form of zwitterionic amidinium carbonate is further hydrogenated to formate employing RhCl₃/DPEphos as the catalyst (**Scheme 6**). In the same time, we find that

the CO₂ capture product of potassium phthalimide in PEG₁₅₀, can also be *in situ* hydrogenated to formic acid catalyzed by RhCl₃·3H₂O/CyPPh₂ (**Scheme 6**) (Zhang et al., 2014).

Hydrogenation Using Ru- and Fe-Based Catalysts

Ru-based catalysts are also promising candidates for the hydrogenation of captured CO₂. In the study of Yadav et al., CO₂ is captured by DBU and an alcohol to form the alkyl carbonate ionic liquid and the resulting alkyl carbonate is hydrogenated into [DBUH⁺] formate and methyl formate facilitated by RuCl₂(PPh₃)₃ (**Scheme 7**) (Yadav et al., 2014). Although the reactive species (i.e., alkyl carbonates or CO₂) cannot be identified at this stage, this result indicates that alkyl carbonates may be a substrate for hydrogenation, in addition to free CO₂.

In 2015, Sanford group combined CO₂ capture to form a carbamate salt with hydrogenation to generate CH₃OH (Rezayee et al., 2015). In their study, NHMe₂ is used to capture CO₂ and a homogeneous Ru-based catalyst is used to facilitate the hydrogenation of the captured CO₂ to a mixture of DMF and CH₃OH (**Scheme 7**). Although the formation of carbamate salt can decrease the electrophilicity of CO₂, causing the captured CO₂ difficult to hydrogenate, the existence of the equilibrium between DMC (Dimethylammonium dimethylcarbamate) and



CO₂ allows the release of CO₂ possible, thus promoting the CO₂ hydrogenation.

By employing pentaethylenhexamine (PEHA) as CO₂ absorbent and Ru-based complexes as catalyst, Olah and Surya Prakash group develops a process that combines CO₂ capture and the following hydrogenation in an ethereal solvent for the production of MeOH (Kothandaraman et al., 2016a). CO₂ from air can be captured by an aqueous solution of PEHA and up to 61% yield of MeOH can be obtained in the triglyme/H₂O mixtures at 155°C in the following hydrogenation (Scheme 7). The resulting MeOH can be easily separated by simple distillation from the reaction mixture.

Later, the same group captures CO₂ with aqueous amine solution and then *in situ* hydrogenates the resulting ammonium bicarbonate/carbonate utilizing Ru- and Fe-based pincer complexes in a biphasic solvent system (water/Me-THF) (Kothandaraman et al., 2016b). The superbases (DABCO, TMG, and DBU) shows to be efficient for both CO₂ capture and hydrogenation with more than 90% yield of formate under moderate reaction conditions (50 bar H₂ at 55°C) (Scheme 7). The biphasic system features easy separation of product and catalyst and the catalyst can be reused for at least five cycles.

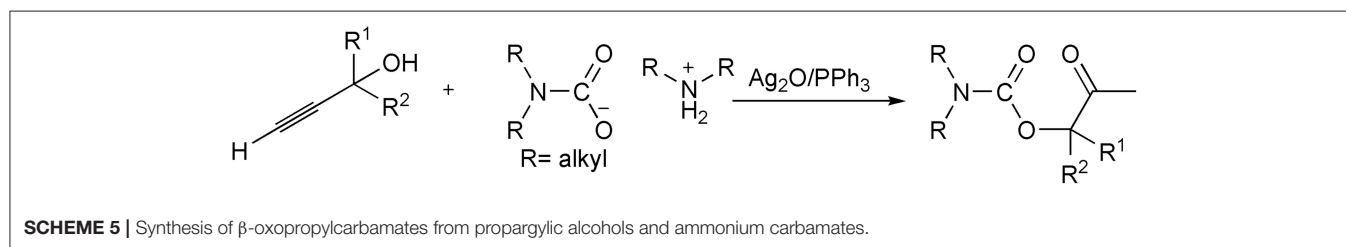
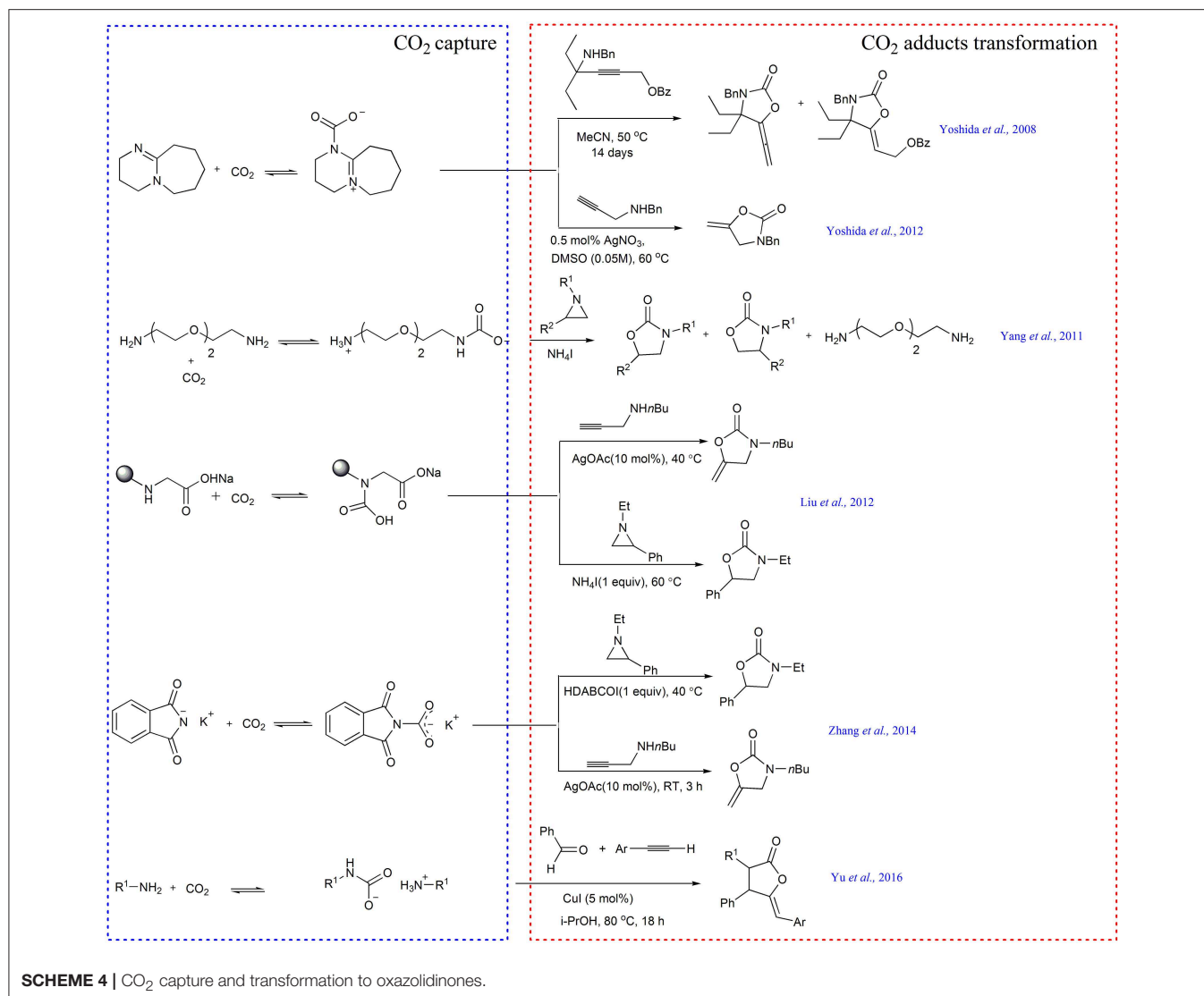
Hydrogenation Using Heterogeneous Catalysts

Besides homogeneous catalysts, the heterogeneous catalysts were also used in the hydrogenation of CO₂ capture products. For example, H. Lin group applies Pd/AC catalyst to the hydrogenation of CO₂ capture products originated from ammonia. In the hydrogenation step, the dependence of the activity of CO₂ capture products on the solvent is observed (Su et al., 2015a,b). For example, the ammonium bicarbonate in water and ammonium carbamate in 70 wt% ethanol-water

solution can offer more than 90% yield of formate under high H₂ pressure (5.52 and 2.75 MPa, respectively) at 20°C. The ammonium carbonate presents similar activity with ammonium carbamate. Identification of the species in the reactant solutions suggests the bicarbonate ion and ethyl carbonate ion, instead of the carbamate ion, are the activation forms of CO₂ in the hydrogenation (Scheme 8). Coincidentally, Enthaler finds that sodium bicarbonate in methanol can be hydrogenated to sodium formate catalyzed by the nickel hydride complex while CO₂ cannot be hydrogenated in the identical conditions, which further confirms the activity of the captured CO₂ in hydrogenation (Enthaler et al., 2015).

