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# Homogeneous catalytic hydrogenation of CO<sub>2</sub> – amino acid-based capture and utilization

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In this review, we provide an overview of research efforts to integrate carbon dioxide capture specifically using amino acid-based sorbents with its thermocatalytic hydrogenation promoted by homogeneous metal complexes. Carbon capture and utilization (CCU) is a promising strategy for the production of fuels, chemicals and materials using CO<sub>2</sub> scrubbed from point sources and the atmosphere as a C1 feedstock while mitigating CO<sub>2</sub> emissions. Compared to established (alkanol)amines, amino acids offer some advantages as CO<sub>2</sub> capture agents due to their lower volatility, higher oxygen stability and lower regeneration energies. We report how the structural diversity of amino acids and the possibility of combining them with cations in salts and ionic liquids have been exploited in the design of absorbers for improved absorption kinetics and capacity. Furthermore, we discuss selected examples from the literature illustrating the use of 1°/2° (poly)amines, since the 1°/2° amino groups are mainly responsible for CO<sub>2</sub> chemisorption in amino acid-based capture media, the nature of the corresponding adducts, and the most promising catalysts capable of converting the latter to formate and methanol while regenerating the scrubber. General trends regarding the influence of catalyst structure and reaction parameters on the efficiency, productivity, and selectivity of such processes will be highlighted. We will detail how this knowledge has informed the design of novel processes in which CO<sub>2</sub> is chemisorbed by amino acid-based solvents and hydrogenated *in situ* to formate and methanol, or alternatively used as a fuel to implement a "hydrogen battery" where, after metal-catalyzed H<sub>2</sub> release from formate, CO<sub>2</sub> is retained by the amino acid-based solvent in the "spent battery" which can then be recharged by hydrogenation of the retained CO<sub>2</sub> promoted by the same catalyst. The topic is still in its infancy, and several issues have emerged that will be critically discussed in the final section of this review. These issues need to be addressed in order to improve performance and provide a playground for researchers whose interest we hope to have aroused with this review.

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## 1. Introduction

The Paris Agreement, negotiated by 196 parties, finally entered into force in November 2016 with the goal of keeping global warming well below 2 °C above pre-industrial levels. There is growing public, scientific and political awareness of the impact of CO<sub>2</sub> emissions from fossil fuel combustion on global warming and ecosystems. However, the development and deployment of renewable energy technologies has not yet reached a level where they can fully meet the high energy demands of modern society. Therefore, fossil fuels will remain the primary source of energy for the foreseeable future, and significant amounts of CO<sub>2</sub> from their combustion will be emitted into the atmosphere. In this scenario, CO<sub>2</sub> capture from point

sources and from the atmosphere will be one of the key strategies to mitigate the adverse effects of CO<sub>2</sub> emissions and to achieve the target set by the convention, along with the development of new technologies for improved energy efficiency and renewable energy production.

Currently, CO<sub>2</sub> capture technologies can be divided into four categories, including physical adsorption, chemical absorption, membrane and cryogenic separation. Among these technologies, chemical absorption is the most efficient and has been implemented in power plants using alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyl diethanolamine (MDEA), as absorbents, with MEA being widely used as the benchmark absorbent. The captured CO<sub>2</sub> is then typically desorbed and compressed to either be used as a C1 feedstock producing chemicals and fuels, or sequestered underground. The alkanolamine based solvents have been shown to be quite efficient, capturing up to 90% of the CO<sub>2</sub> present in power plant flue gas streams.<sup>1</sup> However, the energy required for solvent regeneration (CO<sub>2</sub> desorption)

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ranges between 2.4 and 4.2 GJ per ton of CO<sub>2</sub>, accounting for 60–70% of the total capital investment of the capture process.<sup>2</sup>

To circumvent the high energy penalty of the desorption and compression steps, processes are being investigated that can be collectively referred to as reactive CO<sub>2</sub> capture (Scheme 1), where the captured CO<sub>2</sub> is used directly as a C1 feedstock for the synthesis of value-added products. Currently, the fertilizer industry uses about 230 Mt CO<sub>2</sub> per year for urea production (~130 Mt) and enhanced oil recovery (~80 Mt).<sup>3</sup> Among the possible applications within the reactive CO<sub>2</sub> capture concept, the direct hydrogenation of the captured CO<sub>2</sub> to formate and

methanol is the most promising from an economic point of view. One reason is that green H<sub>2</sub> derived from water electrolysis using renewable energy or from photocatalysis is much more sustainable compared to the production of other precursors used in CO<sub>2</sub> fixation, such as epoxide, alkenes and alkynes.<sup>4</sup> In addition, formic acid and methanol can also be used as liquid organic hydrogen carriers (LOHC).<sup>5</sup> Moreover, methanol is one of the most important organic feedstocks for the chemical industry<sup>6</sup> which is produced annually on the order of 100 Mt. More specifically, methanol is used in the synthesis of chemicals including acetic acid, formaldehyde, ethylene,



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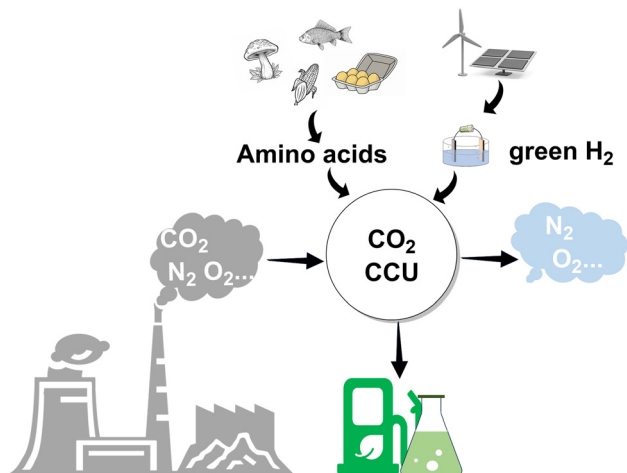


**Matthias Beller**

*Matthias Beller, born in Gudensberg (Germany) in 1962, obtained his PhD in 1989 working with Lutz F. Tietze at the University of Göttingen. After one year of postdoctoral research with Barry Sharpless at MIT (USA), from 1991 to 1995 he worked at Hoechst AG in Frankfurt. Then, he started his academic career at TU Munich. In 1998, he relocated to Rostock to head the Leibniz-Institute for Catalysis. Matthias Beller is also Vice-president of the*

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Scheme 1 Schematic illustration of the CO<sub>2</sub> reactive capture concept.

methyl methacrylate, and propylene *via* the methanol-to-olefin (MTO) route. It can also be used as a fuel, either by itself, in a blend with gasoline, to produce biodiesel, or in the form of methyl *tert*-butyl ether (MTBE) and dimethyl ether (DME). Although reactive CO<sub>2</sub> capture is a relatively new topic, several research groups, for instance, Prakash,<sup>6b,7</sup> Milstein,<sup>8</sup> Leitner,<sup>9</sup> Gademann,<sup>10</sup> He,<sup>11</sup> Nielsen,<sup>12</sup> Sanford,<sup>13</sup> and our group<sup>14</sup> have advanced this field and demonstrated the applicability of the *in situ* conversion of captured CO<sub>2</sub> for the synthesis of methanol, formates, oxazolidinones, and urea. In these studies, mostly organic amines were used as the base for CO<sub>2</sub> capture and subsequent hydrogenation.

Although the alkanolamine-based capture technologies can be easily retrofitted to existing post-combustion power plants and have been shown to be highly efficient in capturing CO<sub>2</sub> from flue gas, they suffer from some fatal drawbacks, such as volatile loss, thermal degradation by O<sub>2</sub> in the flue gas and thus the formation of corrosive by-products. Therefore, many efforts have been made to develop alternative absorbents to alkanolamines. Among the developed absorbents, amino acid-based absorbents, whose amino groups can bind to CO<sub>2</sub> in a similar manner to amines, show the advantages in terms of their low volatility due to their ionic properties, high oxygen resistance and low regeneration energies. There are more than 500 amino acids in nature, offering a wide range of possibilities in terms of basicity and steric hindrance, which have been shown to be the most important parameters determining absorption kinetics, type of CO<sub>2</sub> adducts, and uptake capacity, *etc.*<sup>15</sup> In addition, since the amino groups can only react with CO<sub>2</sub> in their neutral form after the amino acid zwitterions have been neutralized/deprotonated, the choice of counter cations can also influence the absorption performance, and thus offer another possibility for absorbent design, as will be discussed in detail in Section 3.

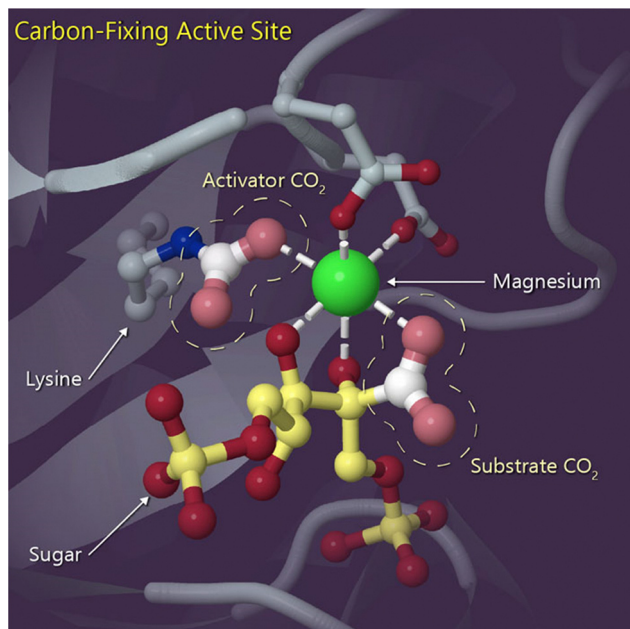
Amino acids are the building blocks of carboxylases, the key enzymes in photosynthesis and the global carbon cycle, that capture CO<sub>2</sub> from the atmosphere and convert it into

organic biomass.<sup>16</sup> Carboxylases promote the formation of a C–C bond between CO<sub>2</sub>, the electrophile, and a substrate, which act as the nucleophile. To overcome the thermodynamic and kinetic inertness of CO<sub>2</sub>, most carboxylases activate the substrate (for example, a thioester,  $\alpha$ -ketoacid, or ketone) by transforming it into an enol(ate), which is a stronger nucleophile. On the other hand, the electrophilic CO<sub>2</sub> molecule is closely positioned in the active site through interaction with amino acids to allow nucleophilic attack. This interaction relies on a variety of binding elements that exploit the difference in electronegativity between carbon and oxygen: CO<sub>2</sub> binds through metals, hydrogen bonds and hydrophobic interactions.

Molecular dynamics calculations suggest that the diffusion of CO<sub>2</sub> around and into carboxylases to access the active site is dominated by hydrophobic interactions with amino acids with small hydrophobic side chains, such as alanine (ALA), valine (VAL), leucine (LEU), and isoleucine (ILE), and the sulfur-containing cysteine (CYS) residue.<sup>16</sup> Within the active site, catalysis requires tight control of the reaction between the enolate and CO<sub>2</sub>. This is realized by a network of hydrogen bonds, or more precisely acid/base motifs, provided by strategically located amino acid residues. Bioinformatic analysis shows that the highly basic amino acids, such as lysine (LYS) (pI 9.5), arginine (ARG) (pI 10.8), and histidine (pI 7.6), are the most abundant in the crystal structures of CO<sub>2</sub> protein binding sites.<sup>17</sup> In enoyl-CoA carboxylase/reductases, the carboxylases with the highest turnover frequencies, four amino acid residues anchor and position the CO<sub>2</sub> molecule for attack by a reactive enolate formed during the catalytic cycle. The amide group of an asparagine residue (ASN) holds the CO<sub>2</sub> in place from one side, while a water grid, starting from a water molecule secured between a residue of histidine (HIS) and glutamic acid (GLUA), serves as an additional anchoring point for CO<sub>2</sub> from the opposite side.

The aromatic ring of a phenylalanine (PHE) residue actively prevents the diffusion of water into the active site which would trigger the competitive protonation/reduction of the enolate, the alternative reaction catalyzed by enoyl-CoA carboxylase/reductases in the absence of CO<sub>2</sub>. It is noteworthy that CO<sub>2</sub> is bound to the protein environment through the two oxygen atoms leaving the carbon atom relatively free for any incoming substrate. This is an aspect that should be considered in the design and application of biomimetic catalysis for CO<sub>2</sub> capture and utilization (*vide infra*). CO<sub>2</sub> can also react with unprotonated *N*-primary amine or LYS- $\epsilon$ -amino groups in proteins affording the corresponding carbamates/carbamic acid.<sup>18</sup> This post-translational modification plays a crucial role in regulating oxygen binding in hemoglobin and activating the CO<sub>2</sub>-fixing enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO).<sup>19</sup> It is estimated that 400 Gt of CO<sub>2</sub> are fixed annually by RuBisCO which is ultimately responsible for virtually all the organic carbon present in the biosphere.<sup>20</sup> The active site of RuBisCO is centered on a magnesium ion which is held tightly by an ASN residue, a GLUA and the carbamate group formed by carbamylation of the  $\epsilon$ -amino group of a LYS residue.<sup>21</sup> A second CO<sub>2</sub> molecule is then fixed





**Fig. 1** The active site of RuBisCO is centered on a magnesium ion. It is held tightly by three amino acids: an asparagine, glutamic acid, and the carbamate group formed by carbamylation of the  $\epsilon$ -amino group of a lysine residue. The carbon dioxide molecule (left, dotted outline) attached to this lysine serves as an activator in the carbon fixing reaction. This activator carbon dioxide is different from the carbon dioxide molecule that is fixed to the ribulose 1,5-bisphosphate. Reproduced with permission from ref. 22: Image from the RCSB PDB (<https://rcsb.org>) November 2000 Molecule of the Month feature by David Goodsell.

through nucleophilic attack by the enolate of ribulose 1,5-bisphosphate, generated by H3 proton abstraction by the activated LYS carbamate (Fig. 1).<sup>22</sup>

Inspired by the unique properties of amino acids in the natural process and some favorable features compared to alkanolamines, we believe that amino acid-based absorbents can be attractive alternatives for reactive CO<sub>2</sub> capture. In recent years, our group has focused on using amino acid salts (AAS) and amino acid-based ionic liquids (AAILs) as the basis for CO<sub>2</sub> hydrogenation, and productivities (TONs) for formate superior to amine and alkanolamine based systems have been achieved.<sup>23</sup> Based on these promising results, we feel compelled to highlight this emerging field by summarizing the recent progress in CO<sub>2</sub> capture and hydrogenation realized in amino acid-based systems.

In this review, we summarize recent advances in the application of amino acid-based absorbents for CO<sub>2</sub> capture and subsequent *in situ* hydrogenation. As readers will note, amino acid-based reactive CO<sub>2</sub> capture has only emerged in the last five years, whereas earlier developments were largely focused on conventional amine/hydroxide-based systems. To provide a comprehensive overview, we also briefly discuss advances in reactive CO<sub>2</sub> capture using non-amino acid-based systems and the guiding principles behind these approaches. To facilitate the understanding of the relationship between CO<sub>2</sub> properties and CO<sub>2</sub> reactivity in capture and hydrogenation, we present

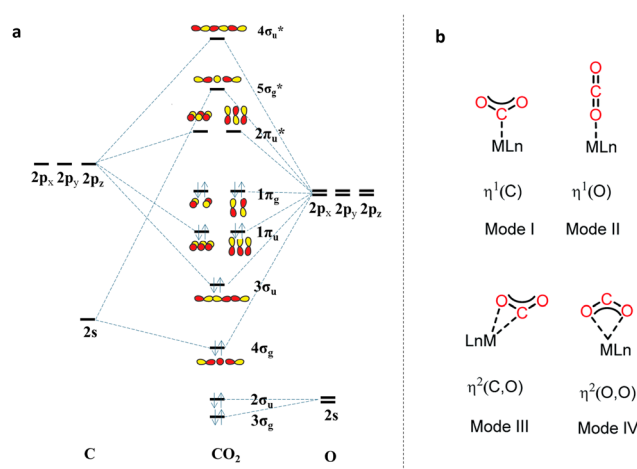
the essential background information on the physical and chemical properties of CO<sub>2</sub> in Section 2. Furthermore, we highlight the distinct advantages of amino acid-based absorbents by discussing recent advances in this field in Section 3. Following this, recent advances in reactive CO<sub>2</sub> capture in non-amino acid-based systems are discussed in Section 4. Finally, the achievements of reactive CO<sub>2</sub> capture with amino acid-based absorbents are highlighted in Section 5.

## 2. CO<sub>2</sub> properties and activation

CO<sub>2</sub> is a linear triatomic molecule in which the sp-hybridized central carbon is bonded to two peripheral oxygen atoms *via*  $\sigma$  and  $\pi$  bonds, making it highly thermodynamically stable ( $\Delta G_f^\circ = -396$  kJ mol<sup>-1</sup>). The symmetric dipole moments and linear geometry determine the overall nonpolar property. However, due to the electronegativity differences between carbon and oxygen, the bonds are polar, resulting in a partial positive charge on the carbon atom and a partial negative charge at the oxygen atoms. The positive carbon center can thus act as electrophile, allowing nucleophilic attack by a base, for instance, hydroxide or amines, which is the basis for CO<sub>2</sub> capture *via* chemical absorption.

The Lewis basic and acidic properties of CO<sub>2</sub> can also be explained by the orbital structure at its ground state, as shown in Fig. 2a. The HOMO ( $1\pi_g$ ) orbitals contain only the contribution from the 2p orbitals of the O atoms, corresponding to their out-of-phase orbitals including lone electron pairs. The LUMO ( $2\pi_u^*$ ) comprises contributions from the 2p<sub>x</sub> and 2p<sub>y</sub> orbitals of the C and O atoms, with significant carbon character and localization on the carbon atom, while the corresponding bonding orbitals ( $1\pi_u$ ) have an energy level slightly lower than the O 2p orbitals, due to the higher electronegativity of the O element.

The disruption of the linear geometry and symmetric electron distribution of the molecule can be an indicator of CO<sub>2</sub>



**Fig. 2** (a) Molecular orbitals of CO<sub>2</sub> at the ground state. (b) Common binding modes of the CO<sub>2</sub> molecule with metal. Reproduced from ref. 24 and 25 with copyright permission.



activation. In general, chemisorption is the first step prior to the activation. As shown in Fig. 2b, CO<sub>2</sub> can be coordinated to an isolated activation site by four different modes: (1) when the carbon center is bonded to a Lewis base or metal surface, the backward electron donation to the anti-bonding orbital of CO<sub>2</sub> ( $2\pi_u^*$ ) leads to the bending of the O–C–O angle to less than 180°, and to a lowering of the  $2\pi_u^*$  orbital energy;<sup>26</sup> (2) when the O center is end-on adsorbed on a Lewis acid site, *i.e.*, metal oxide or electron-deficient metal surface, the CO<sub>2</sub> molecule can maintain its linear structure or be slightly distorted;<sup>27</sup> (3) in the case of  $\eta^2(\text{C,O})$  side-on adsorption on the active site, both back-donation from the active site, and donation to the active site, occur at the same time, resulting in a bent O–C–O bonds; (4) both O atoms can simultaneously bind to the active center, forming a bidentate species. In a system with multiple active sites, for instance, metal clusters/nanoparticles, organometallic complexes, the mode III and mode IV in Fig. 2b can be further extended to a bridge-on absorption mode.

In the heterogeneous hydrogenation of CO<sub>2</sub>, one pathway for further conversion of the adsorbed intermediates is the dissociation of CO<sub>2</sub> into CO and O species, resulting from the weakening of the C–O bond. Further hydrogenation of the adsorbed CO can then result in formate, methanol, methane and C<sub>2+</sub> hydrocarbons, depending on the reaction conditions and catalysts.<sup>28</sup> Alternatively, the hydride adsorbed on the active surface can migrate and nucleophilic attack the carbon center of the bound CO<sub>2</sub> to form adsorbed formate species. For example, a case study by Bowen and colleagues demonstrated the activation of CO<sub>2</sub> by platinum hydride clusters using mass spectroscopy and photoelectron spectroscopy (Fig. 3a). Combining experimental data with DFT calculations, they confirmed that the insertion of CO<sub>2</sub> into the Pt–H bond of [PtH<sub>3</sub>]<sup>–</sup>

is energetically favorable, leading to the formation of formate anion/[PtH<sub>2</sub>] adducts (Fig. 3b). In contrast, [PtH]<sup>–</sup> was found to only activate CO<sub>2</sub> (Fig. 3c).<sup>29</sup>

Compared to heterogeneous catalytic CO<sub>2</sub> upgrading, the homogeneous pathway typically allows the conversion under milder conditions with easier control of selectivity.<sup>30</sup> The general modes of CO<sub>2</sub> coordination and subsequent activation on transition metal complexes are shown in Fig. 2b. The reduction of CO<sub>2</sub> to formate requires the insertion of the CO<sub>2</sub> molecule into a M–H bond. The respective mechanism is shown in Fig. 4, where a side-on coordination of CO<sub>2</sub> to the metal center occurs (activation mode I in Fig. 4), followed by hydride transfer to the carbon center (nucleophilic attack).<sup>31</sup> For a coordinatively saturated metal complex, a vacant site made available by the dissociation of an ancillary ligand may be a prerequisite for the CO<sub>2</sub> coordination and subsequent insertion step into the M–H bond. Since the reaction for the formation of formic acid is endergonic ( $\Delta G_{298}^\circ = +33 \text{ kJ mol}^{-1}$ ), a base is always added to shift the reaction equilibrium. It should be noted that the direct nucleophile attack by the hydride (activation mode II in Fig. 4) has also been proposed, which does not require coordination of CO<sub>2</sub> to the metal, and is therefore possible also for coordinatively saturated metal catalysts such as the Nozaki pyridine-based PNP-ligated iridium(III) trihydride.<sup>32</sup> More recently, functional ligands have been developed which incorporate a functional group besides the donor atoms. Hazari and co-workers demonstrated that the presence of an H-bond donor incorporated in the second coordination sphere of an Ir complex favors CO<sub>2</sub> insertion and conversion.<sup>33</sup> As shown in Fig. 5, the aliphatic PNP ligand in the iridium trihydride catalyst contains an –NH motif that can form a hydrogen bond with the oxygen of an incoming CO<sub>2</sub> molecule, thereby increasing the electrophilicity of its central carbon to facilitate hydride transfer. DFT calculations were performed to explore the pathway for CO<sub>2</sub> insertion. It was calculated that of the three available hydrides, axial H<sub>a</sub>, *syn* to the N–H bond, is preferentially transferred (Fig. 6). The hydrogen bond, which is also present in the Ir–formate complex, makes the insertion thermodynamically and kinetically more favourable. Indeed, complex **1** (Fig. 5) was found to readily insert CO<sub>2</sub> at room temperature, leading to the highly moisture and air stable formate–Ir complex **2**. For the catalytic hydrogenation of CO<sub>2</sub> in alkaline water promoted by **1**, nucleophilic attack of CO<sub>2</sub> by the hydride was calculated to be the rate-determining step, requiring no pre-coordination of CO<sub>2</sub> to iridium. Similar transition states and intermediates have been calculated for the insertion of CO<sub>2</sub> into the Ru–H bond of a ruthenium dihydride complex carrying an aliphatic bisphosphinoamino pincer ligand.<sup>34</sup>

Nucleophilic attack may not always be an activation when considering the target hydrogenation product. For example, the adsorption of CO<sub>2</sub> onto an oxygen-rich surface, such as an oxide support, could form a stable and strongly adsorbed carbonate intermediate species, which may not be favorable for further hydrogenation. The same applies to CO<sub>2</sub> absorbed in solution, either in water or an organic solvent, in the form of bicarbonate and/or carbamate, which are thermodynamically poorer hydride

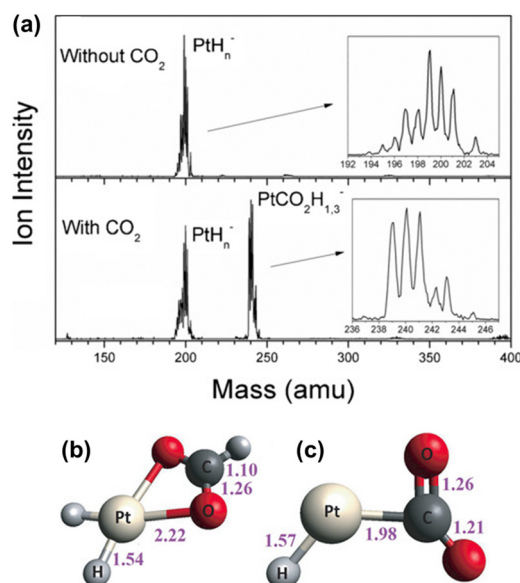


Fig. 3 Illustration of the activation of CO<sub>2</sub> by PtH<sub>n</sub><sup>–</sup> cluster: (a) mass spectra with and without the presence of CO<sub>2</sub>, (b) PtCO<sub>2</sub>H<sub>3</sub><sup>–</sup> and (c) PtCO<sub>2</sub>H<sup>–</sup>. Bond lengths (Å). Reproduced from ref. 29 with copyright permission.



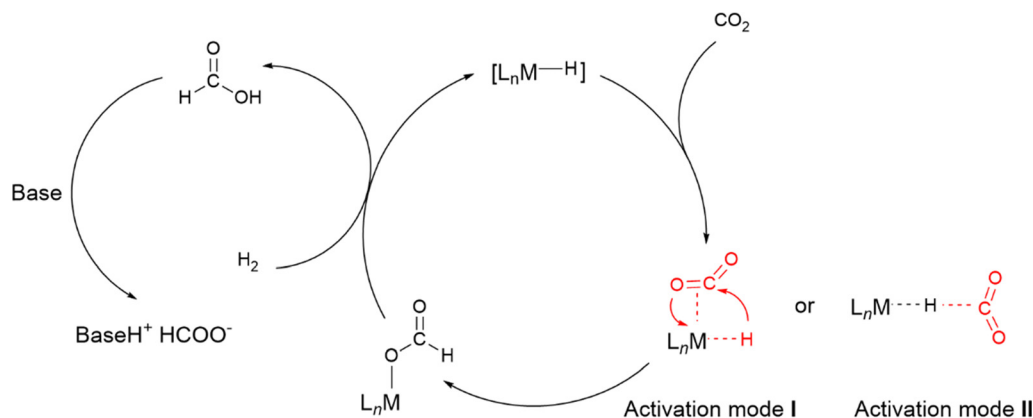


Fig. 4 General mechanism of CO<sub>2</sub> hydrogenation by metal hydrides. Adapted from ref. 35 and 30 with copyright permission.

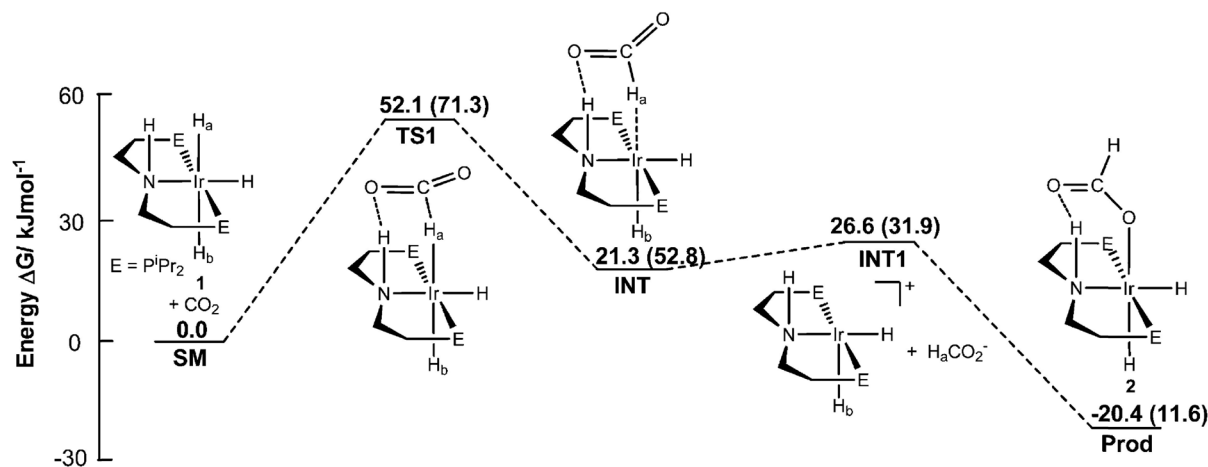


Fig. 5 Reaction pathway for insertion of CO<sub>2</sub> into **1**. All energies are solvent corrected (THF) Gibbs free energies. Numbers in parentheses are for insertion into H<sub>b</sub>. For which hydrogen bonding between the entering CO<sub>2</sub> and the ligand NH is not available. E = P<sup>i</sup>Pr<sup>2</sup>. Reproduced with permission from ref. 33.

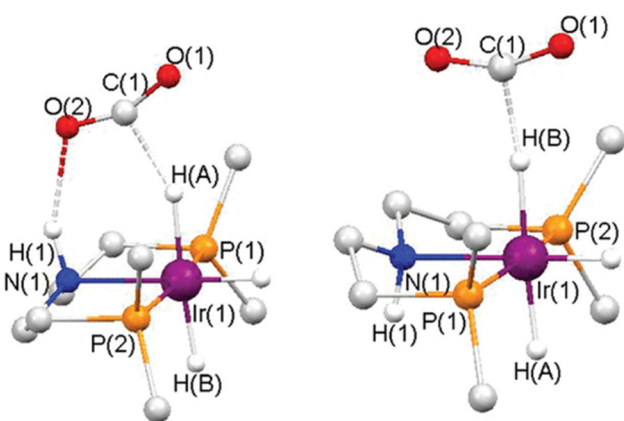


Fig. 6 Calculated transition state for CO<sub>2</sub> insertion into (a) H<sub>a</sub> and (b) H<sub>b</sub> respectively of complex **1** shown in Fig. 4. Selected hydrogen atoms and isopropyl groups have been removed for clarity. The smaller Ir–H<sub>a</sub>–C bond angle for H<sub>a</sub> attack on CO<sub>2</sub> (152.2°) compared to the corresponding bond angle Ir–H<sub>b</sub>–C for H<sub>b</sub> attack on CO<sub>2</sub> (172.4°) allows for a stabilizing H-bonding interaction between O(2) and H(1). As a result, the former process is thermodynamically and kinetically favoured. Reproduced with permission from ref. 33.

acceptors than CO<sub>2</sub> itself. Yet, anionic carboxylates/carbamates can coordinate to cationic metal complexes and become charge neutral, allowing reduction. Alternatively, ion pairing can be used to tune the properties of the anions and should be considered in reaction design. Whether the hydrogenation within a given solvent proceeds on the CO<sub>2</sub>-adduct formed after CO<sub>2</sub> scrubbing or on free CO<sub>2</sub> in equilibrium with the latter under the experimental conditions of the hydrogenation reaction is questionable and specific to the system under investigation.<sup>36</sup> In the case of bicarbonate hydrogenation, claims can be made in either case or a combination of both can be put forward based on either the successful hydrogenation of (bi)carbonate without CO<sub>2</sub> overpressure and the detection of a metal-(bi)carbonate resting state,<sup>34,37</sup> or the higher TON achieved in the presence of pressurized CO<sub>2</sub>.<sup>38</sup> In natural photosynthesis catalyzed by RuBisCO, CO<sub>2</sub> released from bicarbonate is the species which undergoes nucleophilic attack by the negatively charged enolates.<sup>22</sup> It has recently been demonstrated that alkylcarbonates are more reactive toward ruthenium hydride complexes than CO<sub>2</sub> under comparable conditions when the catalyst operates *via* an inner-sphere mechanism in

which the substrate alkylcarbonate is coordinated to the metal center.<sup>39</sup> It is likely that carbamates have a similar reactivity, although with coordinatively saturated metal hydrides which cannot bind the substrate, formate is more likely to result from preferential hydride transfer to free CO<sub>2</sub> in equilibrium with carbamate, due to the higher electrophilicity of the former.<sup>13</sup>

### 3. CO<sub>2</sub> capture with amino acid-based absorbents

As discussed in the introduction, current industrial-scale carbon capture, utilization, and storage (CCUS) technologies use alkanolamines as absorbents. However, these amine-based systems suffer from several disadvantages, such as high regeneration energy, low resistance to oxygen degradation, corrosiveness, and volatility. In comparison, amino acids could potentially overcome the above-mentioned disadvantages and have thus attracted considerable attention from both academia and industry. In addition to high CO<sub>2</sub> loading capacity, low regeneration energy, resistance to O<sub>2</sub> degradation, and high-boiling point, the amino acid-based absorbents are also biodegradable, and can be obtained from biomass, making them environmentally friendly. The evaluation criteria for CO<sub>2</sub>-capture and -storage solvents include the capture capacity/equilibrium constants, cyclic capacity, density and dynamic viscosity, heat capacity, dissociation constant, and CO<sub>2</sub> mass transfer. However, since the focus of this review is on valorization of CO<sub>2</sub>, only the capture capacity, absorption kinetics and equilibrium constant will be considered and discussed.

Amino acids can be considered as analog of amines when in the active form (Scheme 2a), as the amino group serves as the active center for CO<sub>2</sub> capture, and thus, the capture mechanisms of amines can be applied to amino acid-based systems. Specifically, the dissolved CO<sub>2</sub> undergoes nucleophilic attack by the amino group, forming a C–N bond (Scheme 2b, eqn (1)) in a zwitterionic form, after which, another base, either the amino acid itself, H<sub>2</sub>O, as Brønsted base, or a hydroxide, present in the solution, can abstract a proton from the protonated amino group to form a carbamate (Scheme 2b, eqn (2) and (3)). Thus, the maximum loading capacity is 0.5 moles CO<sub>2</sub> per mole of amino acid in the carbamate form when another molecule of amino acid acts as the counter cation. In addition, if an additional base, usually hydroxide, or water, is present, it may also promote the formation of bicarbonate (Scheme 2b, eqn (4)) or carbamic acid (Scheme 2b, eqn (5)), and therefore, the theoretical maximum load can exceed 0.5 (eqn (3) and (5)) or even 1 (Scheme 2b, eqn (4)). However, the amino acids are inactive in CO<sub>2</sub> capture over a wide pH range. For example, in a medium with a pH between pK<sub>a</sub>(–COOH) and pK<sub>a</sub>(–NH<sub>2</sub>), amino acids exist in a zwitterionic form with a net charge of zero, and the protons from the carboxyl groups protonate and deactivate the amino groups. Under more acidic conditions, the amino groups would be protonated by external protons with a net charge of +1, which would also result in a deactivated amino group. Therefore, to activate the amino groups, the amino acids

must be neutralized, or ionized by a base, such as alkali metal hydroxides, or strongly basic amines. Scheme 2a illustrates the effect of pH on the transitions between different forms of amino acids. Based on the type of cations, the amino acid-based absorbents for CO<sub>2</sub> capture can be classified into three categories, namely, amino acid salts, amino acid ionic liquids, and amino acids mixtures. In the following three subsections, the state-of-the-art reference work on amino acid-based absorbents for CO<sub>2</sub> capture mainly published within the last 5 years will be discussed.

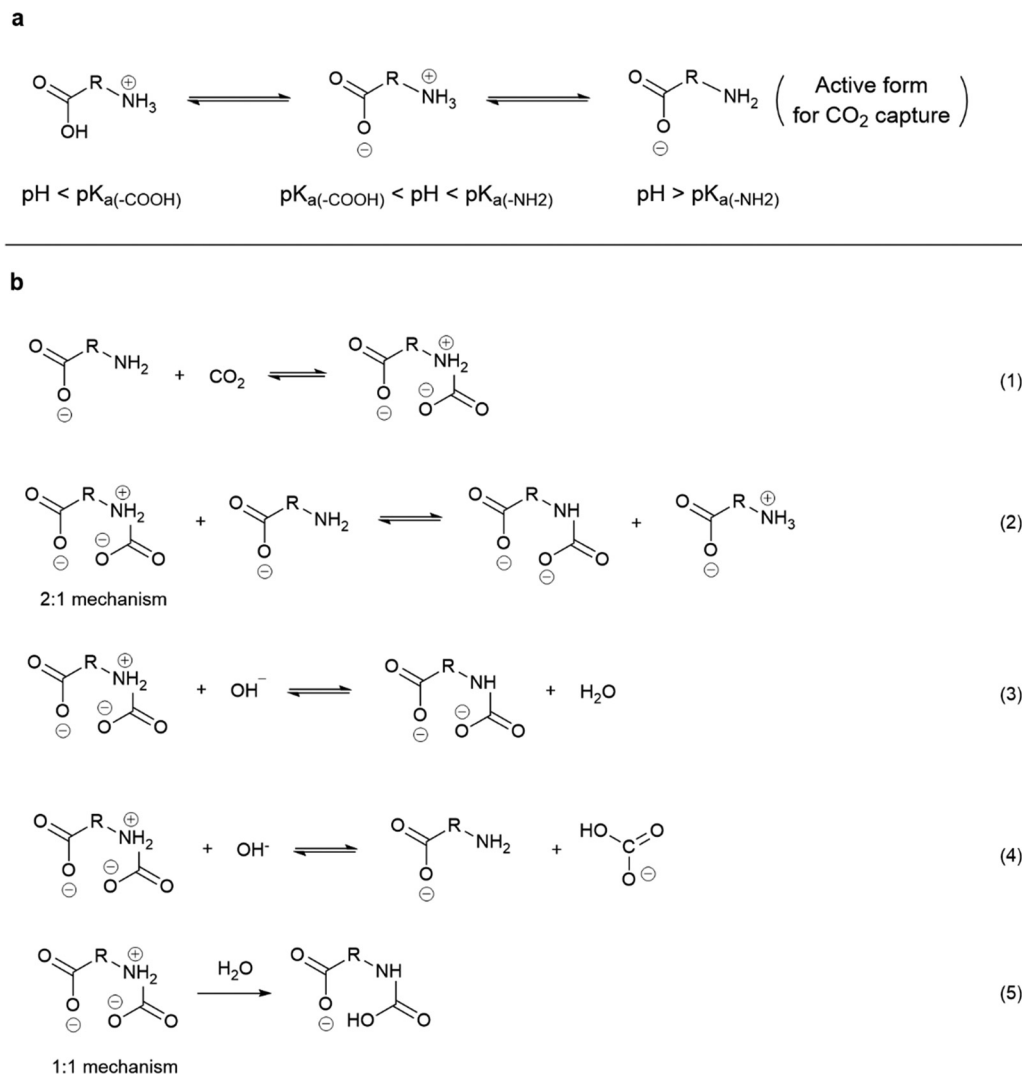
#### 3.1. Amino acid salts for CO<sub>2</sub> capture

Amino acid salts (AAS) can be obtained simply by neutralizing the amino acids with an equimolar amount of alkali hydroxides in an aqueous solution. There are 20  $\alpha$ -amino acids that are the building blocks of proteins, with the amine and carboxylic group located on the same carbon. However, the properties and CO<sub>2</sub>-binding capacities vary depending on the side group. For example, potassium lysinate (LYSK), potassium arginate (ARGK), and potassium histidinate (HISK) are reported to have the highest capture capacity and by far exceed the performance of 30 wt% of MEA (benchmark), due to the high pK<sub>a</sub> of the additional primary or secondary amine groups on the side chain.<sup>15,40</sup> Potassium proline (PROK) was also reported to possess high capacity due to the instability of the corresponding carbamate and its tendency to hydrolyze to bicarbonate, which, in turn, shifts the equilibrium toward amine-CO<sub>2</sub> bond formation. To make it easier for the reader to compare the amino acid properties and their correlation with the CO<sub>2</sub> capture performance of the corresponding salts, a list of the structure and pK<sub>a</sub> of the amino acids, as well as the reported CO<sub>2</sub> loading capacities, and the pseudo-first-order reaction constant ( $K_{ov}$ ) are summarized in Table 1.

The CO<sub>2</sub> absorption rate is one of the critical parameters for evaluating a good absorbent for CO<sub>2</sub> capture, as fast kinetics results in a smaller absorption column size, or lower absorbent concentration, thus reducing the operating cost of the stripping process. The Hogendoorn's group studied the overall pseudo-first order reaction rate constant ( $K_{ov}$ ) of the potassium salt of various amino acids, including taurine (TAU), methionine (MET), glycine (GLY), GLUA, alanine (ALA), 6-aminohexanoic acid, sarcosine (*N*-methyl glycine, NMGLY), PRO, and ARG, as a function of the amino acid pK<sub>a</sub>.<sup>51</sup> The results show that NMGLY, GLY and PRO exhibit comparatively higher  $K_{ov}$  than MEA and DEA at a concentration of 0.5 M, demonstrating the great potential of amino acids salts as a replacement for conventional alkanolamines for industrial-scale application (Fig. 7). However, ARG exhibited a similar apparent rate constant despite having a pK<sub>a</sub> as high as 13.8.<sup>51</sup> They further studied the influence of alkali cations on the apparent absorption rate and found that the rate is independent of the alkali counterions in the case of NMGLY, while the potassium salt exhibited a faster rate than the lithium salt with PRO as the counterion.

Song *et al.* studied the influence of steric hindrance on the CO<sub>2</sub> absorption and desorption rate, and the net cyclic capacity.<sup>15</sup>





**Scheme 2** (a) The dependence of aqueous amino acid form on the pH; (b) possible reactions for CO<sub>2</sub> capture with active amino acid absorbents.

As shown in Fig. 8a, the authors claimed that the stability of the zwitterionic products is influenced by the R groups attached to the amines, as they exert a steric repulsion on the two oxygen atoms of CO<sub>2</sub>. Therefore, sterically hindered amino acids allow for easier CO<sub>2</sub> desorption. Based on this model, the authors tested 16 amino acids with different R groups, including, linear amino acids [GLY, TAU and β-alanine (BALA)], sterically hindered amino acids [ALA, aminobutyric acid (AABA), serine (SER), α-methyl alanine (AMALA) and CYS], cyclic amino acids [proline (PRO), hydroxyproline (HYPRO) and pyroglutamic acid (PGA)], and polyamino acids [(ASN, glutamine (GLN), diglycine (DIGLY) and ARG). The authors found that the ease of CO<sub>2</sub> desorption increases when the distance between the CO<sub>2</sub>-bonded amino group and the carboxyl group decreases or in the presence of bulkier substituents, which is consistent with the predicted model (Fig. 8b and c). However, exceptional cases not following the rule were also observed: for example, the presence of a carbonyl group adjacent to the amino group (*e.g.*, ASN and GLUA), leads to nitrogen lone pair delocalization and reduced

nucleophilicity, which results in lower CO<sub>2</sub> loading capacity. It should be noted that the net cyclic capacity of ARG is similar to that of NMGLY, despite its loading capacity being the highest among those of the tested amino acids. The authors speculated that the lower net cyclic capacity of arginate salts can be rationalized by the fact that they form stable carbamates which cannot be completely decomposed under the stripping conditions applied in this study.