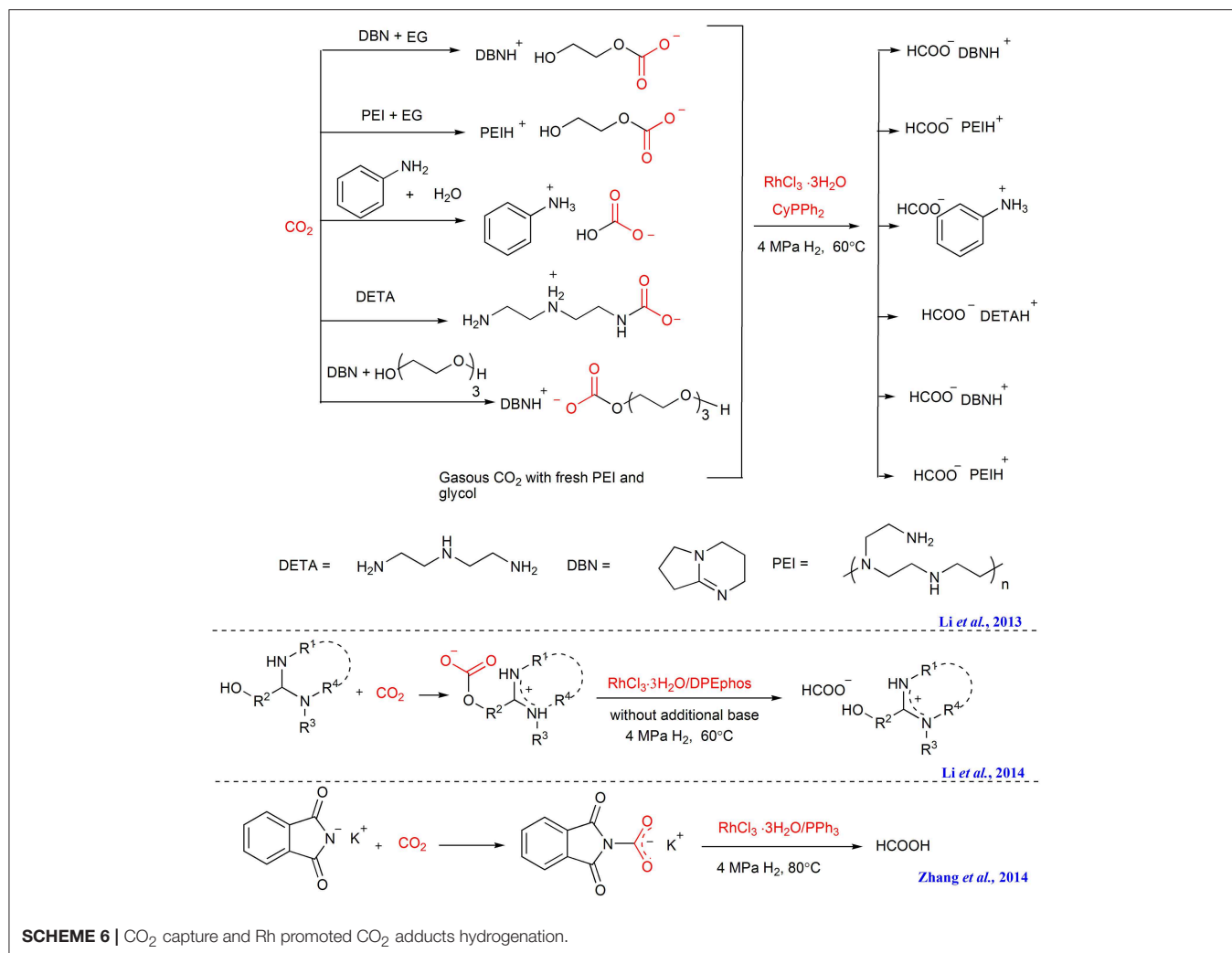
Mertens and coworkers report the *in situ* hydrogenation of the captured CO₂ using Cu/ZnO-Al₂O₃ as catalyst under retrieval of the CO₂ capture reagent N,N-diethylethanolamine (DEEA) (Reller et al., 2014). In the reaction, DEEA can also function as a trapping reagent for the resulting formic acid and drives the hydrogenation forward. The authors find that the generation of the products 2-diethylaminoethylformate and methanol can be regulated by the reaction temperature (Scheme 9). The combination of CO₂ capture and hydrogenation realizes the energy integration by using the reaction heat of CO₂ hydrogenation in the energy demanding CO₂ stripping process.

In addition to the liquid absorption system, the alkali metal and alkali earth metal based solid CO₂ adsorbents are also developed (Li et al., 2010, 2011; Lee et al., 2011) and applied in the CCU strategy recently. Duyar et al. design a series of novel dual function materials (DFM) consisting of the catalyst and adsorbent components to couple the endothermic CO₂ desorption step with the exothermic hydrogenation of CO₂ (Duyara et al., 2016). The results show that DFM with the composition of 5% Ru 10% K₂CO₃/Al₂O₃ and 5% Ru



10% Na₂CO₃/Al₂O₃ have a methanation capacity of 0.91 and 1.05 g-mol/kg DFM, respectively. Similarly, A. Urakawa group develops the catalyst consisting of earth-abundant chemical elements (FeCrCu/K/MgO-Al₂O₃), which can trap CO₂ from fuel gas in the form of surface carbonates and subsequently hydrogenated the adsorbed CO₂ to CO (Bobadilla et al., 2016). Accordingly, these DFMs are identified as promising candidates for CO₂ capture and direct utilizations.

Hydrogenation of captured CO₂ to energy chemicals can facilitate turning hydrogen gas to liquid fuel as well as realize carbon cycling. Albeit the hydrogenation of captured CO₂ has been extensively investigated and various capture reagents and catalysts have been developed, the identification of CO₂ activation forms is still controversial. For example, the CO₂ capture products alkyl carbonate ammonium salts are considered as the activated CO₂ species (Li et al., 2013, 2014; Su et al.,



2015a,b). However, the results of Jessop group show that [DBUH][OC(O)OMe] salt is less active than free CO₂ when using RuCl(O₂CMe)(PMe₃)₄ as catalyst in MeOH solution (Munshi et al., 2002). Thus, the relationship between the activity of CO₂ capture products and the catalyst is still underdeveloped.

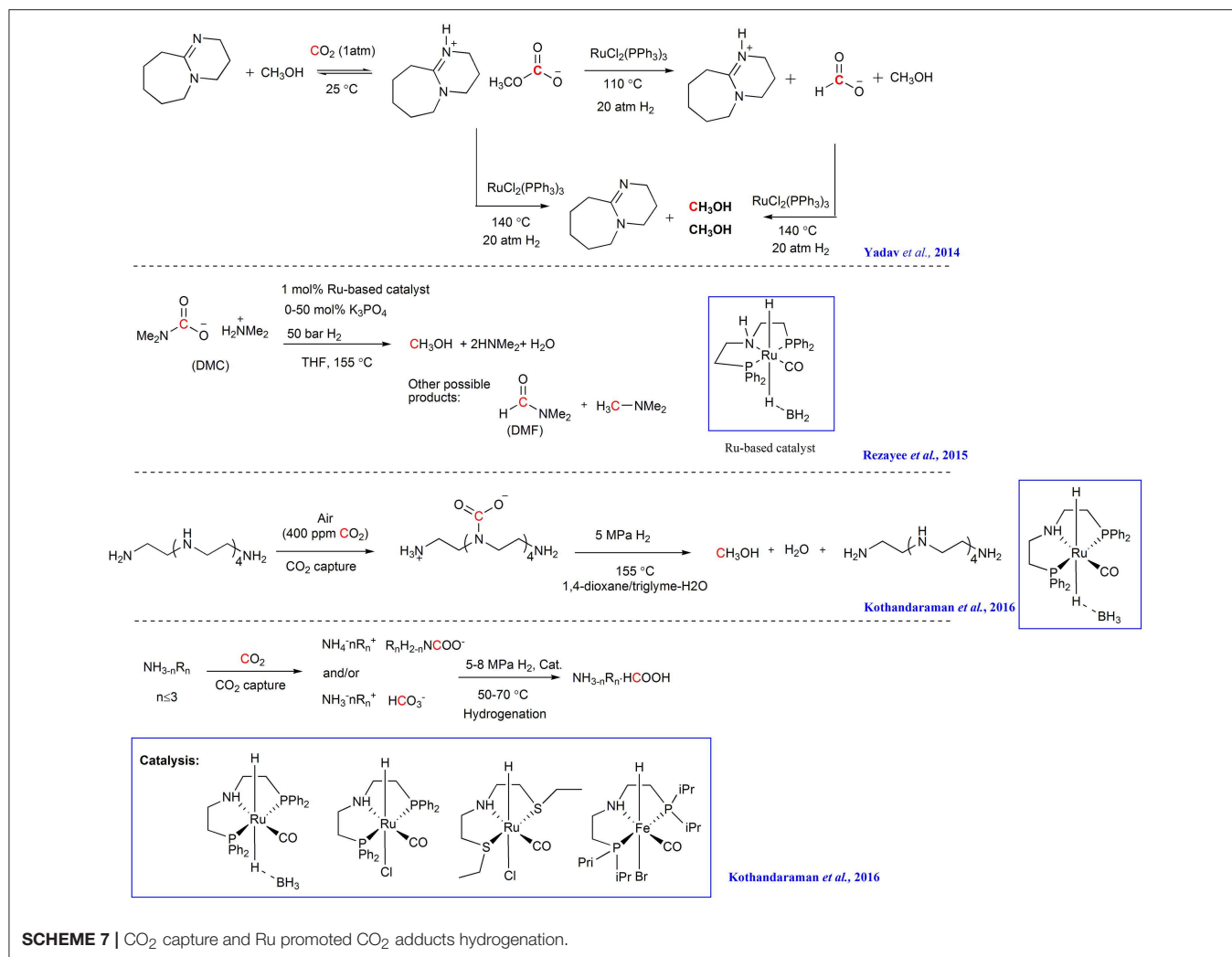
N-HETEROCYCLIC CARBENES AND N-HETEROCYCLIC OLEFINS

It has been verified that *N*-heterocyclic carbenes and *N*-heterocyclic olefins can react with CO₂, forming the CO₂ adduct which can be used as “all-in-one” carboxylating agent (Zhou et al., 2008; Kelemen et al., 2014; Dong et al., 2015; Talapaneni et al., 2015; Finger et al., 2016; Saptal and Bhanage, 2016). For example, Tommasi group shows the CO₂ adduct 1-butyl-3-methylimidazolium-2-carboxylate and 1,3-dimethylimidazolium-2-carboxylate behaves as active CO₂-carriers and reacted with CH₃OH and acetophenone for the synthesis of methylcarbonate and benzoylacetate. The other organic compounds with active hydrogen (acetone,

cyclohexanone, benzylcyanide, and propargyl alcohols) can also be carboxylated with these CO₂-transfer agents for the synthesis of carboxylates of pharmaceutical interest (Tommasi and Sorrentino, 2005, 2006, 2009) (Scheme 10). Similarly, the transcarboxylation of IPrCO₂ (1,3-bis(2,6-diisopropylphenyl)-imidazolium-2-carboxylate) to acetophenone with NaBPh₄ to yield sodium benzoylacetate and direct dicarboxylation of MeCN using I^tBuCO₂ (1,3-bis(tert-butyl)-imidazolium-2-carboxylate) are also reported (Van Ausdall et al., 2011) (Scheme 10).