Clearly, the CO<sub>2</sub> absorption rate and loading capacity varies among amino acid salts, influenced by factors such as steric hindrance, pK<sub>a</sub> value, and viscosity. Liao's group suggested that a blend of different amino acid salts in a solvent mixture could lead to a synergistic improvement, resulting in a higher CO<sub>2</sub> loading capacity.<sup>52</sup> To verify this hypothesis, four different types of amino acids, including GLY, with low steric hindrance on the amine group, ALA, with a methyl group in the vicinity of the amine group, PRO, with a cyclic secondary amine, and LYS, with two primary amine groups, were selected for their study. For aqueous solutions of a single amino acid salt,



**Table 1** Molecular structure and chemical properties of different amino acids, and CO<sub>2</sub> capture capacity of the corresponding alkali salts

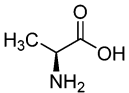
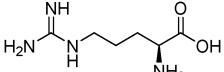
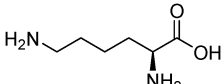
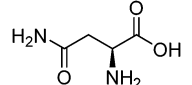
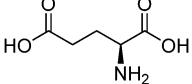
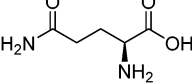
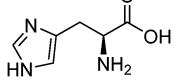
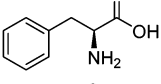
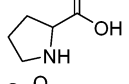
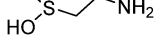
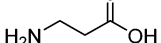
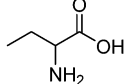
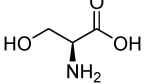
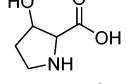
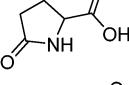
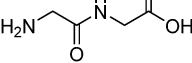
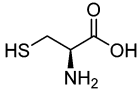
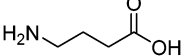
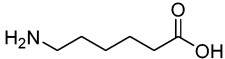
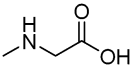
| Name                     | Structure                                                                           | pK <sub>a</sub> at <sup>a</sup><br>298.15 K | Loading<br>temperature<br>and pressure | Concentration | Absorption<br>kinetics <sup>c</sup><br>[K <sub>ov</sub> (S <sup>-1</sup> )] | Loading capacity <sup>b</sup><br>(mol <sub>CO<sub>2</sub></sub> mol <sub>AAS</sub> <sup>-1</sup> ) | Ref. |
|--------------------------|-------------------------------------------------------------------------------------|---------------------------------------------|----------------------------------------|---------------|-----------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|------|
| Alanine (ALA)            |    | 10.01                                       | 30 kPa<br>298–313 K                    | 2.5 M         | —                                                                           | 0.68                                                                                               | 41   |
| Arginine (ARG)           |    | 13.88 <sup>42</sup>                         | 15 kPa<br>298–333 K                    | 1 M           | 4203 (0.5 M)                                                                | 1.107                                                                                              | 15   |
| Lysine (LYS)             |    | 10.67                                       | 1 atm<br>298–313 K                     | 0.5–2.5 M     | —                                                                           | 0.17–1.063                                                                                         | 43   |
| Asparagine (ASN)         |    | 8.80                                        | 5–950 kPa<br>313–353 K                 | 8.5–34 wt%    | —                                                                           | 0.17–1.22                                                                                          | 44   |
| Glutamic acid (GLU)      |    | 9.98                                        | 25–225 kPa<br>293–313 K                | 2–10 wt%      | 1442 (0.5 M)                                                                | 0.3–1.6                                                                                            | 45   |
| Glutamine (GLN)          |    | 9.13                                        | 5–950 kPa<br>313–353 K                 | 9.2–36.8 wt%  | —                                                                           | 0.28–1.44                                                                                          | 44   |
| Glycine (GLY)            |    | 9.73                                        | 293–351 K<br>0.1–100 kPa               | 0.1–3 M       | —                                                                           | 0.1–1.4                                                                                            | 46   |
| Histidine (HIS)          |   | 9.17                                        | 313–353 K<br>154–4000 kPa              | 1–2 M         | —                                                                           | 0.6–2.4                                                                                            | 47   |
| Phenyl-alanine (PHE)     |  | 9.13                                        | 303–333 K<br>200–2500 Pa               | 10–25%        | —                                                                           | 0.2–1.9                                                                                            | 48   |
| Proline (PRO)            |  | 10.64                                       | 313–353 K<br>1–1000 kPa                | 7.5–27.4 wt%  | 7218 (0.5 M)                                                                | 0.24–1.16                                                                                          | 49   |
| Taurine (TAU)            |  | 11.1 <sup>50</sup>                          | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.573                                                                                              | 15   |
| β-Alanine (BALA)         |  | 10.24                                       | 313 K<br>15 kPa                        | 1 M           | 1499 (0.5 M)                                                                | 0.721                                                                                              | 15   |
| Aminobutyric acid (AABA) |  | 9.83                                        | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.728                                                                                              | 15   |
| Serine (SER)             |  | 9.15                                        | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.619                                                                                              | 15   |
| Hydroxy proline (HYPRO)  |  | —                                           | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.655                                                                                              | 15   |
| Pyroglutamic acid (PGA)  |  | —                                           | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.224                                                                                              | 15   |
| Diglycine (DIGLY)        |  | 10.864                                      | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.510                                                                                              | 15   |



Table 1 (continued)

| Name                       | Structure                                                                         | pK <sub>a</sub> at <sup>a</sup><br>298.15 K | Loading<br>temperature<br>and pressure | Concentration | Absorption<br>kinetics <sup>c</sup><br>[K <sub>ov</sub> (S <sup>-1</sup> )] | Loading capacity <sup>b</sup><br>(mol <sub>CO<sub>2</sub></sub> mol <sub>AAS</sub> <sup>-1</sup> ) | Ref. |
|----------------------------|-----------------------------------------------------------------------------------|---------------------------------------------|----------------------------------------|---------------|-----------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|------|
| Cysteine (CYS)             |  | 10.28                                       | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.485                                                                                              | 15   |
| γ-Aminobutyric acid (GABA) |  | 10.556                                      | 313 K<br>15 kPa                        | 1 M           | —                                                                           | 0.749                                                                                              | 15   |
| 6-Aminohexanoic acid       |  | 10.95                                       | 298 K<br>0–10 kPa                      | 0.5 M         | 1266                                                                        | —                                                                                                  | 51   |
| Sarcosine (NMGLY)          |  | 10.21                                       | 298 K<br>0–10 kPa                      | 0.5 M         | 2973                                                                        | —                                                                                                  | 51   |

<sup>a</sup> Relative to the most basic group in the amino acid. <sup>b</sup> The loading capacity means the maximum CO<sub>2</sub> capture capacity of the amino acid under the given conditions in each entry. <sup>c</sup> All the absorption kinetic data are taken from ref. 50.

the percentage of CO<sub>2</sub> captured as carbamate decreases with increasing steric bulk, with glycinate exhibiting the highest, and alaninate, with a methyl group on the alpha carbon, the lowest. Nevertheless, the absorption capacities were similar, about 0.58 mol<sub>CO<sub>2</sub></sub> mol<sub>AAS</sub><sup>-1</sup> for the three monoamine amino acids, and 0.74 mol<sub>CO<sub>2</sub></sub> mol<sub>AAS</sub><sup>-1</sup> for LYS. Interestingly, the blended mixture, containing combinations of different AAS, showed an absorption capacity of 0.91 mol<sub>CO<sub>2</sub></sub> mol<sub>AAS</sub><sup>-1</sup>, which is over 19% higher than any of the single component systems at the same amino group concentration. The authors attributed the enhancement to a synergistic effect of the structure and basicity properties of each component, although a deeper understanding of the role of each component is needed. Based on these findings, Liao further studied the employment of microalgal biomass as the precursor for a blended mixture of AAS for CO<sub>2</sub> capture.<sup>53</sup> The compositional analysis revealed that ALA, GLY, GLUA, aspartic acid (ASP), LYS, LEU, and PRO are the main amino acids with a total amino acid concentration of 0.592 M obtained from microalgal hydrolysis. Most importantly, the cyclic capacity obtained from this system is as high as 1.27 mol<sub>CO<sub>2</sub></sub> mol<sub>amine</sub><sup>-1</sup>, three times higher than the benchmark MEA solution.

A potential disadvantage of using an amino acid-based salt as an absorbent at high concentrations is the decreased solubility after CO<sub>2</sub> loading, as this leads to increased viscosity and consequently to higher energy input, as well as reactor clogging and fouling. On the other hand, if the captured CO<sub>2</sub> precipitates along with the amino acid salt, the equilibrium will be shifted towards the formation of carbamate, and thus higher CO<sub>2</sub> loading capacity can be achieved. In addition, the CO<sub>2</sub>-rich phase can be separated for stripping, while the CO<sub>2</sub>-lean phase can be recirculated directly to the capture reactor. Such a strategy might contribute to a reduction of the capital cost for the regeneration process. The first example of using an amino acid salt-based biphasic system for CO<sub>2</sub> capture was reported by Li's group.<sup>54</sup> In this study, aqueous solutions of one of five different amino acid salts were tested as the absorbents,

including ALA, ARG, LYS, SER, and ASP. After CO<sub>2</sub> bubbling, only ALA underwent a phase change, forming a clear phase at the top and a milky phase at the bottom (Fig. 9a–c). Further studies on the composition of these two phases were performed by NMR spectroscopy, and by using tetramethylammonium chloride as an internal standard, it was confirmed that 90% of the adsorbed CO<sub>2</sub> was concentrated in the milky phase in the form of NaHCO<sub>3</sub> and carbamate. Benefiting from the self-concentration phenomenon, the cyclic capacity reached 0.62 mol<sub>CO<sub>2</sub></sub> mol<sub>ALA</sub><sup>-1</sup>. With such a system, only the CO<sub>2</sub>-rich phase needed the stripping process for solvent regeneration, while the CO<sub>2</sub>-lean phase could be directly reused (Fig. 9a), thus reducing the energy consumption for the regeneration step.

Due to their high heat capacity, aqueous solutions always result in higher energy penalty during the regeneration process. The use of an organic solvent, such as ethanol, is advantageous because of the lower heat capacity and binding energy, thus, requiring less energy input during the CO<sub>2</sub> stripping process. Based on this consideration, Shen *et al.* developed a proline potassium (PROK)/ethanol phase-change system for CO<sub>2</sub> capture under post-combustion conditions.<sup>55</sup> Compared to the aqueous PROK solvent, the ethanol/PROK exhibited a more than four-fold higher absorption rate, reaching 18.06 kmol m<sup>-2</sup> s<sup>-1</sup>, which was confirmed to have benefited from the three-fold higher solubility of CO<sub>2</sub> in the ethanol solution. During CO<sub>2</sub> loading, the solution underwent a phase change, with the bottom phase enriched with 55–60% of the captured CO<sub>2</sub>, consisting of PRO carbamate, ethyl carbonate, and bicarbonate salts. To minimize solvent loss due to the low boiling point character of ethanol, Shen and co-workers reported in 2020 the alternative use of 2-methoxyethanol (EGME) and 2-ethoxyethanol (EGEE) as antisolvent to trigger the precipitation.<sup>56</sup> The authors suggested that a lower dielectric constant favors the precipitation of hydrophilic CO<sub>2</sub> captured products, and, consequently, the absorption capacity of both PROK and sarcosinate potassium (NMGLY-K)-based systems using EGME or EGEE solvent were enhanced by about 15–20% compared to their aqueous solutions. XRD and NMR analysis showed that 50–80%



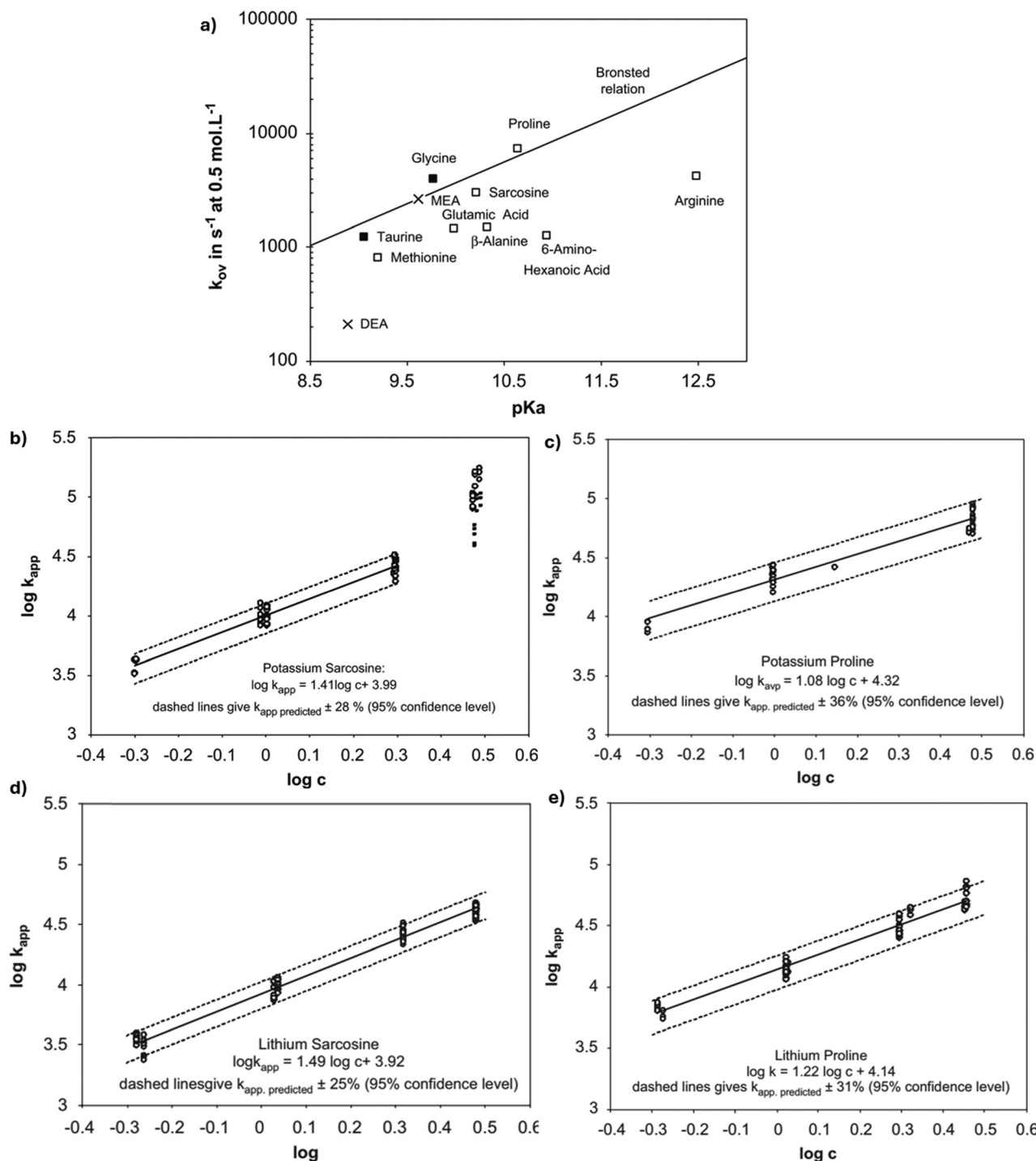
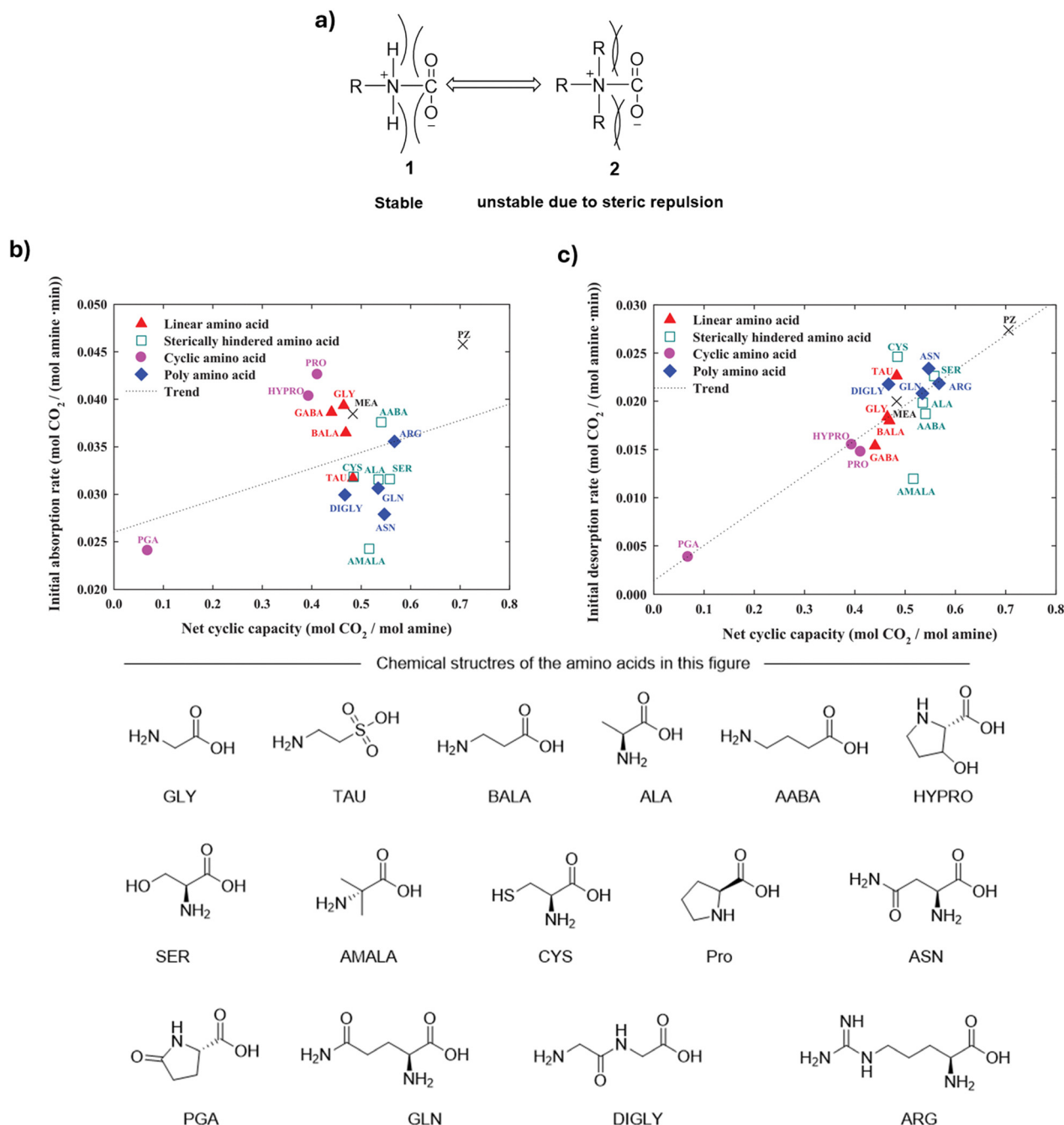


Fig. 7 (a)  $K_{ov}$  vs.  $pK_a$  for various potassium salts of amino acids; (b) and (c) results for ( $K_{app}$ , pseudo-first-order rate constant,  $S^{-1}$ ) as a function of the potassium concentration of (b) sarcosine, (c) proline. (d) and (e) Results for ( $K_{app}$ ) as a function of the lithium concentration of (d) sarcosine, (e) proline. Figures reproduced from ref. 51 with copyright permission.

of the captured  $CO_2$  is precipitated in the form of bicarbonate and carbamate. Impressively, the PROK/EGME system exhibited a very low energy penalty for the regeneration of 1.87–2.61 GJ per t  $CO_2$ , which is almost half the amount required for the benchmark MEA system, demonstrating the advantages of amino acid salt-based solvents for the  $CO_2$  capture applications.

A further improvement of the amino acid-based biphasic system was reported by Rahimpour and his colleagues in 2021.<sup>57</sup> Using potassium glycinate in combination with either *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), ethanol, or EGEE as the phase change solvent, all of the captured  $CO_2$  was concentrated in one phase while no bicarbonate or



**Fig. 8** (a) Illustration of the influence of the amino acid side chain on the stability of corresponding carbamate species; (b) the relationship of the net cyclic capacity and the initial absorption rate of different amino acid salts; (c) the relationship of the net cyclic capacity and the initial desorption rate of different amino acid salts. Figures reproduced from ref. 15 with copyright permission.

carbamate were detected in the  $\text{CO}_2$ -lean phase. Additionally, they observed that the  $\text{CO}_2$  absorption capacity exhibited a non-linear response to variations in co-solvent percentages. For example, with NMP as the co-solvent, the loading capacity initially decreased with increasing amount of co-solvent compared to the neat aqueous potassium glycinate solution, scoring the lowest value of  $0.60 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{AAS}}^{-1}$  at 10 wt% NMP. Further increasing the percentage of NMP resulted in an increased loading capacity, reaching the highest value of

$0.74 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{AAS}}^{-1}$  at 50 wt% NMP. The authors suggested that the lower loading capacity of the solvent resulting from co-solvent addition in the range 0–30 wt% as compared to neat aqueous solution is due to a less favorable carbamate hydrolysis to bicarbonate in the presence of the co-solvent, while a further increase of the amount of added co-solvent would promote phase separation and precipitation, consequently shifting the reaction equilibrium and enhancing the loading capacity accordingly. It is clear from the above examples that by



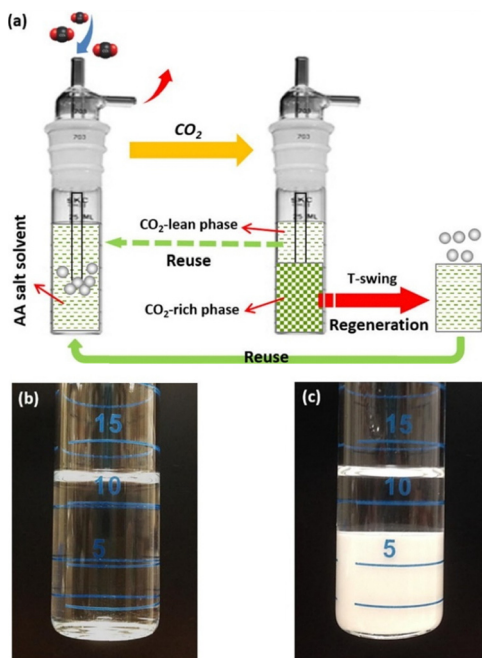


Fig. 9 (a) Illustration of the CO<sub>2</sub> capture and regeneration process with a biphasic system, (b) the homogenous amino acid salt solution before, and (c) after CO<sub>2</sub> loading, showing the formation of two phases. Reproduced from ref. 54 with copyright permission.

carefully choosing AAS and co-solvent, a biphasic system with higher CO<sub>2</sub> capture capacity and lower re-generation energy penalty can be achieved.

### 3.2. Amino acid-based ionic liquid as the absorbent for CO<sub>2</sub> capture

In addition to alkanolamines and amino acid salts, ionic liquids are another promising type of absorbent.<sup>58</sup> Like amino acid salts, ionic liquids exhibit high thermal stability, low volatility, and excellent CO<sub>2</sub> solubility.<sup>59</sup> Unfunctionalized ILs capture CO<sub>2</sub> by physical interaction and the absorption rate/capacity is very low, although low energy input is required for the regeneration.<sup>59b</sup> One common strategy to improve the absorption performance of ionic liquids is to functionalize the constituent cation or anion with amine groups, thus enabling the same chemical CO<sub>2</sub> absorption that occurs in amine-based systems *via* the formation of carbamate and bicarbonate species.

Among the functionalized ILs, AAILs have attracted considerable attention by the research community because they combine the advantages of both ILs and AAS. In 2015, Li and co-workers investigated the CO<sub>2</sub> capture ability of an aqueous solution of the amino acid-based ionic liquid (AAIL) featuring hydroxyethyl methyl imidazole as the hydrophilic cation and GLY as the anion (denoted as [C<sub>2</sub>OHmim][GLY]).<sup>60</sup> For comparison, solutions of MEA and sodium glycinate with the same concentration (0.4 M) were tested, and the results showed that the CO<sub>2</sub> loading capacities of MEA, sodium glycinate, and [C<sub>2</sub>OHmim][GLY] are 0.457, 0.26, and 0.575 mol<sub>CO<sub>2</sub></sub> mol<sub>absorbent</sub><sup>-1</sup> respectively, demonstrating the superior performance of the

AAIL. In addition, the latter shows higher stability compared to the other two absorbents after a multiple regeneration process under high O<sub>2</sub> concentration conditions. This demonstrates the high potential of this type of absorbents to overcome the disadvantages of amine-based solvents.

In 2014, Khanna and co-workers reported the application of a series of AAILs combining the butyl methyl imidazolium (BMIM)<sup>+</sup> cation with nine different amino acids. It should be noted that these studies were performed under moisture-free conditions using the lean AAILs. The loading capacity increased in the order ARG > LYS > HIS > MET > LEU > GLY > VAL > ALA > PRO (Table 2). The authors speculated that the lowest CO<sub>2</sub> loading capacity of PRO is due to the steric hindrance of its 5-membered ring, whereas the highest activity of AAILs based on ARG, LYS and HIS can be explained by the presence of an additional amine functional group in their side chains. According to the authors, the absorption as carbamate follows the 2:1 model (see Scheme 2b), rather than the 1:1 one. Noteworthy, it has been demonstrated that the CO<sub>2</sub> absorption capacity of ILs with amine-functionalized cations is lower than that of anion-functionalized ILs, which also include amino acid-based ILs, highlighting a further advantage of the use of AAILs for this application.

Comparing the behavior of different AAILs, it can be concluded that the CO<sub>2</sub> absorption capacity is mainly determined by the number of amine groups and the structure of the amino acid side chain (Table 2): the more amino groups, the more potential binding sites for CO<sub>2</sub> chemical sorption are present, which on the other hand, can be negatively affected by the bulkiness of the side chain, hindering the CO<sub>2</sub> access to the amine groups. Thus, in most of the reports on AAILs, ARG shows the highest absorption capacity, followed by LYS and HIS, regardless of the cation which was either 1-butyl-4-methyl pyridinium,<sup>61</sup> vinyl imidazolium, or butyl methyl imidazolium.<sup>62</sup> PRO was reported to be the least active amino acid among those without a second amino functionality, due to the high steric hindrance of the five-membered ring. An exception was reported by Dai and co-workers: [P<sub>4444</sub>][PRO] showed a higher capacity compared to [P<sub>4444</sub>][GLY] and [P<sub>4444</sub>][ALA] due to the lowest stability of the deprotonated dianion of PRO-carbamic acid, and thus the absorption is dominated by a 1:1 reaction mechanism.<sup>67</sup>

The values of the CO<sub>2</sub> loading capacities of different AAILs reported in the literature show that the cation also affects the performance, as well as the reaction mechanism. For example, Dai and co-workers systematically investigated the absorption mechanism of pure AAILs under moisture-free conditions.<sup>67</sup> In this study, AAILs were prepared using tetra-alkyl phosphonium cation and amino acid-derived anions, including, ALA, isoleucine (ILE), GLY, MET and PRO. Contrary to the 2:1 absorption model observed in Khanna's work,<sup>64</sup> they claimed that the 1:1 model dominates in all the cases, with carbamic acid as the main CO<sub>2</sub> absorption product, which was confirmed by IR and NMR studies. [P<sub>4444</sub>][PRO] (P<sub>4444</sub>, tetrabutylphosphonium cation) shows the highest absorption capacity of (0.91 mol<sub>CO<sub>2</sub></sub> mol<sub>IL</sub><sup>-1</sup>), followed by [P<sub>4444</sub>][GLY] (0.86 mol<sub>CO<sub>2</sub></sub> mol<sub>IL</sub><sup>-1</sup>), and [P<sub>4444</sub>][ALA]



Table 2 Reported CO<sub>2</sub> loading capacities with different amino acid based ILs

| Cation                 | Anion   | Temperature, pressure | Solvent         | CO <sub>2</sub> loading capacity [mol CO <sub>2</sub> per mol IL] | Ref. |
|------------------------|---------|-----------------------|-----------------|-------------------------------------------------------------------|------|
| [B <sub>4</sub> MPyr]  | [L-ARG] | 298 K, 0.2–6 bar      | Pure AAILs      | 0.097–0.613                                                       | 61   |
|                        | [L-LYS] |                       |                 | 0.097–0.554                                                       |      |
|                        | [L-HIS] |                       |                 | 0.062–0.524                                                       |      |
|                        | [L-TYR] |                       |                 | 0.056–0.487                                                       |      |
|                        | [GLY]   |                       |                 | 0.070–0.475                                                       |      |
|                        | [L-ALA] |                       |                 | 0.074–0.469                                                       |      |
|                        | [L-VAL] |                       |                 | 0.066–0.414                                                       |      |
|                        | [L-PRO] |                       |                 | 0.080–0.379                                                       |      |
| [VBIM]                 | [L-ARG] | 283–313 K, 0.2–4 bar  | Pure AAILs      | 0.061–0.990                                                       | 62   |
|                        | [L-LYS] |                       |                 | 0.053–0.761                                                       |      |
|                        | [L-HIS] |                       |                 | 0.034–0.768                                                       |      |
|                        | [GLY]   |                       |                 | 0.048–0.602                                                       |      |
|                        | [L-ALA] |                       |                 | 0.036–0.598                                                       |      |
|                        | [L-VAL] |                       |                 | 0.048–0.507                                                       |      |
|                        | [L-PRO] |                       |                 | 0.044–0.493                                                       |      |
|                        | [L-PRO] |                       |                 | 0.66–0.74                                                         |      |
| [CHO]                  | [GLY]   | 298 K, atm pressure   | 16 wt% in DMSO  | 0.86                                                              | 63   |
| [BMIM]                 | [ARG]   | 298 K, 2 bar          | Pure AAILs      | 0.62                                                              | 64   |
|                        | [LYS]   |                       |                 | 0.48                                                              |      |
|                        | [HIS]   |                       |                 | 0.45                                                              |      |
|                        | [MET]   |                       |                 | 0.42                                                              |      |
|                        | [LEU]   |                       |                 | 0.38                                                              |      |
|                        | [GLY]   |                       |                 | 0.38                                                              |      |
|                        | [VAL]   |                       |                 | 0.39                                                              |      |
|                        | [ALA]   |                       |                 | 0.39                                                              |      |
|                        | [PRO]   |                       |                 | 0.32                                                              |      |
|                        | [GLY]   | 303 K, 10 kPa         | 0.4 M in water  | 0.575                                                             | 60   |
|                        | [LYS]   | 295 K, 1 bar          | 50 wt% in water | 2.2                                                               | 60   |
|                        | [PRO]   | 308 K, 1 bar          | 50 wt% PEG2000  | 0.61                                                              | 65   |
| [C <sub>2</sub> OHmim] | [GLY]   | 298 K, 1 bar          | 50 wt% in DMSO  | 0.78                                                              | 66   |
|                        | [ALA]   |                       |                 | 0.79                                                              |      |
|                        | [SER]   |                       |                 | 0.61                                                              |      |
|                        | [PRO]   |                       |                 | 0.84                                                              |      |
|                        | [PHE]   |                       |                 | 0.70                                                              |      |
|                        | [SAR]   |                       |                 | 0.71                                                              |      |
|                        | [ALA]   |                       |                 | 0.77                                                              |      |
|                        | [ILE]   |                       |                 | 0.85                                                              |      |
|                        | [GLY]   |                       |                 | 0.86                                                              |      |
|                        | [MET]   |                       |                 | 0.93                                                              |      |
|                        | [PRO]   |                       |                 | 0.88                                                              |      |
| [P <sub>4444</sub> ]   | [ALA]   | 298 K, 1 bar          | Pure AAILs      | 0.77                                                              | 67   |
|                        | [ILE]   |                       |                 | 0.85                                                              |      |
|                        | [GLY]   |                       |                 | 0.86                                                              |      |
|                        | [MET]   |                       |                 | 0.93                                                              |      |
| [P <sub>66614</sub> ]  | [PRO]   | 298 K, 1 bar          | Pure AAILs      | 0.88                                                              |      |
|                        | [GLY]   |                       |                 | 0.97                                                              |      |
|                        | [MET]   |                       |                 | 0.99                                                              |      |
|                        | [PRO]   |                       |                 | 0.91                                                              |      |

(0.77 mol<sub>CO<sub>2</sub></sub> mol<sub>IL</sub><sup>−1</sup>). Calculations indicate that the deprotonated form of the PRO-carbamate dianion has a strong repulsion between the two carboxyl groups, making it less stable compared to the ALA-carbamate and GLY-carbamate dianions, and consequently, less carbamate is formed following the 2:1 model (Table 2). This result is in contrast to that reported by Khanna and co-workers,<sup>64</sup> who concluded that the [BMIM]-[PRO] exhibited the lowest capacity, demonstrating the important role of cations in determining the capture capacity. In another example, Riisager and co-workers analyzed the loading capacities of trihexyl(tetradecyl) ammonium lysinate [N<sub>66614</sub>][LYS] and trihexyl(tetradecyl) phosphonium lysinate [P<sub>66614</sub>][LYS], which reached 2.0 and 1.6 mol<sub>CO<sub>2</sub></sub> mol<sub>AAILs</sub><sup>−1</sup>, respectively.<sup>68</sup> The authors demonstrated that the basic carboxyl group of the amino acid acts as the catalyst for rapid CO<sub>2</sub> absorption, and in the case of [P<sub>66614</sub>][LYS], a strong hydrogen bond interaction between the formed carbamic acid and the carboxyl group of the amino acid inhibits the catalytic effect, whereas in the case of [N<sub>66614</sub>][LYS], the interaction is much

weaker, allowing the reaction to proceed in a stoichiometric manner (Fig. 10). Therefore, the above work demonstrates the importance of selecting the right cations when exploring new types of AAILs for CO<sub>2</sub> capture applications.

Choline (CHO) is naturally abundant and biodegradable, making it a potentially more environmentally friendly cation for AAILs compared to pyridine- and imidazole derivatives. In 2019, Bordiga and co-workers reported the synthesis of choline glycinate [CHO][GLY] and choline proline [CHO]-[PRO] AAILs from choline chloride, and their application in CO<sub>2</sub> capture.<sup>63</sup> In this study, the AAILs were diluted in dimethyl sulfoxide (DMSO) to overcome the problem of their high viscosity. Both [CHO][GLY] and [CHO][PRO] showed a CO<sub>2</sub> loading capacity of about 0.70–0.86 mol<sub>CO<sub>2</sub></sub> mol<sub>AAILs</sub><sup>−1</sup>, mostly in the form of carbamate (max. 0.5 mol<sub>CO<sub>2</sub></sub> mol<sub>AAILs</sub><sup>−1</sup>), and carbamic acid species (max. 1 mol<sub>CO<sub>2</sub></sub> mol<sub>AAILs</sub><sup>−1</sup>). The absorption mechanism was further confirmed by ATR-IR. For [CHO][GLY], the authors observed the formation of carbamate in the first step, and then, proton transfer occurred between the



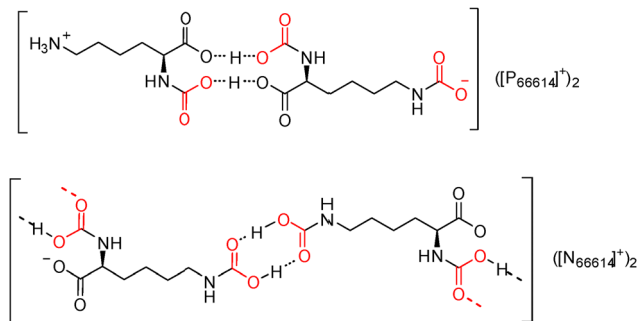


Fig. 10 Structure differences in the CO<sub>2</sub> captured adduct formed by [N<sub>66614</sub>][LYS] and [P<sub>66614</sub>][LYS] absorbents. Figure reprinted from ref. 68 with copyright permission.

zwitterionic GLY and the carbamates, forming carbamic acid and choline glycinate, as shown in Fig. 11a. In the case of [CHO][PRO], carbamic acid was formed directly from [CHO][PRO] via a 1:1 mechanism, in parallel with the formation of carbamates. However, the formation of carbamic acid from carbamate was excluded (Fig. 11b). This work also showed that the steps involved in CO<sub>2</sub> capture are different when using different anions, although the final CO<sub>2</sub> loading is similar. In continuation of this work, Bordiga and Bocchini further evaluated the CO<sub>2</sub> capacity of choline cation-based AAILs with different amino acids in cycling experiments, including PRO, GLY, ALA, SER, PHE, and NMGLY. They showed that [CHO][PRO] has the highest stability with only 15% of capacity loss after 10 cycles. Noteworthy, they have demonstrated that the [CHO][AA]-DMSO system requires a lower temperature (70–80 °C) for CO<sub>2</sub> desorption compared to the classical aqueous solution (over 100 °C).<sup>69</sup>

### 3.3. Blended mixtures of amino acids and other absorbents

Amino acid-based sorbents often have high viscosity compared to the traditional amine solvent, which results in increased resistance to fluid flow, requiring more pumping power and

potentially affecting the overall performance and efficiency. Although increasing the operating temperature can significantly reduce the viscosity in some cases, the energy required and the resulting reduction in CO<sub>2</sub>-absorption capacity cancels the benefits of using a pure amino acid-based solvent. Alternatively, blending the amino acids with other absorbents, such as amines, carbonates, and ILs, can provide a potential replacement for alkanolamine-based solvents. A good example is provided by the technology developed by Siemens,<sup>70</sup> also known as the PostCap<sup>TM</sup> process, in which the mixture of MEA, ammonia, and amino acid salts in aqueous solution is used as absorbent. With the PostCap<sup>TM</sup> absorbent mixture, less than 20% of MEA was lost during one year of operation. Another study reported by Tan and co-workers employed piperazine (PZ) (15 wt%), diethylenetriamine (DETA) (15 wt%), and sodium aliphatic diamine sulphonate (NaADS) (10 wt%) as a blend for CO<sub>2</sub> capture.<sup>71</sup> The results show that, although the viscosity of this mixture is 1.48 times higher than that of the PZ (15 wt%)/DETA (15 wt%) mixture, similar CO<sub>2</sub> absorption rate and capacity were achieved. In this case, an advantage of the amino acid addition is a 7.3% reduction in regeneration energy. Furthermore, the addition of an amino acid to the blend considerably slowed down the degradation rate of the absorbents, as the dissolved oxygen is half compared to the PZ (15 wt%)/DETA (15 wt%) mixture. Similarly, blending AAILs and conventional alkanolamines provides efficient CO<sub>2</sub> capture reagents. For example, Zhang and co-workers demonstrated that the mixture of MDEA and [N<sub>1111</sub>][GLY] has a higher absorption rate compared to MDEA solvent.<sup>72</sup> Zhou's group applied [N<sub>1111</sub>][GLY] as a promoter for the absorbent 2-amino-2-methyl-1-propanol (AMP), which showed a comparable acceleration effect to PZ, MEA, and DEA.<sup>73</sup>

In a very recent work by Zhang and co-workers, a novel absorbent formulation with significant industrial potential was developed.<sup>74</sup> The optimal absorbent composition containing 5.02 wt% [N<sub>1111</sub>][Gly] + 17.06 wt% PZ + 20.00 wt% MDEA + 57.92 wt%

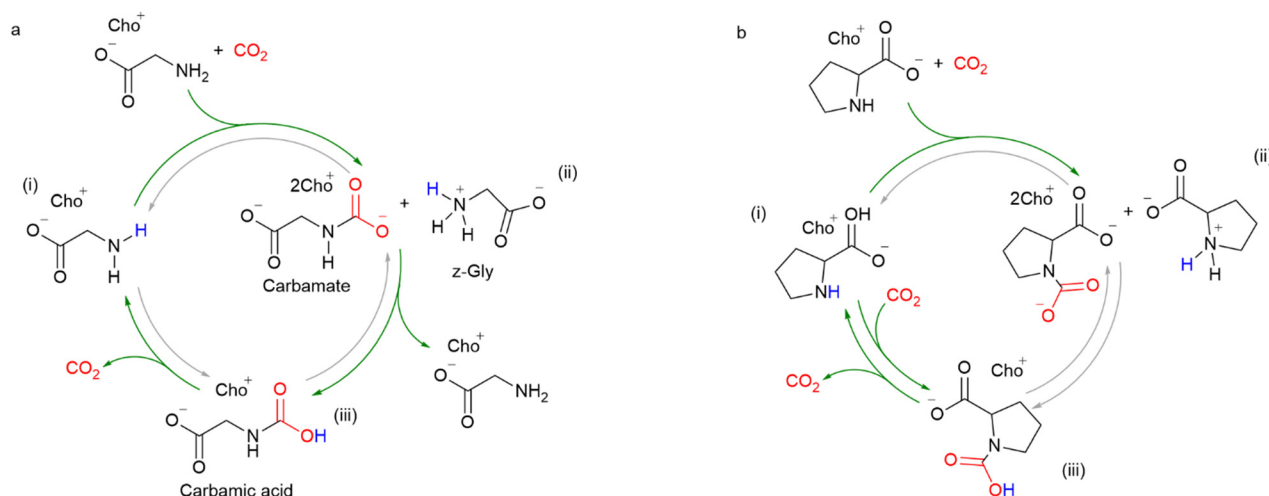


Fig. 11 Confirmed reaction pathway by ATR-IR (green arrow) and reaction pathway not observed (grey arrow) of (a) [CHO][GLY] and (b) [CHO][PRO] for CO<sub>2</sub> capture process. Reproduced from ref. 63 with copyright permission.

H<sub>2</sub>O, noted as IPMH, demonstrated superior capture capacity compared to a conventional 30 wt% MEA solution. More notably, it exhibited a 22.7% higher regeneration efficiency and a 30% reduction in regeneration energy consumption. The authors employed a potentiometric method to identify the absorbed species and found that in the IPMH system, 70% of the captured CO<sub>2</sub> existed as bicarbonate, compared to only 10% in the MEA solution, which explains the lower regeneration energy requirement, as bicarbonate is more readily desorbed than carbamate.