The transcarboxylation capacity of NHOs-CO₂ adducts has also been verified by 1-ethyl-3-methyl-imidazolium-2-methylenecarboxylate through realizing the C-C coupling of CO₂ and MeCN (Scheme 10) (Finger et al., 2016). In this transcarboxylation process, the basicity of NHOs should be strong enough to abstract proton from the CH acid.

As highly efficient carboxylating agents, the NHC-CO₂ and NHO-CO₂ complexes can be easily obtained by reacting NHCs or NHOs with atmospheric CO₂. However, instead of serving as absorbent, NHCs and NHOs are usually used as catalysts to promote the conversion of pure CO₂ by forming transient NHC-CO₂ and NHO-CO₂ complexes (Kayaki et al., 2009; Zhou



et al., 2017). The reason is that NHCs and NHOs are sensitive to air and moisture thus they cannot be used as absorbents for CO₂ in air and industry exhaust. Nowadays, it is found that the imidazolium ionic liquids containing basic anion can absorb CO₂, producing imidazolium carboxylates (Gurau et al., 2011; Wang and Wang, 2016). Considering the imidazolium ionic liquids are stable to air and moisture, it opens a new way for the utilization of NHC-CO₂ and NHO-CO₂ complexes in CCU strategy.

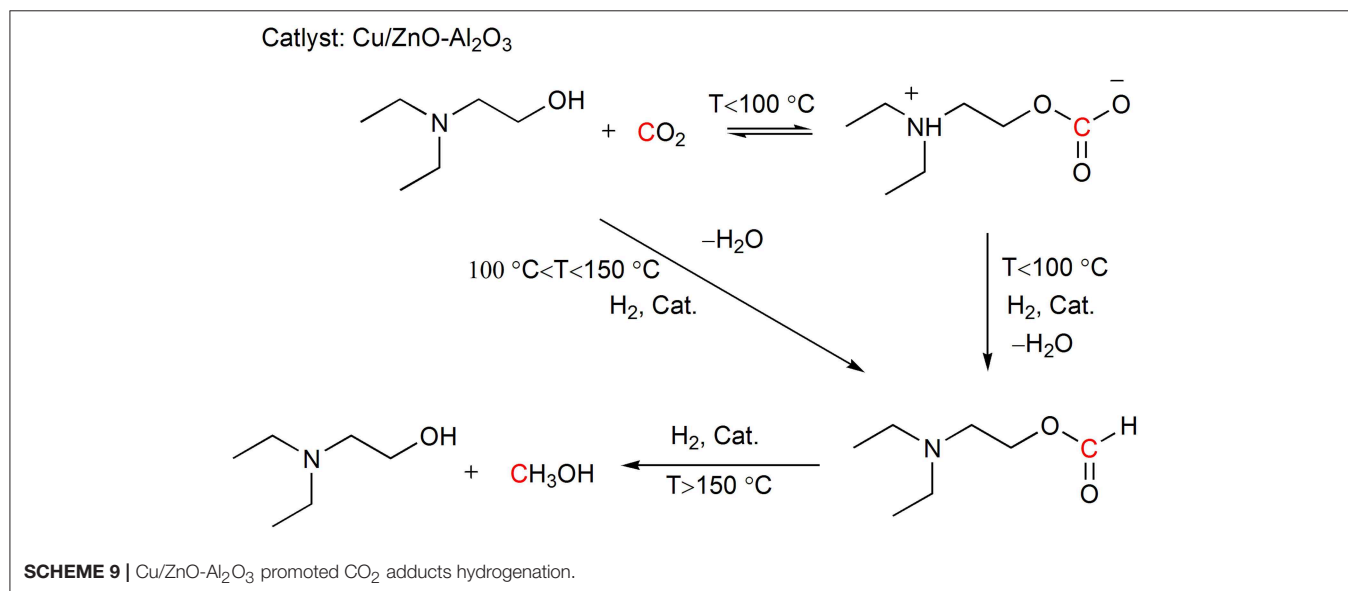
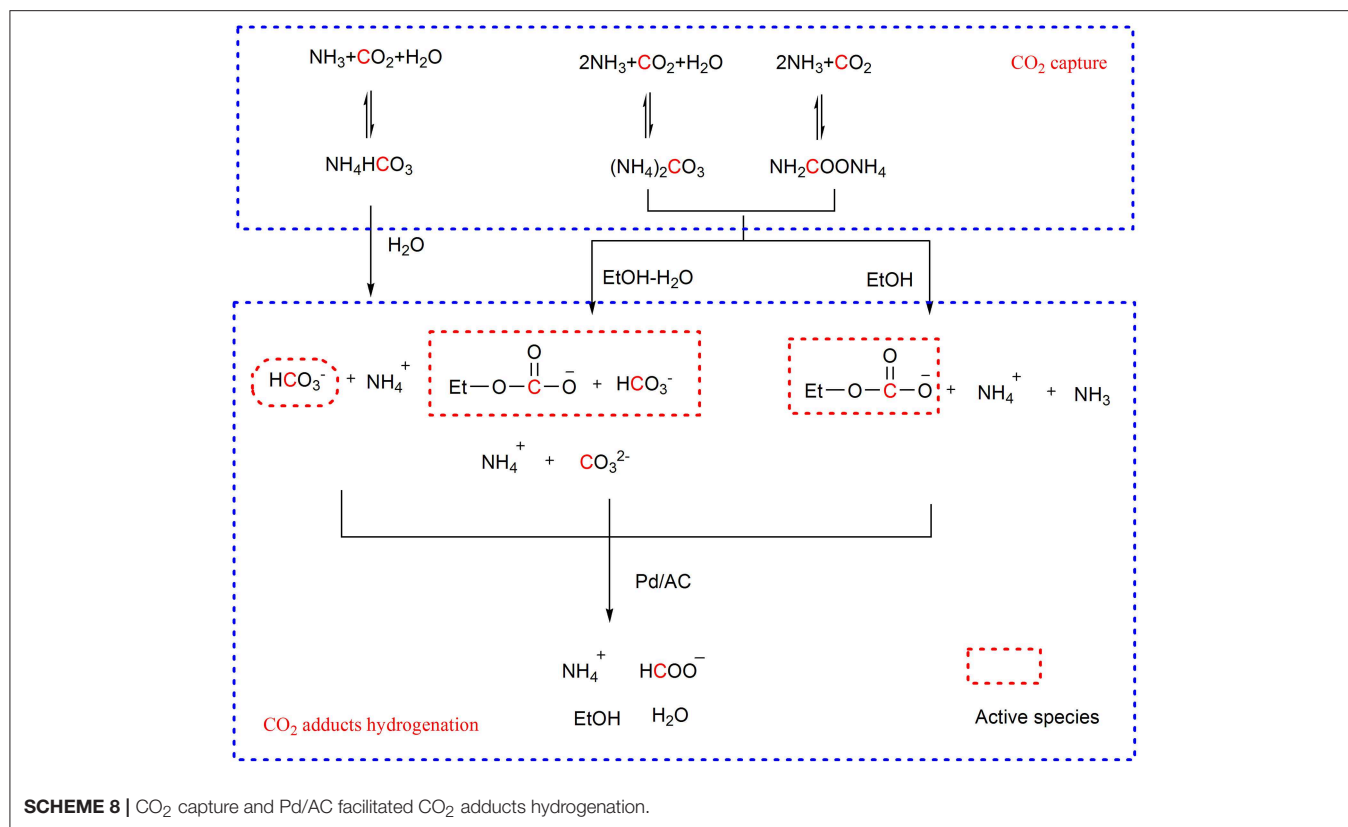
IONIC LIQUIDS (ILS)

Ionic liquids (ILs) offer a new opportunity for developing novel CO₂ capture reagents (Huang and Rüther, 2009; Gurkan et al., 2010; Wang et al., 2011; Yang and He, 2014). Especially, the active site-containing ionic liquids can trap and activate CO₂ through chemical absorption. Besides, IL can also function as catalyst in CO₂ transformation (Lang et al., 2016; Zhang et al., 2017; Xia et al., 2018). Therefore, it is promising to combine the multiple roles of ILs in CCU strategy. Up to now, cyclocarbonates,

oxazolidinones and quinazoline-2,4-(1H,3H)-diones have been synthesized using ILs as CO₂ absorbents and catalysts.

Wang group performs a series of investigation on ILs-based CO₂ capture and conversion. For example, they design bifunctionalized ionic liquids to capture and simultaneously fix CO₂ in the simulation of fuel gas to cyclic carbonates (**Scheme 11**) (Luo et al., 2016). The cation can capture CO₂ and the anion I⁻ can activate the substrate to facilitate CO₂ insertion. In the presence of a small amount of water, the yield of product can be improved, making this reaction more applicable to industrial exhaust.

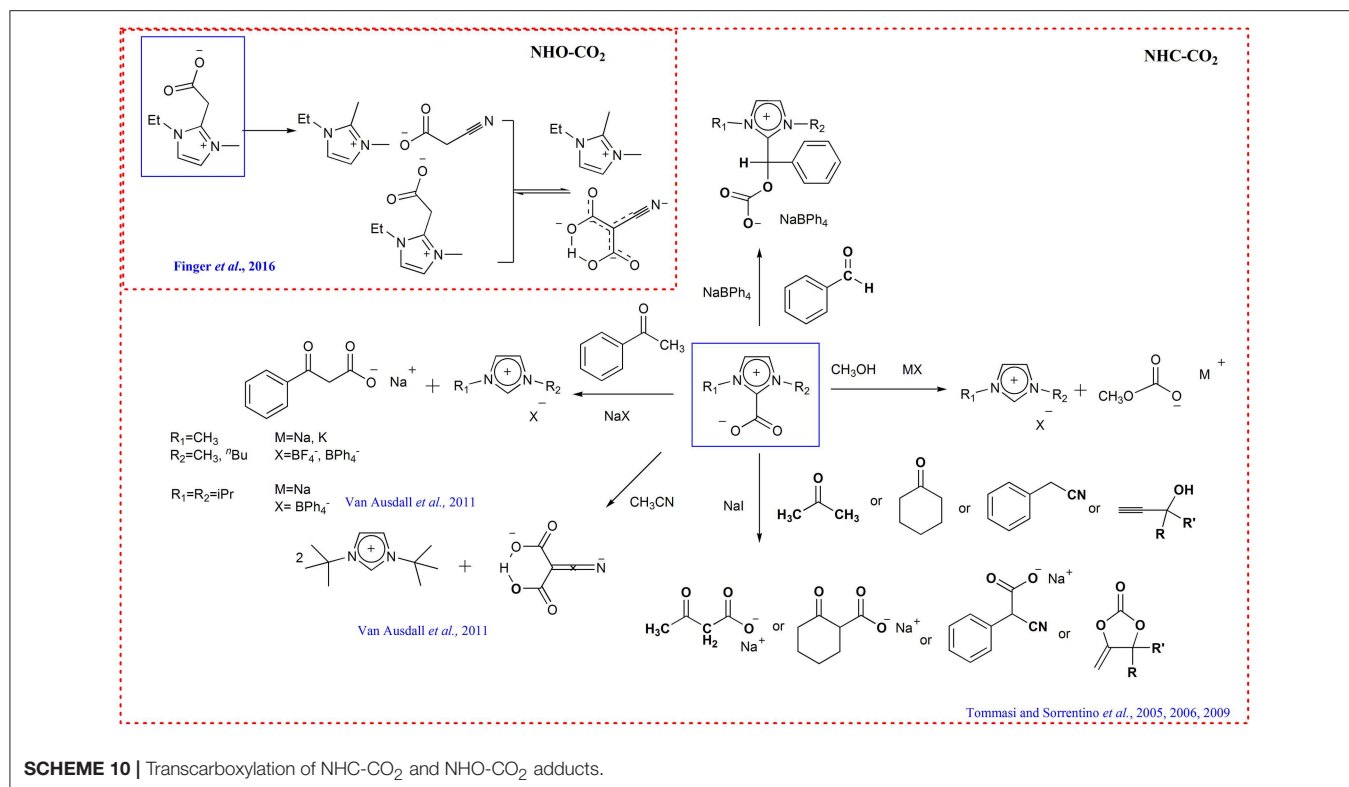
Later, the same group finds that the basicity of anion of ILs is very important for CO₂ capture and transformation. A hydroxyl functionalized aprotic ionic liquid shows high efficiency in synthesis of quinazoline-2,4-(1H,3H)-diones from atmospheric CO₂. The captured CO₂ instead of atmospheric CO₂ is also used and only 13% yield is obtained, being ascribed to the strong interaction between [Im]⁻ and CO₂ (**Scheme 11**) (Shi et al., 2018). They also demonstrate the feasibility of using captured CO₂ as starting material in their another report, where the CO₂ captured by azole-type anion [DEIm]⁻ renders a high



yield of alkylidene carbonates in the carboxylative cyclization of propargyl alcohol due to the weak interaction between CO₂ and the anion (**Scheme 11**) (Chen et al., 2016).

Liu group reports that azole-anion-based ILs with the [Bu₄P]⁺ cation can capture CO₂. With appropriate substrates, the forming carbamate intermediates can be transformed into the α-alkylidene cyclic carbonate, quinazoline-2,4(1H,3H)-diones and

benzimidazolone without other catalysts (**Scheme 11**) (Zhao et al., 2016). Later, the same group reveals that a series of tetrabutylphosphonium ([Bu₄P]⁺)-based ILs with multiple-site for CO₂ capture and activation in their anions can be used in CO₂ capture and conversion, wherein the IL [Bu₄P]₃[2,4-OPym-5-Ac] shows the optimal performance in preparation of α-alkylidene cyclic carbonates from propargylic alcohol substrate



(Wu et al., 2017). The resulting polycarbonates derived from CO₂ and the anion is proved to be the key intermediate in this reaction (**Scheme 11**).

The ILs [HDBU][MIm] and [HDBU][TFE] can capture CO₂ and also show catalytic activity to the reaction of CO₂ and propargylic amines for the synthesis of 2-oxazolidinones and the reaction of CO₂ with 2-aminobenzonitrile derivatives to synthesis quinazoline-2,4-(1H,3H)-diones. By enhancing the mass transfer with gas-liquid laminar flow continuous-flow microreactor, the simultaneous capture and fixation CO₂ to 2-oxazolidinones and quinazoline-2,4-(1H,3H)-diones is realized (**Scheme 11**) (Vishwakarma et al., 2017).

Due to the dual function as CO₂ absorbents and conversion catalysts, ionic liquids can realize the transformation of captured CO₂ with several kinds of substrates. Furthermore, the non-volatility characteristic of ionic liquids can facilitate product separation. Thus, the ionic liquids are considered as promising absorbents for the CCU process.

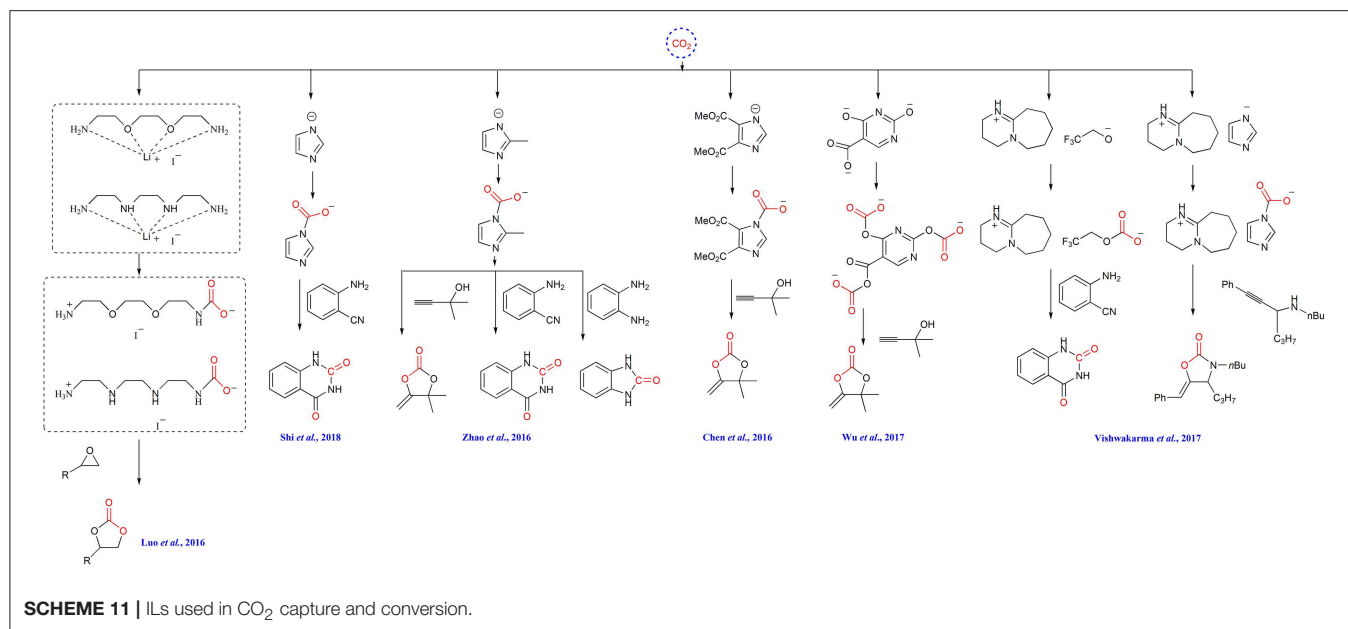
FRUSTRATED LEWIS PAIRS (FLPS)

The CO₂ capture capacity of FLPS has been reported soon after the FLPS concept was in 2006 proposed (Welch et al., 2006; Momming et al., 2009; Travis et al., 2013; Weicker and Stephan, 2015; Wolff et al., 2016). As early as 2010, Stephan group revealed that 1:2 mixtures of PMes₃/AlX₃ (X = Cl or Br) in bromobenzene can react with CO₂, forming CO₂ adduct which can be converted to CH₃OH with ammonia borane as reductant (**Scheme 12**) (Ménard and

Stephan, 2010). In the same year, Piers group found that CO₂ captured by FLP consisting of 2,2,6,6-tetramethylpiperidine (TMP) and B(C₆F₅)₃ can be reduced to methane with triethylsilane (**Scheme 12**) (Berkefeld et al., 2010). Soon, it is found that the FLP composed by bis-borane 1,2-C₆H₄(BCl₂)₂ and PtBu₃ can capture CO₂ and the forming capture product can be reduced to methanol by reductant such as amine-borane Me₂NHBH₃ or [C₅H₆Me₄NH₂][HB(C₆F₅)₂(C₇H₁₁)] (**Scheme 12**) (Sgro et al., 2012). Wang group reports the FLP comprising of bis(2,4,6-tris(trifluoromethyl)phenyl)borane and a secondary amine (such as HN*i*Pr₂ or HNEt₂) readily reacts with CO₂ at 80°C, affording carbamate boryl esters which can function as an intramolecular FLP to activate H₂, affording ammonium borylformate salt and formamide adducts (**Scheme 12**) (Lu et al., 2013).