Aqueous K<sub>2</sub>CO<sub>3</sub> has been demonstrated as another alternative absorbent for CO<sub>2</sub> capture due to its high thermal stability and low regeneration energy. However, the sluggish absorption rate hinders its practical large-scale application. In response, various promoters, such as piperazine, amine, and amino acids,<sup>75</sup> have been added to improve the capture performance. Among these additives, amino acids are superior to the other two in terms of their thermal stability and low vapor pressure. In 2013, Stevens and co-workers showed that the addition of either GLY, NMGLY, or PRO to a 30 wt% K<sub>2</sub>CO<sub>3</sub> aqueous solution with a final amino acid concentration of 1 M, increased the total CO<sub>2</sub> uptake rates by 22, 45, and 14 times, respectively.<sup>76</sup> In addition, they also demonstrated that the promoting effect of amino acids bearing either a primary or secondary amino group is comparable to that of common alkanolamines having a primary (in the case of MEA), or secondary amine (in the case of DEA), respectively. Hu and co-workers further demonstrated that the amino acid-based promoters are more effective than amines in boosting the CO<sub>2</sub> desorption rate and cyclic capacity of K<sub>2</sub>CO<sub>3</sub> solutions.<sup>77</sup>

Non-functionalized ILs are also promising absorbents for CO<sub>2</sub> capture *via* a physical process, albeit with low capacity and high viscosity. On the other hand, the high solubility of CO<sub>2</sub> in ILs can be advantageously exploited by combining it with the chemical sorption exhibited by amines and amino acids, Zhang and coworkers evaluated the use of sodium glycinate (GLY-Na) and butyl methyl imidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) as the absorbents and demonstrated that the blend has a better resistance to oxidative degradation compared to the benchmark MEA solution. In addition, the regeneration energy can be reduced compared to the pure sodium glycinate solution.<sup>2a</sup>

In summary, amino acids with a non-protonated amino group can serve as effective absorbents. The cation can be either a simple metal ion, such as potassium, or more complex ones, *i.e.*, ammonium, phosphonium, imidazolium, to obtain an amino acid-based ionic liquid. Absorbents based on such ionic species exhibit low volatility and minimal solvent loss compared to those based on amines. In addition, their biocompatibility, biodegradability, comparatively high absorption capacity, and efficient capture kinetics make amino acid-based sorbents a promising alternative to traditional alkanolamine sorbents. On the other hand, the high viscosity of AAILs, which further increases after CO<sub>2</sub> absorption, would increase the energy penalty, and thus hinder their practical application. The use of blends, combining AA/AAIL and other sorbents, and biphasic systems have been investigated to mitigate this drawback. However, a reactive CO<sub>2</sub> capture system does not require

the CO<sub>2</sub> regeneration step. Instead, the captured CO<sub>2</sub> is used directly for hydrogenation, forming formic acid/methanol while simultaneously releasing the absorbents, potentially circumventing the viscosity drawbacks. In the following section, the recent progress on the reactive capture of CO<sub>2</sub> to methanol and formic acid will be discussed.

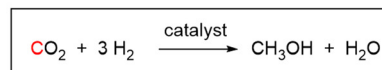
## 4. Conventional amine-based CO<sub>2</sub> transformation to methanol and formates

### 4.1. Basis principles for CO<sub>2</sub> hydrogenation to methanol

On an industrial scale, CH<sub>3</sub>OH is produced from fossil fuel-derived synthesis gas with added CO<sub>2</sub> (CO/H<sub>2</sub>, and CO<sub>2</sub>) over a heterogeneous catalyst comprising copper and zinc oxides, supported on alumina (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) at high pressure and elevated temperature (> 200 °C).<sup>78</sup> Alternatively, CH<sub>3</sub>OH can be obtained by hydrogenation of CO<sub>2</sub> with hydrogen, preferably derived from water splitting using renewable energy.<sup>79</sup> Both heterogeneous<sup>80</sup> and homogeneous metal catalysts<sup>81</sup> are being developed to catalyze this process. Homogeneous molecularly defined catalysts, while far from being ready for practical application, usually operate under milder conditions and are prone to easier structural modification in search of better efficiency and stability. A perusal of the literature shows that such catalysts can be divided into two broad categories, depending on whether they operate in a neutral or slightly acidic medium, or in a basic one. In the first case, HCOOH, formed by the initial reduction of CO<sub>2</sub>, is converted into a formate ester through reaction with an alcohol, used as the solvent, or in catalytic amount to facilitate the reaction in its initial stages. The alcohol can be CH<sub>3</sub>OH itself, thus self-breeding the reaction. Hydrogenation of the ester affords CH<sub>3</sub>OH and regenerates the assisting alcohol.<sup>82</sup>

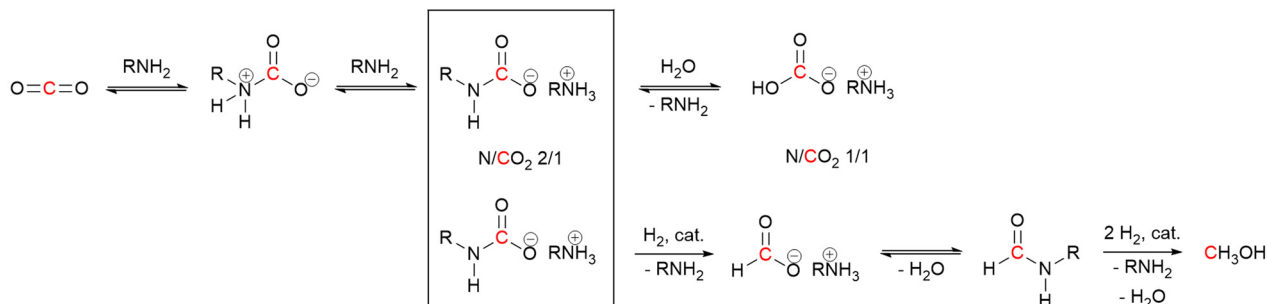
Base-compatible catalysts should be better suited for hydrogenation directly in the basic media used to scrub CO<sub>2</sub>, from flue gas or air. Thus, these catalysts have been more extensively explored for combined CO<sub>2</sub> capture and hydrogenation. Here, the species present in solution following CO<sub>2</sub> capture and the experimental conditions required for the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH depend on the nature of the absorbent, either an inorganic base, such as an alkali hydroxide, or an organic nitrogen base; and the solvent, either water or a water-lean system. In the presence of an organic solvent, a further distinction must be made between an alcohol or a non-protic solvent. Regardless of the reaction medium and the possible reaction intermediates, the hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH generates one equivalent of H<sub>2</sub>O and therefore the consequences of its presence must be considered, especially at higher conversions. Scheme 3 gives an overview of the species which are formed in solution after CO<sub>2</sub> has been captured, depending on the type of base used. Only those cases are illustrated here that were combined with *in situ* homogeneously catalyzed hydrogenation of the captured CO<sub>2</sub> to CH<sub>3</sub>OH. For a more general and in depth description of the various species



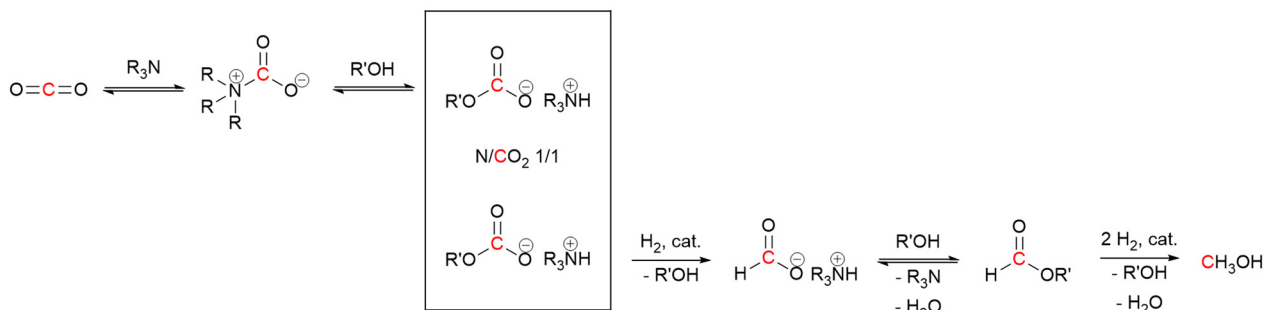
CO<sub>2</sub> capture and hydrogenation

CO<sub>2</sub> capture \_\_\_\_\_ CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH \_\_\_\_\_

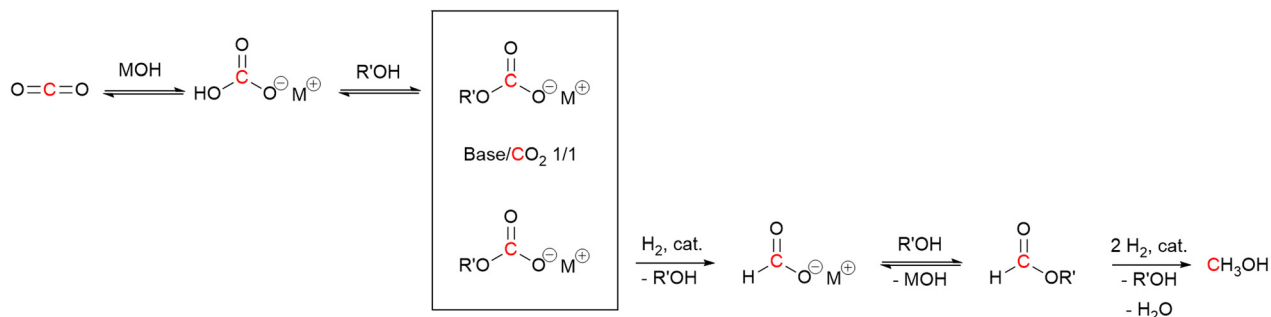
a. with 1°/2° amines \_\_\_\_\_ via formamide \_\_\_\_\_



b. with 3° amines \_\_\_\_\_ via ester \_\_\_\_\_



c. with alkali hydroxide \_\_\_\_\_ via ester \_\_\_\_\_



**Scheme 3** CO<sub>2</sub> capture with amines, either 1°/2° (path a) or 3° (path b), and alkali hydroxides MOH (path c) and integrated metal-catalyzed hydrogenation to formate and methanol. Depending on reaction conditions, formation of methanol can proceed through hydrogenolysis of formamide or ester.

formed in solution following CO<sub>2</sub> capture with amines, their <sup>1</sup>H and <sup>13</sup>C NMR identification, the relative equilibria and how these are influenced by intrinsic properties (Lewis and Brønsted

basicity) and concentration of the amine, by the nature of the solvent, the partial CO<sub>2</sub> pressure and the reaction temperature, the reader is referred to the articles by Kortunov and co-workers.<sup>83</sup>



As mentioned in the introduction, large-scale post-combustion CO<sub>2</sub> separation processes are mainly based on the deployment of aqueous solutions of amines and aminoalcohols such as MEA, DEA, and MDEA.<sup>84</sup> Amines react with CO<sub>2</sub> according to the equilibria depicted in Scheme 3, where a distinction is made between primary/secondary (path a) and tertiary amines (path b). When a primary/secondary amine is used, the nucleophilic amine attacks the electrophilic carbon atom of the CO<sub>2</sub> molecule affording the zwitterionic of the resultant carbamic acid, which is then rapidly deprotonated by a second mole of free amine, acting as a Lewis base, to give a more stable ammonium carbamate (Scheme 3, path a).<sup>85</sup> Under these conditions, the amine/CO<sub>2</sub> ratio is 2:1, *i.e.*, the maximum absorption capacity is 0.5 moles of CO<sub>2</sub> per mole of amine. In the presence of water, the ammonium carbamate can be hydrolyzed, releasing the free amine, to afford the corresponding bicarbonate. In this case, the amine/CO<sub>2</sub> ratio is 1:1, meaning that one mole of CO<sub>2</sub> has been captured per mole of amine. The ratio between carbamate and (bi)carbonate products is influenced by various parameters, for instance the CO<sub>2</sub> up-taking, the Brønsted and Lewis basicity of the amine, and its concentration (*i.e.*, the amine/water stoichiometry). In the presence of a primary/secondary amine, a stepwise pathway to CH<sub>3</sub>OH can be envisioned. The first step is the metal-catalyzed reduction of the captured CO<sub>2</sub> to ammonium formate. Ammonium formate can then be thermally dehydrated to formamide, whose further metal-catalyzed hydrogenolysis yields CH<sub>3</sub>OH and releases the amine for the next capture/hydrogenation cycle.<sup>86</sup>

Unlike primary and secondary amines, tertiary amines cannot form stable carbamates with CO<sub>2</sub> in aqueous or non-aqueous solutions because they lack a transferable proton. They are weak Lewis bases but can be relatively strong Brønsted bases, thus promoting the formation of ammonium bicarbonate, where water acts as the nucleophile (Scheme 3, path b). When an alcohol is used as the solvent, an alkyl carbonate is the prevailing product. In this case, after the first hydrogenation step, further reduction to CH<sub>3</sub>OH can occur by hydrogenolysis of the formate ester, in equilibrium with ammonium formate due to the high alcohol concentration and despite the elevated temperature and the basic conditions.<sup>87</sup> Because of the increasing steric bulk, tertiary amines have kinetically lower efficiencies for CO<sub>2</sub> capture. However, reduction of formate esters should be energetically more favorable than the reduction of formamides, which explains the interest in this approach.<sup>82a</sup>

Due to their high CO<sub>2</sub>-binding affinities, alkali hydroxides are better suited to capture CO<sub>2</sub> at the lower concentration present in air (direct air capture).<sup>88</sup> If an alcohol is used in which both the metal hydroxide and the product of CO<sub>2</sub> capture, the metal alkyl carbonate, are soluble, then this approach can be advantageously exploited to convert CO<sub>2</sub> to CH<sub>3</sub>OH, again through the hydrogenation of an intermediate formate ester (Scheme 3, path c).<sup>89</sup> Key contributions demonstrating the feasibility of the approach described in Scheme 3 are due to Sanford,<sup>13</sup> Milstein,<sup>8</sup> Ding,<sup>90</sup> Prakash<sup>7a,91</sup> and Wass.<sup>92</sup>

Chart 1 illustrates the catalysts and amines they used. The TONs in CH<sub>3</sub>OH are relative to single experiments under the reported conditions. There has been a proliferation of studies documenting efforts to improve solvent (physisorption) and base (chemisorption) CO<sub>2</sub> capture capability, homogeneous catalyst efficiency, productivity and selectivity, and recyclability of active components. Excellent reviews have summarized these studies.<sup>6b,93</sup> Our discussion is not intended to be comprehensive and will focus on selected examples which rely on the use of 1°/2° (poly)amines because primary amino groups are mainly responsible for CO<sub>2</sub> chemisorption in amino acid-based capturing media. Besides, a perusal of the literature shows that Ru-MACHO-BH **1** has been used in several capturing media under a variety of conditions. The steric and electronic properties of this catalyst can be modulated by changing the substituents at the phosphorus and nitrogen of the pincer ligand (Chart 2). In few cases, similar PNP complexes, in which ruthenium was replaced by iron<sup>7a,94</sup> and manganese<sup>94a,95</sup> were tested as well under comparable conditions, allowing a direct comparison with Ru-MACHO-BH. Therefore, as an introduction for amino acid-aided CO<sub>2</sub> capture and following catalytic hydrogenation, we would like to highlight some general trends which emerged from these studies. Here, Ru-MACHO-BH serves as an example how reaction conditions, absorbent medium, and catalyst structure influence the outcome of the integrated CO<sub>2</sub> capture and hydrogenation and how all these parameters can be modified to ease product separation and absorbent/catalyst recyclability.

#### 4.2. Influence of catalyst structure on the efficiency and selectivity in CO<sub>2</sub> hydrogenation to methanol

Ru-MACHO-BH **1** belongs to the family of catalysts that realize their activity through metal–ligand cooperativity,<sup>96</sup> due to the presence of a PNP ligand bearing an –NH group coordinated to ruthenium, which not only defines the steric and electronic properties of the metal center, but also contributes to substrate activation and facilitates catalysis. The –NH group can hydrogen-bond to the incoming substrate,<sup>97</sup> *e.g.* CO<sub>2</sub>, carbamate, and formamide, enhancing its electrophilicity and properly orienting it for the transfer of the metal hydride to the electrophilic carbon, and with the reduced product stabilizing it.<sup>98</sup> This pathway may not require prior coordination of the substrate to the metal and proceeds *via* a so-called outer-sphere mechanism.<sup>99</sup> Cooperativity may also contribute to the activation of H<sub>2</sub>. In a basic environment, the –HN group in the MACHO family catalyst precursor (Chart 2) can be deprotonated with the elimination of HX (X = BH<sub>4</sub><sup>–</sup>, Cl<sup>–</sup>, Br<sup>–</sup>), producing a 16 electron metal-amido species (Scheme 4).<sup>100</sup> Such species are able to heterolytically split H<sub>2</sub>, which adds to the metal–nitrogen bond, thereby regenerating the metal–hydride. Here, the ligand nitrogen acts as an internal base. A reduction in catalyst activity when the hydrogen on the nitrogen is replaced by an alkyl group suggests that ligand–metal cooperativity may indeed be operative, allowing an otherwise energetically more demanding transformation. Alternatively, if a vacant coordination site on the catalyst becomes available, H<sub>2</sub> can coordinate to the metal forming a  $\sigma$ -adduct (Scheme 4). An exogenous base can then abstract a



| Capturing Medium<br>(Absorbent, base, solvent)                                                                                                         | Catalyst  | Conditions                                                                                                  | TON <sub>max</sub><br>(CH <sub>3</sub> OH) | Process              | Reference        |
|--------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|-------------------------------------------------------------------------------------------------------------|--------------------------------------------|----------------------|------------------|
| NHMe <sub>2</sub> , K <sub>3</sub> PO <sub>4</sub> , THF                                                                                               |           | CO <sub>2</sub> 2.5 bar, H <sub>2</sub> 50 bars<br>95 °C, 18 h + 155 °C 36 h                                | 550                                        | One pot<br>T ramp    | Sanford, Ref. 13 |
| <br>1, 1.7 μmol                                                                                                                                        |           |                                                                                                             |                                            |                      |                  |
|                                                                                                                                                        |           | 1. CO <sub>2</sub> 1 bar, 150 °C, 24 h<br>2. H <sub>2</sub> 60 bars, 135 °C, 72 h                           | 21                                         | One pot<br>two steps | Milstein, Ref. 8 |
| Cs <sub>2</sub> CO <sub>3</sub> , <i>t</i> BuOK, DMSO                                                                                                  |           |                                                                                                             |                                            |                      |                  |
| <br>2, 25 μmol                                                                                                                                         |           |                                                                                                             |                                            |                      |                  |
|                                                                                                                                                        |           | 1. CO <sub>2</sub> / H <sub>2</sub> (1 / 1) 70 bars<br>120 °C, 40 h<br>2. H <sub>2</sub> 50 bars, 160°, 1 h | 3600                                       | One pot<br>two steps | Ding, Ref. 90    |
| <i>t</i> BuOK, THF                                                                                                                                     |           |                                                                                                             |                                            |                      |                  |
| <br>1a, 2.5 μmol                                                                                                                                       |           |                                                                                                             |                                            |                      |                  |
| PEHA, Triglyme                                                                                                                                         | 1, 1 μmol | CO <sub>2</sub> / H <sub>2</sub> (1 / 3) 75 bars<br>145 °C, 244 h                                           | 9900                                       | One pot<br>one step  | Prakash, Ref. 91 |
|                                                                                                                                                        |           |                                                                                                             |                                            |                      |                  |
| NH/ <i>i</i> Pr <sub>2</sub> , NaOEt, toluene                                                                                                          |           | CO <sub>2</sub> /H <sub>2</sub> 1/3 40 bars<br>180 °C, 2 h                                                  | 8900                                       | One pot<br>one step  | Wass, Ref. 92    |
|                                                                                                                                                        |           |                                                                                                             |                                            |                      |                  |
| <br>3, 0.05 μmol                                                                                                                                       |           |                                                                                                             |                                            |                      |                  |
| <br>PEHA = H <sub>2</sub> N-CH <sub>2</sub> -(CH <sub>2</sub> -NH-CH <sub>2</sub> -CH <sub>2</sub> -NH) <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub> |           |                                                                                                             |                                            |                      |                  |

**Chart 1** Seminal studies demonstrating the feasibility of combined amine-based CO<sub>2</sub> capture and homogeneously metal-catalysed hydrogenation to CH<sub>3</sub>OH.

|           |           |          |
|-----------|-----------|----------|
|           |           |          |
| <b>1</b>  | <b>4</b>  | <b>5</b> |
| R         | R         |          |
| R'        | R'        |          |
| X         |           |          |
| <b>1a</b> | <b>4a</b> |          |
| R         | R         |          |
| R'        | R'        |          |
| X         |           |          |
| <b>1b</b> |           |          |
| R         |           |          |
| R'        |           |          |
| X         |           |          |
| <b>1c</b> |           |          |
| R         |           |          |
| R'        |           |          |
| X         |           |          |
| <b>1d</b> |           |          |
| R         |           |          |
| R'        |           |          |
| X         |           |          |
| <b>1e</b> |           |          |
| R         |           |          |
| R'        |           |          |
| X         |           |          |

**Chart 2** Range of catalysts belonging to the aliphatic PNP MACHO-type family which have been applied to the combined amine-based CO<sub>2</sub> capture and homogeneously catalyzed hydrogenation to HCOO<sup>-</sup>/CH<sub>3</sub>OH.