Recently, Yan group incorporates FLP acceptor and donor into the styrene-based monomers, respectively to prepare two diblock copolymers consisting of the complementary FLP blocks and common polystyrene block. These two diblock copolymers can bind CO₂, forming nanoparticle. The nanoparticle is then used as CO₂ reservoir and catalyst to facilitate the formylation of amines with phenylsilane (**Scheme 12**) (Chen et al., 2018).

The CO₂ capture and H₂ activation capacity makes FLPS attractive for CCU strategy, especially for the hydrogenation of captured CO₂. However, in the current study, the FLPS promoted CO₂ hydrogenation encounters difficulty in FLPS regeneration (Ashley et al., 2009). By now, the FLPS are merely used as CO₂ capture reagents and reductants are still needed. Thus, the hydrogen activation ability of FLPS hasn't



been utilized. Recently, the breakthrough is made by Jazsar and Bertrand group. By combining the copper catalyst and Lewis pair, hydrogenation of carbon dioxide into formate is realized (Romero et al., 2018). Latter, X. Hu and Y. Wu group reports the first catalytic hydrogenation process of CO₂ to formate using transition metal free catalyst (B(C₆F₅)₃/M₂CO₃, M = Na, K, and Cs) (Zhao et al., 2019). These results open new vistas in the field of FLPs facilitated CO₂ capture and hydrogenation.

CATALYST DESIGN FOR DIRECT CONVERSION OF DILUTED CO₂

In addition to the CO₂ capture and transformation strategy, there are also examples that the CO₂ from waste streams can be directly converted by designing catalysts that tolerate to the contaminants in the waste streams such as exogenous water, nitrogen, SO₂, amine etc. For example, Williams et al. reports the synthesis of poly(cyclohexylene carbonate) using the power station generated CO₂ facilitated by the homogeneous dinuclear Zn or Mg catalysts, which is stable in the presence of contaminants from gas streams (Chapman et al., 2015) (**Scheme 13**). D'Elia and Basset group develops the combination of early transition metal halides (Y, Sc, Zr) and TBAB to quantitatively convert CO₂ from diluted streams and produce cyclic organic carbonates (Barthel et al., 2016). The features of metal-organic frameworks (MOFs) to selectively capture and catalyze CO₂ conversion make them a new type of platform for diluted CO₂ transformation. Recently, Hong group design and synthesize an acid-base resistant Cu(II)-MOF which can convert CO₂ from simulated post-combustion flue gas into corresponding cyclic carbonates (Liang et al., 2017). In direct conversion of diluted CO₂, the stability of the catalysts to the

contaminants in the gas streams is crucial to the success of the process.

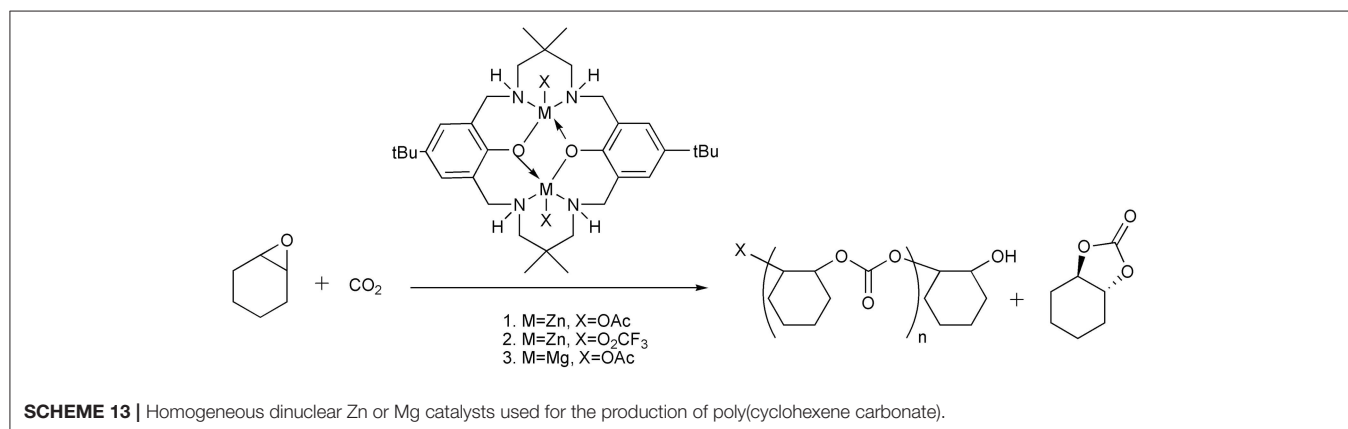
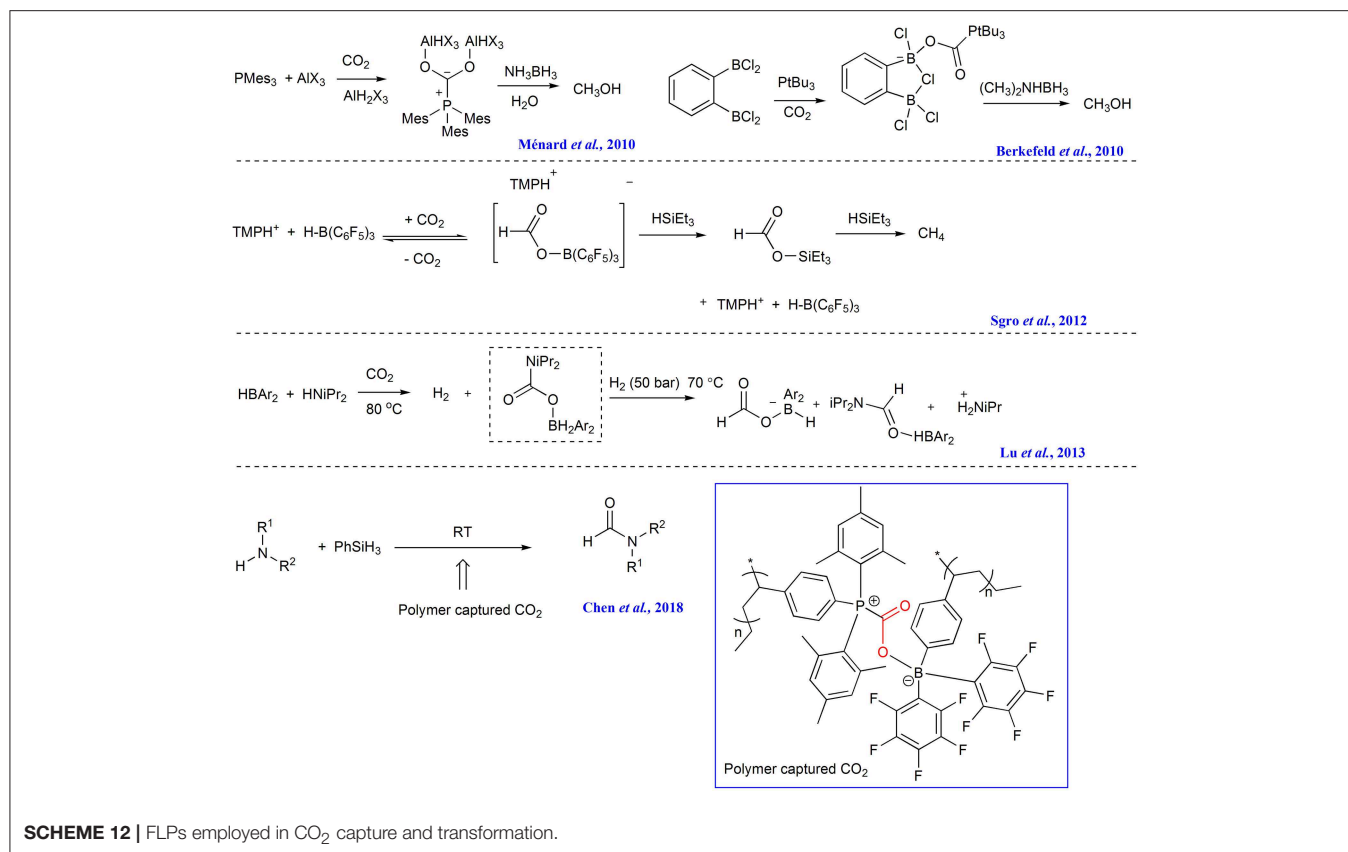
CONCLUSION AND OUTLOOK

The past 10 years have witnessed great advances in CO₂ capture and *in situ* conversion. Different CO₂ absorbents including inorganic and organic bases, NHCs, and NHOs, ILs, FLPs and polymeric functional materials have been employed in this field. As an emerging field, much effort is still desired to explore the potential conversion of the captured CO₂.

Considering amines and CO₂ can be involved in diverse reactions, it is hoped that the conversion of ammonia carbamate can be further extended to other valuable products besides isocyanates, carbamates and ureas.

On the other hand, although the hydrogenation of CO₂ captured by inorganic/organic bases and the combination of base and alcohol has been investigated, the hydrogenation of CO₂ captured by ILs and/or FLPs remains sporadic and underexplored. In light of the successful electrochemical reduction of IL-captured CO₂ and hydrogenation of CO₂ in ILs (Zhang et al., 2008, 2009; Wesselbaum et al., 2012; Scott et al., 2017), it is reasonable to conclude that the captured CO₂ by IL can be hydrogenated by designing appropriate catalyst. Besides, the breakthrough in FLP-mediated CO₂ hydrogenation opens new possibilities for FLP-based CO₂ capture and transformation (Romero et al., 2018; Zhao et al., 2019).

Another important transformation pathway for CO₂ adducts derived from reacting with amines, NHCs, NHOs and ILs is transcarboxylation reaction in the synthesis of cyclocarbonates, oxazolidinones and quinazoline-2,4-(1H,3H)-diones. It is foreseeable that the application of these transcarboxylating reagents will be investigated continuously with the emergence of new CO₂ conversion reactions.



Although a plethora of CO₂ absorbents has been developed and valuable products can be obtained from the resulting CO₂ adducts by different strategy, however, the cost and feasibility must be considered from the viewpoint of industrial application. With this in mind, amines and ionic liquids are considered as promising absorbents for the CCU strategy. For amine absorbents, their features of high absorbing capacity and comerial availability are attractive for industrial application. Besides, the CO₂ adducts derived from amines and CO₂ are non-volatile liquids or solids, which can be used as starting materials instead of the volatile amines and CO₂ gas to develop the gas free

progress. For ionic liquid- based CO₂ absorbents, the acceptable cost, tunable structure as well as their high CO₂ capture capacity make them competent to the commercial CCU process. Moreover, the ionic liquids are nonvolatile and the corrosion of equipment can be avoided by subtly design the structure of ionic liquids, all of which can facilitate the industry operability.

In summary, the CO₂ capture and *in situ* catalytic transformation is still in its infancy. We hope this review can inspire the extensive research on CO₂ capture and *in situ* transformation, which will benefit for the design of efficient CO₂ capture and utilization system (CCU) and realize the

valorization of diluted CO₂ in waste gas streams or directly from the atmosphere.

AUTHOR CONTRIBUTIONS

All authors contributed for the writing of the manuscript. L-NH designed this proposal and determined the contents. H-RL wrote the Abstract, Introduction, Conclusion, and Outlook parts. H-CF wrote the Inorganic/organic bases and Ionic liquids parts. FY wrote *N*-heterocyclic carbenes and *N*-heterocyclic olefins and frustrated lewis pairs parts. H-RL and L-NH revised the manuscript.

REFERENCES

- Alexander, O., Grube, T., Schiebahn, S., and Stolten, D. (2015). Closing the loop: captured CO₂ as a feedstock in the chemical industry. *Energy Environ. Sci.* 8, 3283–3297. doi: 10.1039/c5ee02591e
- Ashley, A. E., Thompson, A. L., and O'Hare, D. (2009). Non-metal-mediated homogeneous hydrogenation of CO₂ to CH₃OH. *Angew. Chem. Int. Ed.* 48, 9839–9843. doi: 10.1002/anie.200905466
- Barthel, A., Saih, Y., Gimenez, M., Pelletier, J. D. A., Kühn, F. E., D'Elia, V., et al. (2016). Highly integrated CO₂ capture and conversion: direct synthesis of cyclic carbonates from industrial flue gas. *Green Chem.* 18, 3116–3123. doi: 10.1039/c5gc03007b
- Berkefeld, A., Piers, W. E., and Parvez, M. (2010). Tandem frustrated lewis pair/tris(pentafluorophenyl)borane-catalyzed deoxygenative hydrosilylation of carbon dioxide. *J. Am. Chem. Soc.* 132, 10660–10661. doi: 10.1021/ja105320c
- Bobadilla, L. F., Riesco-García, J. M., Penelás-Pérez, G., and Urakawa, A. (2016). Enabling continuous capture and catalytic conversion of flue gas CO₂ to syngas in one process. *J. CO₂ Util.* 14, 106–111. doi: 10.1016/j.jcou.2016.04.003
- Chapman, A. M., Keyworth, C., Kember, M. R., Lennox, A. J. J., and Williams, C. K. (2015). Adding value to power station captured CO₂: tolerant Zn and Mg homogeneous catalysts for polycarbonate polyol production. *ACS Catal.* 5, 1581–1588. doi: 10.1021/cs501798s
- Chaturvedi, D., and Ray, S. (2006). Versatile use of carbon dioxide in the synthesis of carbamates. *Monatsh. Chem.* 137, 127–145. doi: 10.1007/s00706-005-0423-7
- Chen, K. H., Shi, G. L., Dao, R. N., Mei, K., Zhou, X. Y., Li, H. R., et al. (2016). Tuning the basicity of ionic liquids for efficient synthesis of alkylidene carbonates from CO₂ at atmospheric pressure. *Chem. Commun.* 52, 7830–7833. doi: 10.1039/c6cc02855e
- Chen, L., Liu, R. J., and Yan, Q. (2018). Polymer meets frustrated lewis pair: second-generation CO₂-responsive nanosystem for sustainable CO₂ conversion. *Angew. Chem. Int. Ed.* 57, 9336–9340. doi: 10.1002/anie.201804034
- Ciamician, G. (1912). The Photochemistry of the future. *Science* 36, 385–394.
- Dong, L., Wen, J., and Li, W. Y. (2015). A theoretical investigation of substituent effects on the stability and reactivity of *N*-heterocyclic olefin carboxylates. *Org. Biomol. Chem.* 13, 8533–8544. doi: 10.1039/c5ob01021g
- Duyara, M. S., Wang, S., Arellano-Treño, M. A., and Farrauto, R. J. (2016). CO₂ utilization with a novel dual function material (DFM) for capture and catalytic conversion to synthetic natural gas: an update. *J. CO₂ Util.* 15, 65–71. doi: 10.1016/j.jcou.2016.05.003
- Enthaler, S., Brück, A., Kammer, A., Junge, H., Irran, E., and Güllak, S. (2015). Exploring the reactivity of nickel pincer complexes in the decomposition of formic acid to CO₂/H₂ and the hydrogenation of NaHCO₃ to HCOONa. *ChemCatChem* 7, 65–69. doi: 10.1002/cctc.201402716
- Finger, L. H., Guschlbauer, J., Harms, K., and Sundermeyer, J. (2016). *N*-heterocyclic olefin-carbon dioxide and -sulfur dioxide adducts: structures and interesting reactivity patterns. *Chem. Eur. J.* 22, 16292–16303. doi: 10.1002/chem.201602973
- Gurau, G., Rodriguez, H., Kelley, S. P., Janiczek, P., Kalb, R. S., and Rogers, R. D. (2011). Demonstration of chemisorption of carbon dioxide in 1,3-dialkylimidazolium acetate ionic liquids. *Angew. Chem. Int. Ed.* 50, 12024–12026. doi: 10.1002/anie.201105198
- Gurkan, B. E., de la Fuente, J. C., Mindrup, E. M., Ficke, L. E., Goodrich, B. F., Price, E. A., et al. (2010). Equimolar CO₂ absorption by anion-functionalized ionic liquids. *J. Am. Chem. Soc.* 132, 2116–2117. doi: 10.1021/ja909305t
- Hampe, E. M., and Rudkevich, D. M. (2003). Exploring reversible reactions between CO₂ and amines. *Tetrahedron* 59, 9619–9625. doi: 10.1016/j.tet.2003.09.096
- Huang, J. H., and Rütger, T. (2009). Why are ionic liquids attractive for CO₂ absorption? An overview. *Aust. J. Chem.* 62, 298–308. doi: 10.1071/CH08559
- Inesi, A., Mucciante, V., and Rossi, L. (1998). A convenient method for the synthesis of carbamate esters from amines and tetraethylammonium hydrogen carbonate. *J. Org. Chem.* 63, 1337–1338. doi: 10.1021/jo971695y
- Kayaki, Y., Yamamoto, M., and Ikariya, T. (2009). *N*-Heterocyclic carbenes as efficient organocatalysts for CO₂ fixation reactions. *Angew. Chem. Int. Ed.* 48, 4194–4197. doi: 10.1002/anie.200901399
- Kelemen, Z., Peter-Szabo, B., Szekely, E., Holloczki, O., Firaha, D. S., Kirchner, B., et al. (2014). An abnormal *N*-heterocyclic carbene-carbon dioxide adduct from imidazolium acetate ionic liquids: the importance of basicity. *Chem. Eur. J.* 20, 13002–13008. doi: 10.1002/chem.201402912
- Kothandaraman, J., Goepfert, A., Czaun, M., Olah, G. A., and Prakash, G. K. (2016a). Conversion of CO₂ from air into methanol using a polyamine and a homogeneous ruthenium catalyst. *J. Am. Chem. Soc.* 138, 778–781. doi: 10.1021/jacs.5b12354
- Kothandaraman, J., Goepfert, A., Czaun, M., Olah, G. A., and Surya Prakash, G. K. (2016b). CO₂ capture by amines in aqueous media and its subsequent conversion to formate with reusable ruthenium and iron catalysts. *Green Chem.* 18, 5831–5838. doi: 10.1039/c6gc01165a
- Lang, X. D., Yu, Y. C., Li, Z. M., and He, L. N. (2016). Protic ionic liquids-promoted efficient synthesis of quinazolines from 2-aminobenzonitriles and CO₂ at ambient conditions. *J. CO₂ Util.* 15, 115–122. doi: 10.1016/j.jcou.2016.03.002
- Lee, J. B., Eom, T. H., Oh, B. S., Baek, J. I., Ryu, J., Jeon, W. S., et al. (2011). CO₂ capture from flue gas using potassium-based dry regenerable sorbents. *Energy Procedia.* 4, 1494–1499. doi: 10.1016/j.egypro.2011.02.016
- Li, L., Li, Y., Wen, X., Wang, F., Zhao, N., Xiao, F., et al. (2011). CO₂ Capture over K₂CO₃/MgO/Al₂O₃ dry sorbent in a fluidized bed. *Energy Fuels* 25, 3835–3842. doi: 10.1021/ef200499b
- Li, L., Wen, X., Fu, X., Wang, F., Zhao, N., Xiao, F., et al. (2010). MgO/Al₂O₃ sorbent for CO₂ capture. *Energy Fuels* 24, 5773–5780. doi: 10.1021/ef100817f
- Li, Y. N., He, L. N., Lang, X. D., Liu, X. F., and Zhang, S. (2014). An integrated process of CO₂ capture and *in situ* hydrogenation to formate using a tunable ethoxyl-functionalized amidine and Rh/bisphosphine system. *RSC Adv.* 4, 49995–50002. doi: 10.1039/c4ra08740b
- Li, Y. N., He, L. N., Liu, A. H., Lang, X. D., Yang, Z. Z., Yu, B., et al. (2013). *In situ* hydrogenation of captured CO₂ to formate with polyethyleneimine and Rh/monophosphine system. *Green Chem.* 15, 2825–2829. doi: 10.1039/C3GC41265B
- Liang, L., Liu, C., Jiang, F., Chen, Q., Zhang, L., Xue, H., et al. (2017). Carbon dioxide capture and conversion by an acid-base resistant metal-organic framework. *Nat. Commun.* 8:1233. doi: 10.1038/s41467-017-01166-3