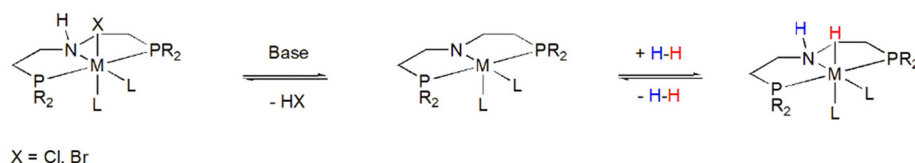
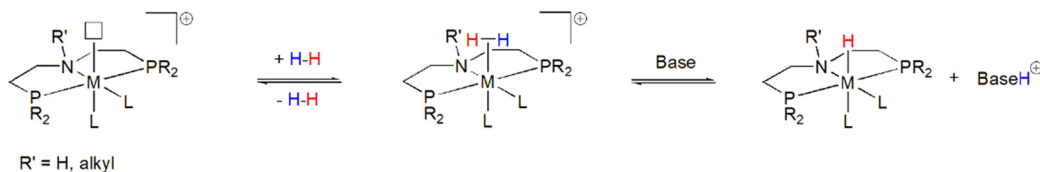
proton from the coordinated dihydrogen and regenerate the metal hydride. This reactivity is also open to catalyst **1e** (Chart 2), which, because its ligand nitrogen is methylated, cannot engage in ligand-metal cooperativity but is still an efficient hydrogenation catalyst.<sup>101</sup> Metal-ligand cooperativity is also possible for catalysts such as **2** (Chart 1), whose pincer ligands contain a pyridyl group that can undergo dearomatization upon deprotonation of a distal carbon (Scheme 4).<sup>102</sup>

In her seminal work reporting the first example of the combined use of a secondary amine Me<sub>2</sub>NH as a capturing agent for CO<sub>2</sub> and Ru-MACHO-BH as a catalyst for the hydrogenation of the resulting carbamate to methanol *via* formamide, Sanford highlighted some key issues that need to be tackled when applying this approach.<sup>13</sup> Scheme 4 illustrates the main steps and the simplified underlying catalytic cycle, as

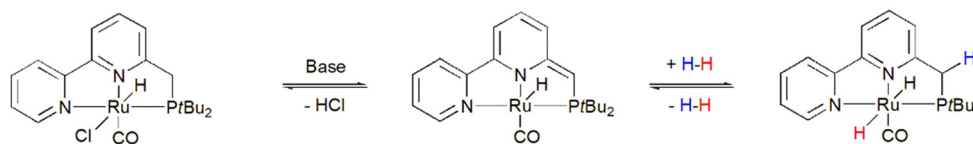


H<sub>2</sub> activation

Metal-Ligand Cooperation - 1,2 addition

H<sub>2</sub>  $\sigma$ -adduct deprotonation

Metal-Ligand Cooperation - Aromatization / Dearomatization

Scheme 4 Pathways accessible to catalysts in Charts 1 and 2 for heterolytic H<sub>2</sub> activation.

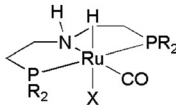
proposed later on by Prakash and co-workers based on mechanistic studies.<sup>91</sup> The reaction was carried out in THF, in the presence of an exogenous base, K<sub>3</sub>PO<sub>4</sub>, without which no catalyst turnover was observed. A temperature ramp from 95 (18 h) to 155 (36 h) °C was applied to optimize the methanol yield while minimizing catalyst decomposition at higher temperature: by applying 2.5 bar CO<sub>2</sub> and 50 bar H<sub>2</sub>, a maximum TON of 550 in CH<sub>3</sub>OH and 1870 in formate/formamide were achieved. The first product, formate, likely arises from preferential reduction of free CO<sub>2</sub> in equilibrium with dimethylammonium dimethylcarbamate, due to the higher electrophilicity of the former. The hydrogenation of CO<sub>2</sub> to HCOOH is an endergonic process which becomes thermodynamically more favorable in the presence of dimethylamine which stabilizes HCOOH as dimethylammonium formate, thus shifting the equilibrium. This reaction is favored at low temperatures while hydrogenolysis of dimethyl formamide is the most energetically demanding step among those which comprise the reduction of captured CO<sub>2</sub> to CH<sub>3</sub>OH and requires high hydrogen pressures. The temperature ramp proposed by Sanford represents the first solution to accommodate these contrasting requirements.<sup>13</sup> 155 °C defines the temperature at which Ru-MACHO-BH decomposition sets in: if the use of a smaller amount of catalyst warrants higher TONs, extension of reaction time to improve CH<sub>3</sub>OH yields should be performed at lower temperature.

Subsequently, Prakash and colleagues pioneered the direct capture of CO<sub>2</sub> from the atmosphere and its subsequent hydrogenation to CH<sub>3</sub>OH using the same catalyst.<sup>7a</sup> This innovative method represented a significant advancement over the previous system, as it employed pentaethylenhexamine, PEHA

(Chart 1), as the capturing agent. This was due to the high nitrogen content and high boiling point of PEHA, which rendered it a more suitable alternative to Me<sub>2</sub>NH. This choice is advantageous for substantial CO<sub>2</sub> absorption, as evidenced by a high CO<sub>2</sub>/amine and subsequent CH<sub>3</sub>OH/mole amine ratio. PEHA is both affordable and readily available. Additionally, its combination with a high-boiling solvent is imperative for facilitating CH<sub>3</sub>OH separation and recovery while minimizing loss of the capturing phase. Through the optimization of reaction conditions, a TON of 1200 in CH<sub>3</sub>OH was achieved in a single experiment using Ru-MACHO-BH<sub>4</sub> (20 μmol), PEHA (5.1 mmol), and triglyme (10 mL) at 145 °C for 200 hours with 75 bars of CO<sub>2</sub>/H<sub>2</sub> (1/9). It was demonstrated that the TON could be elevated to 2150 through the execution of five recycling experiments, each with a duration of 40 hours, under conditions that were otherwise identical. Following each experiment, the produced CH<sub>3</sub>OH and H<sub>2</sub>O were distilled off, and the remaining solution, containing the catalyst and amine, was pressurized again. A number of aspects concerning the catalytic system were highlighted, too.<sup>91</sup> In the absence of amine, traces of CH<sub>3</sub>OH were detected. However, when comparing different amines, higher CH<sub>3</sub>OH yields were obtained with 1,2-diamines, combining a primary and a secondary amine, or polyamines containing this structural motif as repeating unit. Furthermore, the CH<sub>3</sub>OH yield increased with higher amine content (up to a certain extent) and in the presence of a stronger base such as K<sub>3</sub>PO<sub>4</sub>. However, this was not a prerequisite for CH<sub>3</sub>OH formation, contrasting with Sanford's system.<sup>103</sup> The gas phase analysis revealed the presence of 0.2–0.4% CO after the reaction. This amount was found to be reduced by decreasing

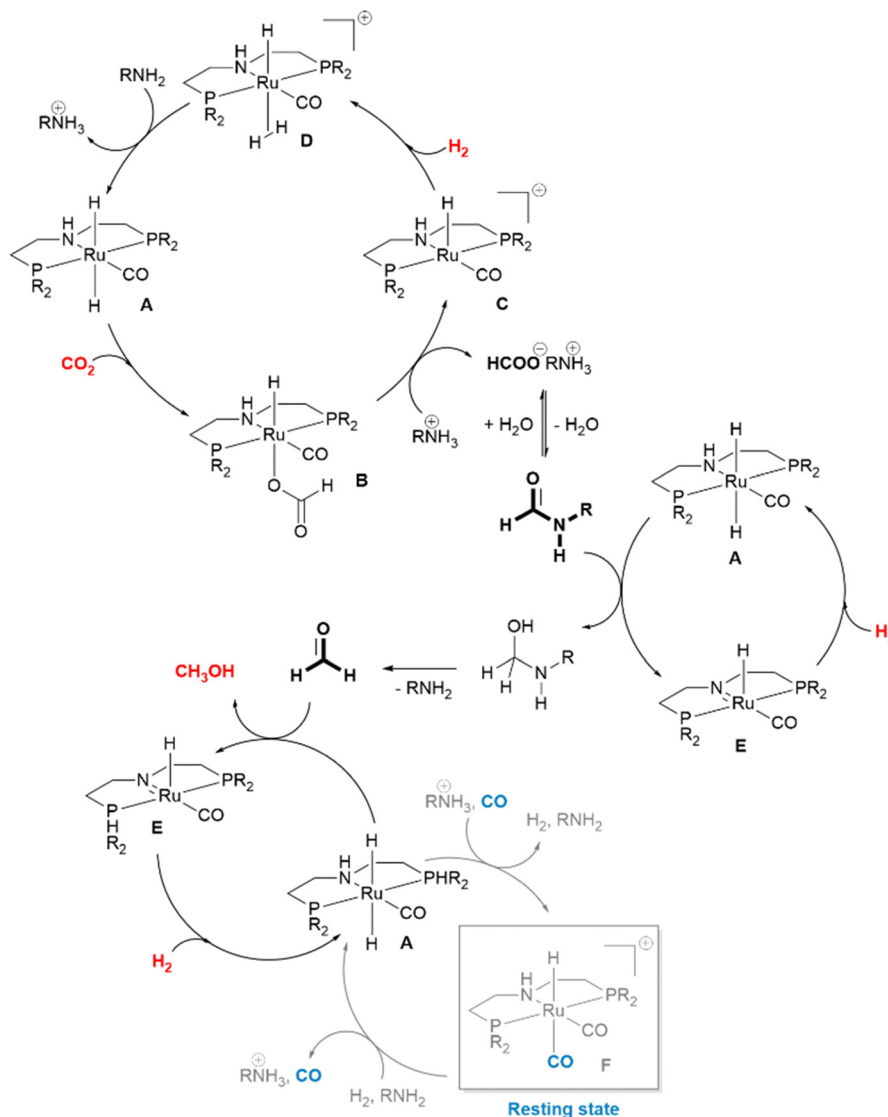


**Table 3** Influence on product distribution of catalyst structure within the Ru-MACHO-type family. Adapted from ref. 14b

|                                                                                                                                                                                                                  |  |  |  |  |  |                                                                                    |             |                 |   |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|--|--|--|------------------------------------------------------------------------------------|-------------|-----------------|---|
| $\text{PEHA} + \text{CO}_2 + \text{H}_2 \xrightarrow[\text{Triglyme, 145}^\circ\text{C, 40h}]{[\text{Ru}], \text{K}_3\text{PO}_4} \text{formate} + \text{formamide} + \text{CH}_3\text{OH} + \text{H}_2\text{O}$ |  |  |  |  |  |  | <b>1</b>    | R               | X |
|                                                                                                                                                                                                                  |  |  |  |  |  | <b>1a</b>                                                                          | Ph          | BH <sub>4</sub> |   |
|                                                                                                                                                                                                                  |  |  |  |  |  | <b>1b</b>                                                                          | Ph          | Cl              |   |
|                                                                                                                                                                                                                  |  |  |  |  |  | <b>1c</b>                                                                          | <i>i</i> Pr | Cl              |   |
|                                                                                                                                                                                                                  |  |  |  |  |  | <b>1d</b>                                                                          | Cy          | Cl              |   |
|                                                                                                                                                                                                                  |  |  |  |  |  | <b>1d</b>                                                                          | <i>t</i> Bu | Cl              |   |

| Entry          | Catalyst  | Formate <sup>a</sup> (mmol) | Formamide <sup>a</sup> (mmol) | CH <sub>3</sub> OH <sup>a</sup> (mmol) | CO <sup>b</sup> (%) | TON formate + formamide | TON CH <sub>3</sub> OH |
|----------------|-----------|-----------------------------|-------------------------------|----------------------------------------|---------------------|-------------------------|------------------------|
| 1 <sup>c</sup> | <b>1</b>  | 1.2                         | 8.0                           | 10.5                                   | 0.21                | 920                     | 1050                   |
| 2              | <b>1a</b> | 1.6                         | 8.1                           | 10.4                                   | 0.21                | 970                     | 1040                   |
| 3              | <b>1b</b> | 1.1                         | 22.6                          | 3.2                                    | nd                  | 2370                    | 320                    |
| 4              | <b>1c</b> | 1.0                         | 14.7                          | 0.5                                    | nd                  | 1570                    | 50                     |
| 5              | <b>1d</b> | 1.6                         | 17.5                          | nd                                     | nd                  | 1910                    | 0                      |

Reaction conditions: PEHA 5.1 mmol; catalyst 10 μmol; K<sub>3</sub>PO<sub>4</sub> 1 mmol; triglyme 10 mL; CO<sub>2</sub>/H<sub>2</sub> 1/3 75 bars; 145 °C, 40 h. <sup>a</sup> Yields were determined from <sup>1</sup>H NMR spectra using 1,3,5-trimethoxybenzene (TMB) as internal standard. <sup>b</sup> CO detection limit 0.099%. <sup>c</sup> No K<sub>3</sub>PO<sub>4</sub> was used. Adapted from ref. 91.

**Scheme 5** Proposed general mechanism for the amine-assisted hydrogenation of CO<sub>2</sub> to methanol promoted by Ru-MACHO-type catalysts. Metal-mediated formaldehyde decarbonylation is a possible source of CO, explaining the formation of the observed resting state F. Adapted from ref. 91.

the CO<sub>2</sub>/H<sub>2</sub> ratio from 1/3 to 1/9, while maintaining a total pressure of 75 bars and a reaction temperature of 145 °C. Moreover, an increase in the H<sub>2</sub> pressure, concomitant with a decrease in the CO<sub>2</sub> pressure, has been observed to enhance the conversion of formamide to CH<sub>3</sub>OH, under conditions of constant total pressure.<sup>91</sup> As illustrated in Table 3, the yields of formate, formamide, and methanol were affected by modifying the structure of Ru-MACHO-BH **1** by replacing the phenyl substituents at phosphorus with more electron-donating alkyl groups.<sup>91</sup> Catalyst **1a**, with a chloride in place of BH<sub>4</sub><sup>−</sup>, is also included for a more consistent comparison with **1b** (iPr), **1c** (Cy) and **1d** (tBu). While all catalysts promoted the formation of formate and formamide, which accumulates in solution, hydrogenation of the latter to CH<sub>3</sub>OH proceeded more efficiently with catalysts **1** and **1a** with TON of 1050 and 1040, respectively (Table 3, entries 1 and 2), while was modest with **1b** (TON 320, Table 3, entry 3) and poor with **1c** (TON 50, Table 3, entry 4). No CH<sub>3</sub>OH was detected with **1d** (Table 3, entry 5). Noteworthy, when comparing the performance of **1/1a** and **1b**, it appears that the latter is overall a better catalyst for the reduction of CO<sub>2</sub> to formate and thus for the build-up of formamide. Table 3 also shows that the formation of higher amounts of CH<sub>3</sub>OH is accompanied by small amounts (0.22%) of CO. Scheme 5 illustrates the catalytic cycle underlying the amine-assisted CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH, as proposed by Prakash and co-workers based on their mechanistic studies. According to the authors, CO likely arises from decarbonylation of formaldehyde, which is the product of formamide hydrogenolysis, and the reduction of which finally leads to CH<sub>3</sub>OH.<sup>91</sup> CO can act as a poison to the catalysts because of the formation of cationic dicarbonyl species **F** (Scheme 5), which were identified as resting states with all the catalysts tested. **F** can be brought back into the catalytic cycle if dihydrogen is able to displace the extra carbonyl ligand. The latter is more labile in the resting state arising from **1/1a** explaining the better performance of **1/1a** in reducing CO<sub>2</sub> to the CH<sub>3</sub>OH level. CO detachment becomes more and more difficult with catalysts **1b–d** which, because of the more electron-donating substituents at phosphorus, possess a metal center that binds CO more tightly through enhanced back-donation. Therefore, even trace amounts of CO can turn **F** into a dead-end, so that less and less of the active catalyst is available for the reduction of formamide to CH<sub>3</sub>OH, as shown by the data in Table 3. Therefore, within this family of catalysts, Ru-MACHO-BH appears to be the catalyst of choice if the captured CO<sub>2</sub> is to be hydrogenated to CH<sub>3</sub>OH. Its robustness was demonstrated by Prakash and co-workers in a long term experiment lasting more than 10 days, when with just 1 μmol of **1**, 5.1 mmol PEHA in triglyme, 10 mL, at 145 °C, 75 bars CO<sub>2</sub>/H<sub>2</sub> 1/3, a total of 9.9 mmol MeOH was obtained, corresponding to a TON of 9900.<sup>91</sup>

Another interesting aspect emerges from a comparison of the performance of Ru-MACHO **1a** with that of its congener **1e** wherein the hydrogen at the ligand nitrogen has been replaced by a methyl group, thereby precluding the possibility of metal–ligand cooperativity. It has been shown that under comparable conditions, **1e** exhibited a level of efficacy in promoting the hydrogenation of the PEHA-captured CO<sub>2</sub> to formate, that was

comparable to that of **1a**. However, in contrast to **1a**, **1e** was unable to catalyze the hydrogenolysis of formamide to CH<sub>3</sub>OH.<sup>7a</sup> A similar behavior has been observed by Weiss and co-workers applying catalyst **3** (Chart 1). Under the conditions outlined in Chart 1, this catalyst has achieved one of the highest TONs, 8900, in the diisopropylamine-aided hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH.<sup>92</sup> Analogous to Ru-MACHO, this catalyst can function through metal–ligand cooperativity. If the amino group at the ligand bears not one but two methyl groups, then the hydrogenation stops at the level of formate, resulting in the exclusive formation of formamide. These two examples support the notion that while for the base-promoted metal-catalyzed hydrogenation of CO<sub>2</sub> to formate two catalytic pathways are open and equally productive, either metal-centred<sup>99</sup> or ligand-assisted, for the metal-catalyzed hydrogenolysis to CH<sub>3</sub>OH the latter seems mandatory.

Pincer PNP complexes<sup>33</sup> **4** and {FeHBr(CO)}[HN(CH<sub>2</sub>CH<sub>2</sub>PiPr<sub>2</sub>)<sub>2</sub>]**5** (Chart 2) based on more abundant and inexpensive metals, were also tested for the integrative amine-assisted CO<sub>2</sub> capture and hydrogenation to CH<sub>3</sub>OH.<sup>94a</sup> After capture with an aqueous solution of PEHA, CO<sub>2</sub> was hydrogenated in a biphasic 2-MTHF/water system. Both catalysts were as efficient as the Ru-MACHO one for the hydrogenation of the captured CO<sub>2</sub> to formate, but only small amounts or no methanol were obtained in the hydrogenation of the accumulated formamide with **4** and **5**, respectively. The reasons behind the poor performance of **4** and **5** were highlighted in two dedicated studies by Prakash<sup>95a</sup> and Bernskoetter,<sup>94b</sup> respectively. It was demonstrated that, when using morpholine as the amine, the two catalysts can promote both the reduction of CO<sub>2</sub> to formyl morpholine and the hydrogenolysis of the latter to methanol, if the two steps are operated separately. If the two steps are to be combined, then residual CO<sub>2</sub> must be discharged after the first step, because CO<sub>2</sub> negatively impacts the subsequent formamide hydrogenolysis. This obviously represents an obstacle for the implementation of practical CO<sub>2</sub> capture and utilization processes. At the molecular level, for both systems, a metal–formato species, similar to the ruthenium–formato species **B** in Scheme 5, was identified as the main catalyst resting state. The strong coordination of the formato ligand, further enhanced by hydrogen bonding with the –NH group of the PNP ligand, renders these species stable. As shown in Scheme 5 for the analogous Ru-species **B**, formate must be displaced to allow H<sub>2</sub> coordination and activation for further catalytic turnover and this process is assisted by the amine. Once the amine is “trapped” as formamide, collapse of the resting state proceeds through de-insertion of CO<sub>2</sub> and reconstitution of the metal–hydride bond. This process is reversible and is influenced by CO<sub>2</sub> in solution. The addition of LiOTf, in combination with DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene, to assist and ease the expulsion of the formato ligand in the formamide hydrogenation step promoted by the iron catalyst **5** improved the yield of methanol, yet was not enough to mitigate the CO<sub>2</sub> effect to realize a one-batch process.<sup>94b</sup> The use of a Lewis acid was not tested in the report by Prakash using the manganese catalyst **4**.<sup>95a</sup> Although this might be beneficial, as recently highlighted by Leitner and co-workers, in a mechanistic



investigation of the **4** Mn-promoted hydrogenation of CO<sub>2</sub> to methanol assisted by alcohols, through the intermediate formation of formate esters.<sup>9b</sup>

The issues that limit the efficiency of catalysts **4** and **5** and prevent their successful application in the combined amine-aided CO<sub>2</sub> capture and straightforward hydrogenation of the captured CO<sub>2</sub> to methanol apparently do not affect catalyst [FeCl<sub>2</sub>{κ<sup>3</sup>-HC(pz)<sub>3</sub>}] **6**, reported by Martins and co-workers (Scheme 6).<sup>104</sup> The catalyst was prepared by reaction of FeCl<sub>2</sub> with hydrotris(1-pyrazolyl)methane, HC(pz)<sub>3</sub>, in water affording a pentacoordinated 16 electrons Fe(II) complex. The authors reported that in the presence of neat PEHA, without any added solvent, the catalyst (15 μmol) promoted the hydrogenation of CO<sub>2</sub> (CO<sub>2</sub>/H<sub>2</sub> 1/3 75 atm) at 80 °C in a one-pot one-step process, achieving a remarkable TON in CH<sub>3</sub>OH of 2387 over 36 hours. After the reaction, a biphasic mixture was obtained consisting of an upper pale-yellow solution and a milky lower phase, probably containing unconverted formate and formamide, although no mention as to their possible detection and quantification is made. The two phases were separated and CH<sub>3</sub>OH recovered by simple distillation from the upper one. No recycling experiments for assessment of amine and catalyst reusability were described and the authors did not report mechanistic investigations to elucidate the structure of the active catalytic species in solution. Instead, they postulated that the activity of the catalyst could be ascribed to the presence of a free coordination site at the metal for any incoming substrate and a basic hemilabile scorpionate ligand. Thus, catalytically active hydride species would be generated through ligand-promoted heterolytic cleavage of coordinated dihydrogen and the protonated ligand could function as proton shuttle around the catalytic cycle. This hypothesis has been recently supported by DFT calculations.<sup>105</sup>

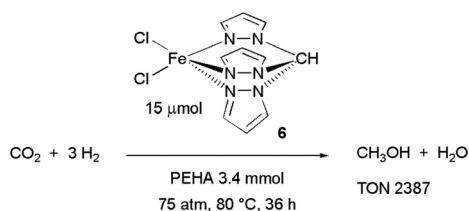
The selected studies reported so far showed how the hydrogenation of the captured CO<sub>2</sub> to CH<sub>3</sub>OH is affected by the catalyst structure and key reaction parameters such as pressure and temperature. For practical applications, the ease of product separation from the reaction medium and the recyclability of both the homogeneous catalyst and capturing amine are other important issues which need to be solved, too. In this respect, the use of high boiling solvents and ionic liquids, the application of biphasic systems to separate or immobilize the organometallic active species in a hydrophobic solvent as the catalyst phase, and the use of polymeric amines or the immobilization of amines on solid support have been described to address

such issues and will be briefly summarized in the following section.