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- Liu, A. H., Ma, R., Song, C., Yang, Z. Z., Yu, A., Cai, Y., et al. (2012). Equimolar CO₂ capture by N-substituted amino acid salts and subsequent conversion. *Angew. Chem. Int. Ed.* 51, 11306–11310. doi: 10.1002/anie.201205362
- Lu, Z., Wang, Y., Liu, J., Lin, Y. J., Li, Z. H., and Wang, H. (2013). Synthesis and reactivity of the CO₂ adducts of amine/bis(2,4,6-tris(trifluoromethyl)phenyl)borane pairs. *Organometallics* 32, 6753–6758. doi: 10.1021/om4007246
- Luo, X., Chen, K., Li, H., and Wang, C. (2016). The capture and simultaneous fixation of CO₂ in the simulation of fuel gas by bifunctionalized ionic liquids. *Int. J. Hydrogen Energy* 41, 9175–9182. doi: 10.1016/j.ijhydene.2015.12.223
- Massoud, S. S., Louka, F. R., Al-Hasan, M. A., Vicenteb, R., and Mautner, F. A. (2015). Magneto-structural properties of carbonato-bridged copper(II) complexes: fixation of atmospheric CO₂. *N. J. Chem.* 39, 5944–5952. doi: 10.1039/c5nj00285k
- Ménard, G., and Stephan, D. W. (2010). Room temperature reduction of CO₂ to methanol by Al-based frustrated lewis pairs and ammonia borane. *J. Am. Chem. Soc.* 132, 1796–1797. doi: 10.1021/ja9104792
- Momming, C. M., Otten, E., Kehr, G., Frohlich, R., Grimme, S., Stephan, D. W., et al. (2009). Reversible metal-free carbon dioxide binding by frustrated lewis pairs. *Angew. Chem. Int. Ed.* 48, 6643–6646. doi: 10.1002/anie.200901636
- Munshi, P., Main, A. D., Linehan, J. C., Tai, C. C., and Jessop, P. G. (2002). Hydrogenation of carbon dioxide catalyzed by ruthenium trimethylphosphine complexes: the accelerating effect of certain alcohols and amines. *J. Am. Chem. Soc.* 124, 7963–7971. doi: 10.1021/ja0167856
- Pérez, E. R., Santos, R. H. A., Gambardella, M. T. P., Macedo, L. G. M., de Rodrigues-Filho, U. P., Launay, J., et al. (2004). Activation of carbon dioxide by bicyclic amidines. *J. Org. Chem.* 69, 8005–8011. doi: 10.1021/jo049243q
- Pérez, E. R., Silva, M. O., da Costa, V. C., Rodrigues-Filho, U. P., and Franco, D. W. (2002). Efficient and clean synthesis of N-alkyl carbamates by transcarboxylation and O-alkylation coupled reactions using a DBU–CO₂ zwitterionic carbamic complex in aprotic polar media. *Tetrahedron Lett.* 43, 4091–4093. doi: 10.1016/S0040-4039(02)00697-4
- Rahman, F. A., Aziz, M. M. A., Saidur, R., Bakar, W. A. W. A., Hainin, M. R., Putrajaya, R., et al. (2017). Pollution to solution: capture and sequestration of carbon dioxide (CO₂) and its utilization as a renewable energy source for a sustainable future. *Renew. Sust. Energ. Rev.* 71, 112–126. doi: 10.1016/j.rser.2017.01.011
- Reller, C., Pöge, M., Lifšner, A., and Mertens, F. O. R. L. (2014). CO₂ capture and hydrogenation in one process step. *Environ. Sci. Technol.* 48, 14799–14804. doi: 10.1021/es503914d
- Rezayee, N. M., Huff, C. A., and Sanford, M. S. (2015). Tandem amine and ruthenium-catalyzed hydrogenation of CO₂ to methanol. *J. Am. Chem. Soc.* 137, 1028–1031. doi: 10.1021/ja511329m
- Romero, E. A., Zhao, T., Nakano, R., Hu, X. B., Wu, Y. T., Jazzar, R., et al. (2018). Tandem copper hydride–lewis pair catalyzed reduction of carbon dioxide into formate with dihydrogen. *Nat. Catal.* 1, 743–747. doi: 10.1038/s41929-018-0140-3
- Saptal, V. B., and Bhanage, B. M. (2016). N-Heterocyclic olefins as robust organocatalyst for the chemical conversion of carbon dioxide to value-added chemicals. *ChemSusChem* 9, 1980–1985. doi: 10.1002/cssc.201600467
- Scott, M., Molinos, B. B., Westhues, C., Francik, G., and Leitner, W. (2017). Aqueous biphasic systems for the synthesis of formates by catalytic CO₂ hydrogenation: integrated reaction and catalyst separation for CO₂-scrubbing solutions. *ChemSusChem* 10, 1085–1093. doi: 10.1002/cssc.201601814
- Sgro, M. J., Domer, J., and Stephan, D. W. (2012). Stoichiometric CO₂ reductions using a bis-borane-based frustrated lewis pair. *Chem. Commun.* 48, 7253–7255. doi: 10.1039/c2cc33301e
- Shi, G. L., Chen, K. H., Wang, Y. T., Li, H. R., and Wang, C. M. (2018). Highly efficient synthesis of quinazoline-2,4(1H,3H)-diones from CO₂ by hydroxyl functionalized aprotic Ionic Liquids. *ACS Sustain. Chem. Eng.* 6, 5760–5765. doi: 10.1021/acssuschemeng.8b01109
- Song, Q. W., Zhou, Z. H., Yin, H., and He, L. N. (2015). Silver(I)-catalyzed synthesis of β-oxopropylcarbamates from propargylic alcohols and CO₂ surrogate: a gas-free process. *ChemSusChem* 8, 3967–3972. doi: 10.1002/cssc.201501176
- Su, J., Lu, M., and Lin, H. F. (2015a). High yield production of formate by hydrogenating CO₂ derived ammonium carbamate/carbonate at room temperature. *Green Chem.* 17, 2769–2773. doi: 10.1039/c5gc00397k
- Su, J., Yang, L. S., Lu, M., and Lin, H. F. (2015b). Highly efficient hydrogen storage system based on ammonium bicarbonate/formate redox equilibrium over palladium nanocatalysts. *ChemSusChem* 8, 813–816. doi: 10.1002/cssc.201403251
- Talapaneni, S. N., Buyukcakir, O., Je, S. H., Srinivasan, S., Seo, Y., Polychronopoulou, K., et al. (2015). Nanoporous polymers incorporating sterically confined N-heterocyclic carbenes for simultaneous CO₂ capture and conversion at ambient pressure. *Chem. Mater.* 27, 6818–6826. doi: 10.1021/acs.chemmater.5b03104
- Tamura, M., Honda, M., Nakagawa, Y., and Tomishige, K. (2014). Direct conversion of CO₂ with diols, aminoalcohols and diamines to cyclic carbonates, cyclic carbamates and cyclic ureas using heterogeneous catalysts. *J. Chem. Technol. Biotechnol.* 89, 19–33. doi: 10.1002/jctb.4209
- Tommasi, I., and Sorrentino, F. (2005). Utilisation of 1,3-dialkylimidazolium-2-carboxylates as CO₂-carriers in the presence of Na⁺ and K⁺: application in the synthesis of carboxylates, monomethylcarbonate anions and halogen-free ionic liquids. *Tetrahedron Lett.* 46, 2141–2145. doi: 10.1016/j.tetlet.2005.01.106
- Tommasi, I., and Sorrentino, F. (2006). Synthesis of 1,3-dialkylimidazolium-2-carboxylates by direct carboxylation of 1,3-dialkylimidazolium chlorides with CO₂. *Tetrahedron Lett.* 47, 6453–6456. doi: 10.1016/j.tetlet.2006.06.106
- Tommasi, I., and Sorrentino, F. (2009). 1,3-dialkylimidazolium-2-carboxylates as versatile N-heterocyclic carbene–CO₂ adducts employed in the synthesis of carboxylates and α-alkylidene cyclic carbonates. *Tetrahedron Lett.* 50, 104–107. doi: 10.1016/j.tetlet.2008.10.107
- Travis, A. L., Binding, S. C., Zaher, H., Arnold, T. A. Q., Buffet, J. C., and O'Hare, D. (2013). Small molecule activation by frustrated lewis pairs. *Dalton Trans.* 42, 2431–2437. doi: 10.1039/c2dt32525j
- Van Ausdall, B. R., Poth, N. F., Kincaid, V. A., Arif, A. M., and Louie, J. (2011). Imidazolide carboxylate bound MBPh₄ complexes (M = Li, Na) and their relevance in transcarboxylation reactions. *J. Org. Chem.* 76, 8413–8420. doi: 10.1021/jo201647b
- Vishwakarma, N. K., Singh, A. K., Hwang, Y. H., Ko, D. H., Kim, J. O., Babu, A. G., et al. (2017). Integrated CO₂ capture-fixation chemistry via interfacial ionic liquid catalyst in laminar gas/liquid flow. *Nat. Commun.* 8:14676. doi: 10.1038/ncomms14676
- Wang, C. M., Luo, X. Y., Luo, H. M., Jiang, D. E., Li, H. R., and Dai, S. (2011). Tuning the basicity of ionic liquids for equimolar CO₂ capture. *Angew. Chem. Int. Ed.* 50, 4918–4922. doi: 10.1002/ange.201008151
- Wang, H., Xin, Z., and Li, Y. H. (2017b). Synthesis of ureas from CO₂. *Top. Curr. Chem.* 375:49. doi: 10.1007/s41061-017-0137-4
- Wang, P. X., Liu, S., and Deng, Y. Q. (2017a). Important green chemistry and catalysis: non-phosgene syntheses of isocyanates – thermal cracking way. *Chin. J. Chem.* 35, 821–835. doi: 10.1002/cjoc.201600745
- Wang, S., and Wang, X. (2016). Imidazolium ionic liquids, imidazolylidene heterocyclic carbenes, and zeolitic imidazolate frameworks for CO₂ capture and photochemical reduction. *Angew. Chem. Int. Ed.* 55, 2308–2320. doi: 10.1002/anie.201507145
- Weicker, S. A., and Stephan, D. W. (2015). Activation of carbon dioxide by silyl triflate-based frustrated lewis pairs. *Chem. Eur. J.* 21, 13027–13034. doi: 10.1002/chem.201501904
- Welch, G. C., Juan, R. R. S., Masuda, J. D., and Stephan, D. W. (2006). Reversible, metal-free hydrogen activation. *Science* 314, 1124–1126. doi: 10.1126/science.1134230
- Wesselbaum, S., Hintermair, U., and Leitner, W. (2012). Continuous-flow hydrogenation of carbon dioxide to pure formic acid using an integrated scCO₂ process with immobilized catalyst and base. *Angew. Chem. Int. Ed.* 51, 8585–8588. doi: 10.1002/ange.201203185
- Wolff, N., von, Lefèvre, G., Berthet, J. C., Thuéry, P., and Cantat, T. (2016). Implications of CO₂ activation by frustrated lewis pairs in the catalytic hydroboration of CO₂: a view using B/Si⁺ frustrated lewis pairs. *ACS Catal.* 5, 4526–4535. doi: 10.1021/acscatal.6b00421
- Wu, Y. Y., Zhao, Y. F., Li, R. P., Yu, B., Chen, Y., Liu, X. W., et al. (2017). Tetrabutylphosphonium-based ionic liquid catalyzed CO₂ transformation at ambient conditions: a case of synthesis of α-alkylidene cyclic carbonates. *ACS Catal.* 7, 6251–6255. doi: 10.1021/acscatal.7b01422
- Xia, S. M., Chen, K. H., Fu, H. C., and He, L. N. (2018). Ionic liquids catalysis for carbon dioxide conversion with nucleophiles. *Front. Chem.* 6:462. doi: 10.3389/fchem.2018.00462

- Yadav, M., Linehan, J. C., Karkamkar, A. J., van der Eide, E., and Heldebrant, D. J. (2014). Homogeneous hydrogenation of CO₂ to methyl formate utilizing switchable ionic liquids. *Inorg. Chem.* 53, 9849–9854. doi: 10.1021/ic501378w
- Yang, Z. Z., and He, L. N. (2014). Efficient CO₂ capture by tertiary amine-functionalized ionic liquids through Li⁺-stabilized zwitterionic adduct formation. *Beilstein J. Org. Chem.* 10, 1959–1966. doi: 10.3762/bjoc.10.204
- Yang, Z. Z., He, L. N., Gao, J., Liu, A. H., and Yu, B. (2012). Carbon dioxide utilization with C–N bond formation: carbon dioxide capture and subsequent conversion. *Energy Environ. Sci.* 5, 6602–6639. doi: 10.1039/c2ee02774g
- Yang, Z. Z., He, L. N., Zhao, Y. N., Li, B., and Yu, B. (2011). CO₂ capture and activation by superbases/polyethylene glycol and its subsequent conversion. *Energy Environ. Sci.* 4, 3971–3975. doi: 10.1039/c1ee02156g
- Yoshida, M., Komatsuzaki, Y., and Ihara, M. (2008). Synthesis of 5-vinylideneoxazolidin-2-ones by DBU-mediated CO₂-fixation reaction of 4-(benzylamino)-2-butynyl carbonates and benzoates. *Org. Lett.* 10, 2083–2086. doi: 10.1021/ol800663v
- Yoshida, M., Mizuguchi, T., and Shishido, K. (2012). Synthesis of oxazolidinones by efficient fixation of atmospheric CO₂ with propargylic amines by using a silver/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) Dual-catalyst system. *Chem. Eur. J.* 18, 15578–15581. doi: 10.1002/chem.201203366
- Yu, B., Cheng, B. B., Liu, W. Q., Li, W., Wang, S. S., Cao, J., et al. (2016). Atmospheric pressure of CO₂ as protecting reagent and reactant: efficient synthesis of oxazolidin-2-ones with carbamate salts, aldehydes and alkynes. *Adv. Synth. Catal.* 358, 90–97. doi: 10.1002/adsc.201500921
- Zhang, S., Li, Y. N., Zhang, Y. W., He, L. N., Yu, B., Song, Q. W., et al. (2014). Equimolar carbon absorption by potassium phthalimide and *in situ* catalytic conversion under mild conditions. *ChemSusChem* 7, 1484–1489. doi: 10.1002/cssc.201400133
- Zhang, Y. G., and Lim, D. S. W. (2015). Synergistic carbon dioxide capture and conversion in porous materials. *ChemSusChem* 8, 2606–2608. doi: 10.1002/cssc.201500745
- Zhang, Z. F., Hu, S. Q., Song, J. L., Li, W. J., Yang, G. Y., and Han, B. X. (2009). Hydrogenation of CO₂ to formic acid promoted by a diamine-functionalized ionic liquid. *ChemSusChem* 2, 234–238. doi: 10.1002/cssc.200800252
- Zhang, Z. F., Xie, Y., Li, W. J., Hu, S. Q., Song, J. L., Jiang, T., et al. (2008). Hydrogenation of carbon dioxide is promoted by a task-specific ionic liquid. *Angew. Chem. Int. Ed.* 47, 1127–1129. doi: 10.1002/ange.200704487
- Zhang, Z. G., Fan, F. J., Xing, H. B., Yang, Q. W., Bao, Z. B., and Ren, Q. L. (2017). Efficient synthesis of cyclic carbonates from atmospheric CO₂ using a positive charge delocalized ionic liquid catalyst. *ACS Sustain. Chem. Eng.* 5, 2841–2846. doi: 10.1021/acsschemeng.7b00513
- Zhao, T., Hu, X., Wu, Y., and Zhang, Z. (2019). Hydrogenation of CO₂ to formate with H₂: transition metal free catalyst based on a lewis pair. *Angew. Chem. Int. Ed.* 58, 722–726. doi: 10.1002/anie.201809634
- Zhao, Y. F., Wu, Y. Y., Yuan, G. F., Hao, L. D., Gao, X., Yang, Z. Z., et al. (2016). Azole-anion-based aprotic ionic liquids: functional solvents for atmospheric CO₂ transformation into various heterocyclic compounds. *Chem. Asian J.* 11, 2735–2740. doi: 10.1002/asia.201600281
- Zhou, H., Wang, G. X., and Lu, X. B. (2017). CO₂ Adducts of α -Carbon Alkylated N-Heterocyclic olefins: highly active organocatalysts for CO₂ chemical transformation. *Asian J. Org. Chem.* 6, 1264–1269. doi: 10.1002/ajoc.201700152
- Zhou, H., Zhang, W. Z., Liu, C. H., Qu, J. P., and Lu, X. B. (2008). CO₂ adducts of N-heterocyclic carbenes: thermal stability and catalytic activity toward the coupling of CO₂ with epoxides. *J. Org. Chem.* 73, 8039–8044. doi: 10.1021/jo801457r

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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