#### 4.3. Influence of base and solvent on the CO<sub>2</sub> hydrogenation to methanol

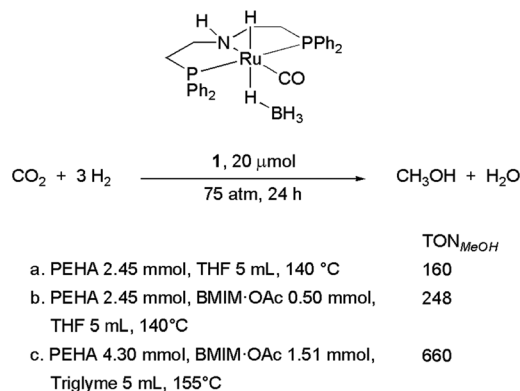
Ionic liquids, which are composed of ions with a melting point below 100 °C by definition, are thermally stable solvents with very low vapor pressure. For these reasons, they have been extensively investigated as CO<sub>2</sub> capturing agents.<sup>106</sup> Solubility of CO<sub>2</sub> in ionic liquids can be modulated through proper choice and combination of the cation and the anion, although it is primarily affected by the anion. Tailored ionic liquids, modified by the introduction of functional groups, such as amino groups, on either the anion or the cation, can boost their CO<sub>2</sub> sorption capacity through chemisorption.<sup>107</sup> Relevant to the present discussion, their use as reaction medium, bare or in combination with another solvent, has proved to be beneficial to the catalytic hydrogenation of CO<sub>2</sub> in some cases.<sup>108</sup> In fact, in the metal-catalyzed hydrogenation of CO<sub>2</sub>, proper solvents, akin to formate salt formation, contribute to formic acid stabilization (thermodynamic drive) *via* hydrogen bonding and ionic interactions. Solvent stabilization of formic acid and formate salts increases in the order: ethers < alcohols < water < ionic liquid. Indeed, the application of imidazolium-based ionic liquids in the hydrogenation of CO<sub>2</sub> using homogeneous ruthenium<sup>12,109</sup> and iridium<sup>110</sup> catalysts led to excellent productivities for formic acid formation.

Recently, Prakash and co-workers have demonstrated the positive effect that the addition of the ionic liquid 1-butyl-3-methylimidazolium acetate (BMIM·OAc) has on the amount of CH<sub>3</sub>OH accessible through the Ru-MACHO-BH **1** catalyzed hydrogenation of CO<sub>2</sub>, 4.96 mmol, TON 248, (1 20 μmol; PEHA 2.45 mmol, BMIM·OAc 0.5 mmol; THF 5 mL; CO<sub>2</sub>/H<sub>2</sub> 1/3 75 bars; 140 °C, 24 h) compared to the use of the sole polyamine PEHA, 3.20 mmol, TON 160, under otherwise identical conditions (Scheme 7, conditions b and a, respectively).<sup>111</sup> After the first explorative experiments, the CH<sub>3</sub>OH yield, and catalyst productivity could be further improved to 13.2 mmol and TON 660, respectively through proper choice and amount of ionic liquid, solvent, amine and adjustment of reaction conditions (Scheme 7, conditions c). A few aspects of this work are worth mentioning: as to the anion in the BMIM-based ionic liquid composition, acetate outperformed bromide and chloride, while in the presence of hydroxide, comparable amounts of CH<sub>3</sub>OH as to the acetate were obtained. However, in the latter case large quantities of formate were obtained, suggesting that hydroxide negatively affects the further reduction to methanol. The reaction could be performed in the neat ionic liquid; however, the addition of a solvent to mitigate viscosity issues following CO<sub>2</sub> capture proved beneficial. Among the tested solvents, triglyme performed best. Although no recycling experiments were described, the high boiling point of this solvent, in combination with the ionic liquid, should facilitate CH<sub>3</sub>OH separation and recovery of capturing medium and catalyst. Increasing the amount of PEHA increased the amount of CH<sub>3</sub>OH. The manganese catalyst **4** was also active, although



**Scheme 6** Amine-aided hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH promoted by an iron(II)-C-scorpionate catalyst.





**Scheme 7** Polyamine-assisted Ru-MACHO-BH catalyzed hydrogenation of CO<sub>2</sub> to methanol: influence of ionic liquid 1-butyl-3-methylimidazolium acetate BMIM·OAc.

to a lower extent than **1**, in the combined CO<sub>2</sub> capture and hydrogenation to CH<sub>3</sub>OH. According to the authors, this is likely due to the cation BMIM acting as Lewis acid, thus favoring the release of formate from a Mn-formate species for subsequent dihydrogen activation and catalyst turnover.

In the interest of enhancing recyclability, the development of a biphasic system that facilitates the segregation of reaction components, catalysts, absorbents, and products into distinct phases is of significant importance. Conventionally, aqueous solutions of amines or alkanolamines have been employed for the purpose of removing carbon dioxide from industrial gas streams. In contrast, homogeneous metal catalysts, unless specifically engineered to enhance hydrophilicity, exhibit preferential solubility in organic solvents. This disparity has been strategically capitalized upon by Prakash and colleagues, who have devised a recyclable system for the tandem capture of CO<sub>2</sub> in water and its subsequent hydrogenation to MeOH, as depicted in Fig. 12.<sup>94a</sup> Here, CO<sub>2</sub> was captured by exposing an aqueous solution of the amine at room temperature either to an atmosphere of pure CO<sub>2</sub> at a constant pressure of 1 psi or to synthetic air containing a CO<sub>2</sub> concentration of 408 ppm. CO<sub>2</sub> was captured both as carbamate and carbonate/bicarbonate. Among the tested (poly)amines, PEHA offered the best trade-off between the amount of captured CO<sub>2</sub> (0.43 mmol of CO<sub>2</sub> per

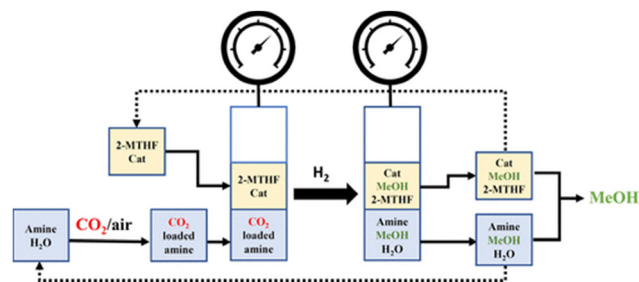
mol of N atom) and CH<sub>3</sub>OH yield. Using Ru-MACHO-BH **1**, 10 μmol, in a Me-THF/H<sub>2</sub>O biphasic mixture containing 11 mmol of absorbed CO<sub>2</sub>, after 72 h at 145 °C under 70 bars H<sub>2</sub>, TON of 231 in HCOO<sup>−</sup>/formamide and 520 in CH<sub>3</sub>OH (yield 47%) were achieved, even though the presence of water as a co-solvent might negatively affect ammonium formate dehydration to formamide. CH<sub>3</sub>OH, which partitioned between the two phases, was recovered by distillation, after which both the catalyst and the amine could be recycled through phase separation. After hydrogenation, it was established that, within the detection limits of <sup>31</sup>P NMR, no catalyst had leached into the aqueous phase. Therefore, the organic phase was separated, and, after removal of volatiles, the catalyst reused four times, with only minimal decrease of TON in subsequent applications, likely due to minute catalyst loss after each work up.

The use of polymeric amines or amines chemically grafted on fumed silica suspended in an organic solvent has also been explored as a mean to ease their recycling. PEI600 (CAS No. 25987-06-8, average *M<sub>w</sub>* ~ 800, average *M<sub>n</sub>* ~ 600) is a branched polyethylenimine containing primary, secondary, and tertiary amino groups. With PEI600 (1.5 mmol N) and Ru-MACHO-BH **1**, 0.05% as to PEI nitrogen content, under optimized conditions, CO<sub>2</sub>/H<sub>2</sub> 1/3 80 bars, THF, 150 °C, 100 h, a maximum catalyst TON of 689 in CH<sub>3</sub>OH was achieved. After the reaction, the polymeric amine could be recovered by simple filtration.<sup>112</sup>

Alternatively, polyamines were immobilized on a solid support and the functionalized support was used neat for CO<sub>2</sub> capture. More specifically, polyethylenimines were either physically impregnated on or covalently bound to fused silica. The CO<sub>2</sub> loading capacity was directly correlated to the number of nitrogen atoms per gram of solid supported amine (SSA). The physically impregnated SSA afforded better yield in CH<sub>3</sub>OH than the chemically grafted ones, but this could be directly correlated to the concentration of amines leaching in the organic solvent for the former materials. Among the tested supported amines, the covalently attached SSA, obtained by reacting trimethoxysilylpropyl-modified polyethylenimine (*M<sub>w</sub>* 1500–1800) with fused silica, was selected owing to its high leaching resistance and amine content. However, under optimized conditions, 500 mg of the SSA, Ru-MACHO-BH **1** 10 μmol, THF 5 mL, CO<sub>2</sub>/H<sub>2</sub> 1/3 80 bars, 145 °C, 40 h, a maximum TON of just 90 in CH<sub>3</sub>OH was achieved, although the possibility of both SSA and catalyst recovery and reuse was demonstrated.<sup>113</sup>

#### 4.4. Basic principles in CO<sub>2</sub> hydrogenation to formate/formic acid

So far, we have described catalytic homogeneous systems which warrant access to CH<sub>3</sub>OH and, as such, are obviously competent for the reduction of CO<sub>2</sub> to formate as well. Formic acid is an important bulk chemical in itself, the global market of which has reached around 750 thousand tons in 2022. Formic acid and its salts find applications in animal forage, grass silaging, leather tanning, and antifreezing,<sup>114</sup> and in the synthesis of a range of products including dyes and finishes, drilling fluids, natural rubber and food additives. The production of



**Fig. 12** Schematic representation of a biphasic system for CO<sub>2</sub> capture from air using an amine aqueous solution and hydrogenation of the captured CO<sub>2</sub> to MeOH through combination of the absorbing aqueous solution with an organic phase containing the homogeneous hydrogenation catalyst. Reproduced with permission from ref. 94a.



formic acid on an industrial scale is mainly based on a two-stage process which comprises first the carbonylation of methanol to afford methyl formate, and then hydrolysis of the later. The by-product methanol is recycled back to the first step. Free formic acid can also be obtained from its salts, mainly sodium formate and calcium formate. The acidolysis is normally carried out with sulfuric acid or phosphoric acid. The atom economy of the process is obviously poor because of the formation of calcium salts as by-product. For this reason, the industrial scale of this process is quite limited.

A greener route to formic acid is based on the hydrogenation of CO<sub>2</sub>, using green hydrogen, promoted by metal catalysts. Relevant to the current discussion, a plethora of homogenous catalysts, based mainly on noble metals such as iridium and ruthenium, have been described<sup>115</sup> which are competent for such transformation, although examples which demonstrate the possibility to use non-precious metals have also been reported.<sup>116</sup> These catalysts have been studied especially in the contest of a hydrogen economy where formic acid is intended as a sustainable storage medium and liquid vector for hydrogen, as it contains 4.4 wt% H<sub>2</sub> and its volumetric storage density is 53 g H<sub>2</sub> per L.

In the discussion so far, it has been shown that while catalysts which operate through metal–ligand cooperativity have so far proved better suited for converting CO<sub>2</sub> to CH<sub>3</sub>OH, metal–ligand cooperativity is not mandatory if amine-aided CO<sub>2</sub> hydrogenation is intended to stop at the formate level. Lower temperatures can and should then be applied as the hydrogenation of CO<sub>2</sub> to formate in the presence of a base becomes an exergonic process, the equilibrium of which can be further shifted towards the products by applying high hydrogen pressures. The produced ammonium formate can be thermally cleaved to afford free HCOOH and recover the amine. A process based on this approach has been developed at BASF which relies on the use of [Ru(H)<sub>2</sub>(PnBu<sub>3</sub>)<sub>4</sub>] and a tertiary amine in alcohol.<sup>117</sup> The formic acid–amine complex is thermally dissociated at 150 °C and recovered through distillation under reduced pressure.

Tertiary amines are commonly used for this purpose because formate salts of primary and secondary amines are thermally dehydrated to formamide at higher temperatures. Therefore, a profitable use of amino acids to capture CO<sub>2</sub> and aid its subsequent metal-catalysed hydrogenation to formate should preferentially involve a direct application of the amino acid formate solution as, for example, the implementation of a “hydrogen battery” (*vide infra*), where following metal-catalysed H<sub>2</sub> release from formate, CO<sub>2</sub> is retained by the amine in the “spent battery” which can then be recharged through hydrogenation of the retained CO<sub>2</sub> promoted by the same catalyst.<sup>118</sup> This would have the added advantage that a separation step to remove CO<sub>2</sub> before feeding H<sub>2</sub> into a PEM fuel cell would not be necessary.

#### 4.5. Recent examples of reactive CO<sub>2</sub> capture to formates

Here we would like to highlight a few selected examples which, because of the use of 1°/2° amines to capture CO<sub>2</sub> and aid its further metal-catalysed hydrogenation to formate and the use of aqueous solutions as reaction medium, can serve to

highlight some key issues related to this transformation which are relevant to the use of amino acids as well.

He and co-workers provided the first demonstration that CO<sub>2</sub>, captured by PEI 600 in methanol as ammonium carbamate and alkylcarbonate, could be directly hydrogenated *in situ* with a RhCl<sub>3</sub>·3H<sub>2</sub>O/PPH<sub>2</sub>Cy system in CH<sub>3</sub>OH, providing the corresponding ammonium formate with a TON as high as 852.<sup>119</sup>

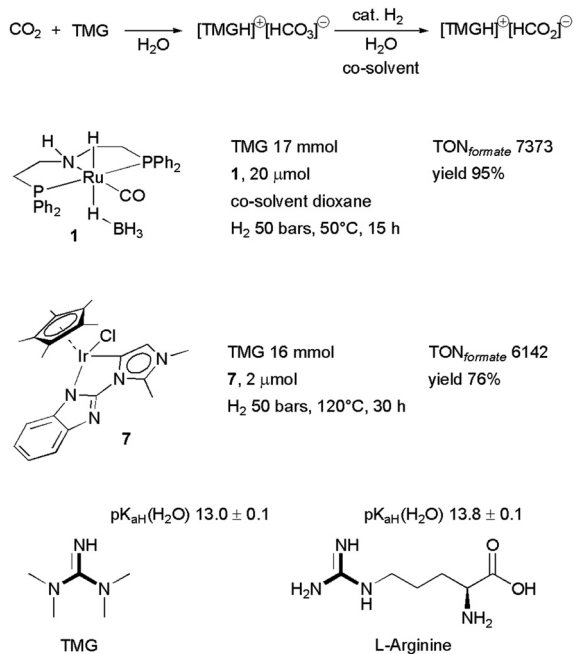
Prakash and co-workers investigated the capturing ability of various amines in aqueous media and the hydrogenation of the captured CO<sub>2</sub> to formate promoted by Ru-MACHO-BH. CO<sub>2</sub> was bubbled through the amine aqueous solutions at room temperature and then an organic co-solvent such as THF or dioxane was added to improve catalyst solubility for the subsequent hydrogenation.<sup>120</sup> Superbases such as 1,1,3,3-tetramethylguanidine TMG and 1,4-diazabicyclo[2.2.2]octane DABCO proved particularly efficient for both CO<sub>2</sub> capture and hydrogenation of the *in situ* formed bicarbonate/carbonate. As with ammonium carbamate, evidence of whether hydrogenation proceeds through hydride transfer from the catalytic active species to a negatively charged bicarbonate species or free CO<sub>2</sub> in equilibrium with the latter is lacking.<sup>36b</sup>

With TMG, 0.92 mmol of CO<sub>2</sub> per mmol of base were captured as bicarbonate/carbonate. When using 17 mmol TMG, in an aqueous/dioxane solution, Ru-MACHO-BH 1 20 μmol, H<sub>2</sub> 50 bar, 50 °C, for 15 hours, a TON as high as 7375 was achieved, corresponding to a 95% yield in formate as to the captured CO<sub>2</sub> (Scheme 8).<sup>120</sup> In the same study, the authors reported the implementation of a biphasic water/Me-THF system for catalyst recovery and recycling, the optimization of which was however realised using the tertiary amine DABCO.<sup>87</sup>

TMG was likewise used as CO<sub>2</sub> capturing agent in combination with a water-soluble iridium catalyst bearing a chelating N-heterocyclic carbene 7, Scheme 8, which therefore did not require the use of an organic co-solvent.<sup>122</sup> Notably, the catalyst was found to be air-stable and could be handled without rigorous exclusion of air also in solution. When using 16 mmol TMG in water, 7.2 μmol, H<sub>2</sub> 50 bar, 120 °C, for 30 hours, a TON of 6142 was achieved, corresponding to a 76% yield in formate as to the captured CO<sub>2</sub> (Scheme 8). Interestingly, a guanidino group is present in the basic side chain of the amino acid arginine (Scheme 8).

Finally, we would like to report about the study by Leitner and co-workers who implemented a biphasic system in combination with the ruthenium catalyst precursor *cis*-[Ru(dppm)<sub>2</sub>Cl<sub>2</sub>] (dppm = bis-diphenylphosphinomethane) to ease product and catalyst separation and recovery.<sup>9a</sup> Here, a few amine/organic solvent combinations were tested for CO<sub>2</sub> hydrogenation to formate. High catalyst activity and stability were achieved using an aqueous solution of MEA and methyl isobutyl carbinol (MIBC). MEA is a prototypical example of a scrubbing amine applied on commercial scale and MIBC is a protic yet water-immiscible solvent with some favourable properties such as being a stable, medium boiling (bp 131.6 °C), affordable and industrially acceptable liquid. Hydrogenation was carried out at 70 °C on a 20% MEA aqueous solution, pre-saturated with CO<sub>2</sub>, under a total





**Scheme 8** TMG-aided CO<sub>2</sub> capture and hydrogenation to formate catalysed by Ru-MACHO-BH **1** and water-soluble Ir catalyst **7**. A guanidino group is present in the basic side-chain of L-arginine which could operate in the same fashion. pK<sub>aH</sub>(H<sub>2</sub>O) from ref. 121 (TMG) and ref. 42 (L-arginine).

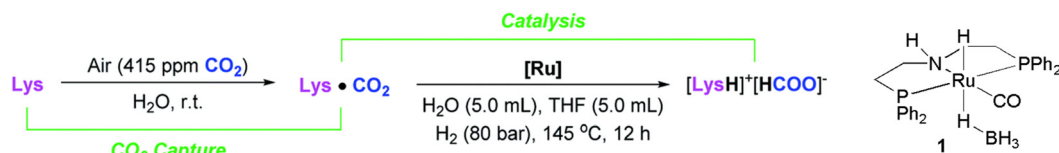
pressure of 90 bars (5/85 CO<sub>2</sub>/H<sub>2</sub>). After the reaction, the amine/formate adduct was almost completely retained in the aqueous phase and a TON of about 1550 in a single run could be achieved. The catalyst remained in the organic phase with less than 0.26% Ru and 1% P leaching in the aqueous phase as established by inductively coupled plasma mass spectrometry (ICP-MS). Based on these premises, a semicontinuous process was realized, to demonstrate the potential applicability and recyclability of the system. After each run, the product phase was removed through a valve at the bottom of the reactor, which was then reloaded with a fresh solution of MEA pre-saturated with CO<sub>2</sub>. Over 11 runs, a total turnover number (TTON) of approximately 150 000 was achieved.

## 5. Recent developments of amino acid-based reactive CO<sub>2</sub> capture to formate and methanol

As it has been discussed above, since one example reported by our group in 2011 on the hydrogenation of bicarbonate to

formate, an analogue concept of reactive capture of CO<sub>2</sub>,<sup>14a</sup> and the first real example in 2015 reported by Sanford and co-workers,<sup>13</sup> the last decade has witnessed significant progress in the optimization of processes for the combined CO<sub>2</sub> capture and hydrogenation, as to (1) catalyst design, from the use of noble metal-based catalysts to the exploration of non-noble metal-based alternatives, (2) the application of different solvent media, especially biphasic systems, to ease catalyst separation and recyclability, (3) the development of various absorbents, among which a range of amines and hydroxides, for the efficient capture of CO<sub>2</sub> and its selective hydrogenation to formates and methanol. However, most systems rely on amines as capturing agents which are volatile: to overcome this limitation strategies have been devised employing high molecular weight polyamines, tethering amines on solid supports, and replacing them with hydroxides. In 2021 our group reported the first example of the use of amino acids to combine CO<sub>2</sub> capture with the direct hydrogenation of the resulting adducts to formate (Fig. 13).<sup>23a</sup> In this study, the CO<sub>2</sub> capture efficiency of various amino acids in water was first evaluated. LYS, having a basic side chain for the presence of a second amino group, proved to be the best absorbent among the amino acids tested, even capable of direct CO<sub>2</sub> capture from air, affording up to 98% of the initial molar amount of LYS in the form of bicarbonate and carbamate. Subsequently, the captured CO<sub>2</sub> was hydrogenated *in situ* to formate using Ru-MACHO **1** as catalyst, reaching a TON of about 55 000 (Lys 5 mmol, **1** 0.02 μmol, H<sub>2</sub>O/THF 1/1 10 mL, H<sub>2</sub> 80 bar, 145 °C, 12 h), thus clearly demonstrating the potential of amino acids for the direct air capture and valorization. Here an organic co-solvent as THF, miscible with water, was added to help catalyst solubilization.

Indeed such potential was further exploited by our group in 2022 with the development of a rechargeable “hydrogen battery” based on a non-noble Mn-pincer catalyst (Fig. 14a).<sup>23b</sup> To fulfil both the H<sub>2</sub> storage and the H<sub>2</sub> release steps within the same cell without switching the catalytic system, the applied catalyst must be active for both the charging (CO<sub>2</sub> hydrogenation) and discharging (formate dehydrogenation) processes. A perusal of the relevant literature showed that only a few noble metal-based catalysts are able to promote both processes efficiently,<sup>123</sup> while Mn-based ones show high activity either for the hydrogenation or the dehydrogenation process. Through informed screening, a Mn pincer complex bearing a triazine backbone pincer PNP ligand was selected which, in combination with LYS as base showed unprecedented high activity towards CO<sub>2</sub> hydrogenation to formate with TON up to 230 000 (Lys 5.0 mmol, Mn catalyst R = NH-C<sub>3</sub>H<sub>5</sub> 0.02 μmol; H<sub>2</sub>O/THF



**Fig. 13** Illustration of the direct air capture of CO<sub>2</sub> using LYS as the absorbent/base and its hydrogenation to formate with the Ru-MACHO-BH catalyst. Reproduced from ref. 23a with copyright permission.



1/1 10 mL, CO<sub>2</sub>:H<sub>2</sub> 20:60 bar, 115 °C, 12 h), and the reverse formic acid dehydrogenation with TON up to 29 400 (Lys 5.0 mmol, Mn catalyst R = NH-C<sub>3</sub>H<sub>5</sub> 0.02 μmol, H<sub>2</sub>O/THF 1/1 10 mL, 90 °C, 12 h). In the dehydrogenation process, under the conditions reported above, 28% of the produced CO<sub>2</sub> was released together with H<sub>2</sub>. The essential role of LYS in achieving high activity was also demonstrated, in fact with the widely used organic amines, like pentaethylenehexamine (PEHA), tetramethylguanidine (TMG), 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), much lower activities were scored. In order to combine the two steps in the “hydrogen battery” and increase the CO<sub>2</sub> absorbing capacity of the reaction medium, potassium lysinate, obtained by treating lysine with one equivalent of KOH, was used instead of LYS. In the developed system, CO<sub>2</sub> can be directly captured from air with potassium lysinate as absorbent, and the subsequent hydrogenation results in over 90% of formate yield. In the dehydrogenation phase, 99.9% of CO<sub>2</sub> is retained in solution which has a two-fold advantage: pure uncontaminated hydrogen is produced, and no CO<sub>2</sub> recharge step is required. Mechanistic studies revealed that potassium lysinate facilitates catalyst activation *via* N-H deprotonation and dearomatization of the triazine moiety (Fig. 14b). Furthermore, it was demonstrated that the combined presence of the α-amino acid moiety and a suitable basic side chain in the amino acid molecule is essential for the Mn-catalysed CO<sub>2</sub> hydrogenation reaction, as well as for the CO<sub>2</sub> capture processes.

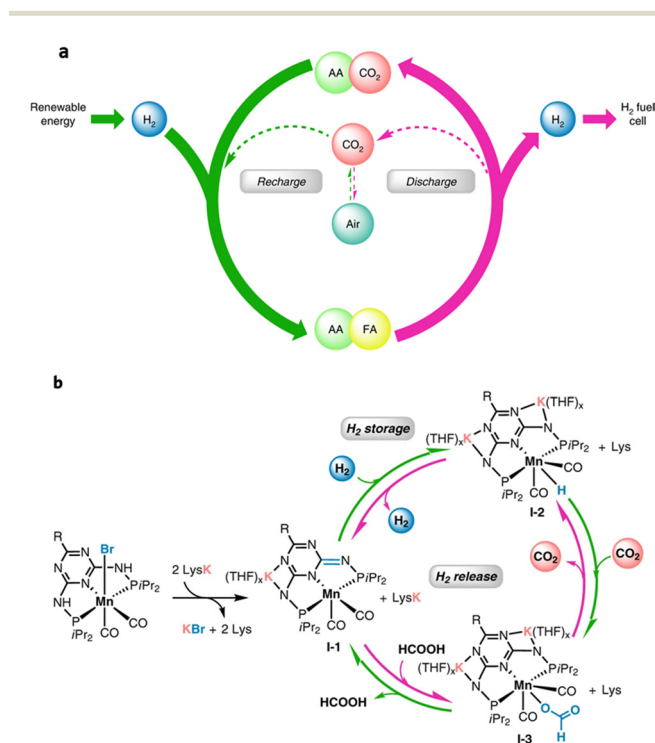


Fig. 14 (a) Potassium lysinate promoted H<sub>2</sub> storage and release cycle in a carbon-neutral fashion. (b) Proposed mechanism for catalyst activation and formic acid/CO<sub>2</sub> (de)hydrogenation promoted by a Mn pincer complex with a triazine backbone PNP ligand. Reproduced from ref. 23b with copyright permission.

Inspired by the fact that amino acids are common supplements of poultry and pig feed, and formic acid/formates are used for the preservation of animal feeds, Leitner and co-workers proposed to integrate the CO<sub>2</sub> capture with its hydrogenation to formate using amino acids.<sup>124</sup> The resulting formate/amino acid mixture can be directly used as additive for animal feeds. For this specific purpose, metal contamination of the product must be avoided. The use of a biphasic reaction medium, whereby the catalyst can be retained in the organic phase while the product stays in the aqueous phase, was applied. Initially the catalyst precursor *cis*-[Ru(dppm)<sub>2</sub>Cl<sub>2</sub>] (dppm = bis-diphenylphosphinomethane) was used in the biphasic mixture of methylisobutylcarbinol (MIBC) and water. The reactions were carried out under 90 bar total pressure at room temperature (CO<sub>2</sub>:H<sub>2</sub> 1:2) and a reaction temperature of 70 °C. The proteinogenic amino acids ARG, HIS, and LYS were used in the aqueous phase because they carry basic side groups which contribute further to CO<sub>2</sub> capture and HCOOH stabilization, rendering the reaction thermodynamically more favourable. In the screening tests, ARG secured both the highest activity and conversion with values comparable to those obtainable with MEA under similar conditions. The HIS based system exhibited relative lower reaction rate. LYS, despite its high pK<sub>a</sub> value, provided the lowest activity and formate yield (Fig. 15). The authors found that, after the reaction, 2.2% of the catalyst had cross-dissolved into the aqueous phase, which would increase the cost for downstream purification. To reduce the catalyst solubility in water and ensure its exclusive partitioning in the organic phase, catalyst [Ru(C12-dppm)<sub>2</sub>Cl<sub>2</sub>] containing the lipophilic-tagged ligand bis(bis(4-dodecylphenyl)phosphanyl)methane (C12-dppm) was used. After a screening of various organic solvents, they found that dodecanol meets the system design criteria of high catalytic activity, biocompatibility and no cross-solubility into the aqueous solution. Based on the dodecanol/H<sub>2</sub>O biphasic system, the authors further tested the reactive capture of CO<sub>2</sub> to formate, using a CO<sub>2</sub> saturated aqueous solution of 6 M Arg: the capture capacity of Arg was determined as 0.94 mol CO<sub>2</sub> per mol Arg under 2 bar. This solution was fed into an autoclave as a part of a semi-batch process. Under 70 bars H<sub>2</sub> at 70 °C, after 5 hours no further pressure drop was detected. The aqueous phase could be removed for analysis under pressure at 70 °C and a new batch of aqueous CO<sub>2</sub>-saturated ARG recharged. The process was repeated ten times affording a final formic acid-to-amino acid ratio of 1:1 (average of 0.91 ± 0.03:1, and 9.0–10.8 wt% of FA) demonstrating a quantitative conversion of the captured CO<sub>2</sub> to FA with practical reusability. They also showed that the tenfold cycle production of FA corresponds to a total TON of 102 282, and the production of FA (in kg) per g of ruthenium is as high as 46.6. It should also be noted that only 3.3% of the Ru catalyst had leached out to the product phase with a total loss of only 1% in runs 2–10, demonstrating excellent catalyst retainability.

AILs have been shown to be a potential absorbent for CO<sub>2</sub> capture, but it was not until 2022 that our group published the first report on the use of such a system for the reactive capture and conversion of CO<sub>2</sub> to formates.<sup>23c</sup> In this study, it was



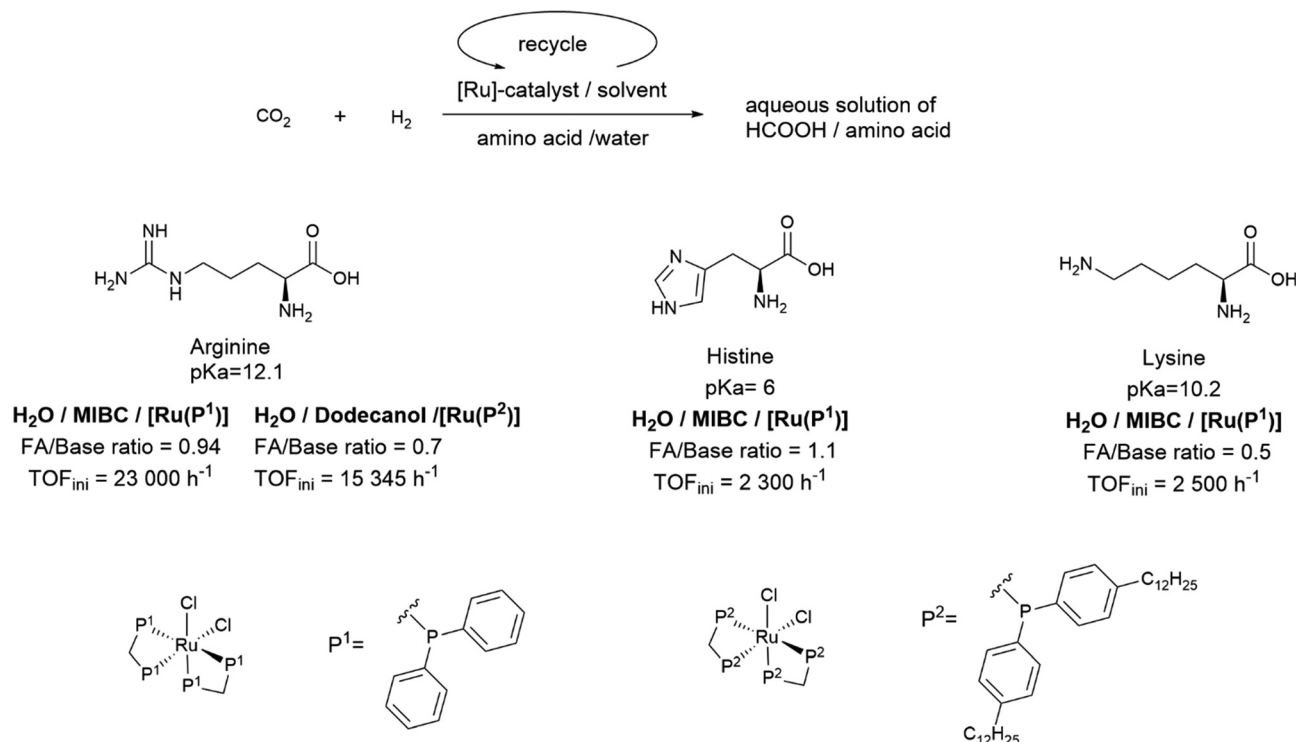


Fig. 15 The reaction system for the CO<sub>2</sub> hydrogenation to product HCOOH/amino acids mixture as the animal feeds additive using a biphasic system with *cis*-[Ru(dppm)<sub>2</sub>Cl<sub>2</sub>] (P<sup>1</sup> ligand) and *cis*-[Ru(C<sub>12</sub>-dppm)<sub>2</sub>Cl<sub>2</sub>] (P<sup>2</sup> ligand) catalysts. MIBC, methyl isobutyl carbinol. Reproduced from ref. 124 with copyright permission.

shown that the CO<sub>2</sub> capture capacity of the AAIL is influenced by both the cation and the anion. With the ionic liquid [TBA][ARG], prepared by reaction of ARG with an aqueous solution of tetrabutyl ammonium (TBA) hydroxide, a capture capacity of 1.94 mol<sub>CO<sub>2</sub></sub> mol<sub>absorbent</sub><sup>-1</sup> was achieved under 2 bars of CO<sub>2</sub>. [TBA][LYS], prepared in the same way from LYS, showed a capturing capacity of 1.80 mol<sub>CO<sub>2</sub></sub> mol<sub>absorbent</sub><sup>-1</sup>. The loading capacity was evaluated after dissolving the AAIL in water to alleviate the problem of increased viscosity after CO<sub>2</sub> loading, which would limit gas diffusion and mass transfer. It should be noted that the loading capacity of ARG in the ILs form is even higher than that of the corresponding potassium salt and [TBA][OH], demonstrating again the advantage of using amino acids as components of ionic liquids for CO<sub>2</sub> capture. The subsequent hydrogenation step was carried out using Ru-MACHO-BH 1, achieving a conversion of over 60% from captured CO<sub>2</sub> to formate (CO<sub>2</sub> capture step: [TBA][ARG] 5 mmol, CO<sub>2</sub> 20 bars, absorbed CO<sub>2</sub> 10.1 mmol; hydrogenation step: Ru-MACHO-BH 1 10 μmol, H<sub>2</sub>O/THF 1/1 10 mL, H<sub>2</sub> 60 bars, 80 °C, 6 h). If no CO<sub>2</sub> overpressure is applied and CO<sub>2</sub> is directly captured from air at room temperature, then a final formate to absorbent ratio of 0.5 can be achieved demonstrating the general capability of amino acid-based ionic liquids for the reactive capture of CO<sub>2</sub>.

The use of amino acid as the absorbent for capture and *in situ* hydrogenation has just been studied within the last 5 years, but it has showcased the high potential of such biocompatible and thermostable absorbents for achieving

highly efficient CO<sub>2</sub> hydrogenation transformation. The water-soluble iridium catalyst 7 described in Scheme 8, reported in 2022 by Choudhury and co-workers, while performing best in combination with TMG, was likewise tested with LYS as absorbent. After CO<sub>2</sub> capture from air (7.5 mmol captured with 10 mmol LYS after 1 h at room temperature), hydrogenation of the loaded aqueous solution with 7 (7 4.3 μmol, H<sub>2</sub>O 10 mL, H<sub>2</sub> 50 bars, 120 °C, 8 h) afforded a 71% yield in formate as to the captured CO<sub>2</sub>.<sup>122</sup>

Very recently, Prakash has demonstrated that also ARG, beside PEHA, in combination with the ionic liquid 3-butyl-1-methyl imidazolium acetate (BMIMOAce) can aid the Ru-MACHO-BH 1-catalyzed hydrogenation of CO<sub>2</sub> to methanol. However, only a meager TON of 42.5 was recorded compared to that achieved with PEA, 410, under otherwise identical conditions (1 20 μmol, BMIMOAce 1.5 mmol, L-Arg 2.6 mmol, triglyme 5 mL, 75 bar CO<sub>2</sub>:3H<sub>2</sub>, 155 °C, 24 hours).<sup>111</sup> Very recently our group could greatly improve this result achieving a maximum TON in methanol of 700 (1 2 μmol, [TBA][ARG] 5.0 mmol, THF 10 mL, 80 bar CO<sub>2</sub>:3H<sub>2</sub>, 150 °C, 24 hours) by directly incorporating the ARG anion in the structure of the ionic liquid [TBA][ARG] used as the CO<sub>2</sub> capturing medium.<sup>125</sup> The study revealed the peculiar advantage provided by ARG: in fact, although the two basic amino acid ARG and LYS when combined with the TBA cation were equally effective in the capture of CO<sub>2</sub> and its further 1-catalyzed hydrogenation to formate, more methanol could be produced with [TBA][ARG]. The main difference between the two amino acids is the



presence of the highly basic guanidino group in ARG which, being protonated under the conditions of the AAIL synthesis and application, can likely establish hydrogen bonding interactions with the intermediate formamide and enhance its electrophilic character thus favoring its reduction. Yet the system suffers from some limitations such as the limited stability of the tetrabutylammonium cation under the harsher conditions required for CO<sub>2</sub> hydrogenation beyond the formate stage.

While a proof of concept has been demonstrated, further investigation is obviously needed to disclose the potential of amino acids-based CO<sub>2</sub>-capturing media for the reactive conversion of the captured CO<sub>2</sub>.

## 6. Discussion

As demonstrated by the aforementioned examples, the process of amino acid-assisted CO<sub>2</sub> capture<sup>126</sup> and *in situ* hydrogenation to either formate or methanol, while still in its nascent stages, is both viable and feasible. The former method has exhibited a higher degree of success compared to the latter. Research in this domain has successfully substantiated the concept, yet further investigation is imperative to address the various challenges that have surfaced during the review of existing publications and to achieve practical applications with high levels of selectivity and efficiency.

It has been demonstrated that CO<sub>2</sub> captured directly from air at room temperature with aqueous solutions of basic amino acids such as LYS and ARG can be directly pressurized with hydrogen in the presence of selected catalysts to yield aqueous solutions of formate. Productivities (TON) are positively affected by higher CO<sub>2</sub> pressures and/or concentrations (up to a certain level). Therefore, the same approach could, at least in theory, be applied to reactive CO<sub>2</sub> capture from flue gases after combustion (0.03–0.14 bar CO<sub>2</sub> partial pressure) and from industrial sources such as cement production (0.14–0.33 bar) and stainless steel plants (0.2–0.6 bar) and hydrogen production (3–5 bar), all of which have higher CO<sub>2</sub> content and partial pressure than air.<sup>127</sup> In addition, the high temperature of post-combustion CO<sub>2</sub> flue gas streams could be advantageously used to support subsequent hydrogenation if the capture process can be performed at such a temperature.

One problem, however, is related to the kinetics of CO<sub>2</sub> absorption: measurements of the capturing ability of aqueous solutions of LYS showed that in air at room temperature up to 4 days are required for reaching a 0.5/1.0 CO<sub>2</sub>/LYS molar ratio, with CO<sub>2</sub> trapped in solution as the exclusive carbamate.<sup>23b</sup> However, the process of CO<sub>2</sub> capture can be accelerated and gradually increased to nearly 1/1 CO<sub>2</sub>/LYS molar ratio with increasing CO<sub>2</sub> pressure up to 20 bar by forming bicarbonate besides carbamate. Such an approach to improve kinetics and process productivity would require an additional energy input if to be applied to a post-combustion CO<sub>2</sub> capture process. Alternatively, when the basic amino acids LYS and ARG are applied in the form of the corresponding ionic liquids<sup>23c</sup> in combination with the TBA cation, the CO<sub>2</sub>/AA ratio can be increased

up to 1.80 and 1.94 for LYS and ARG, respectively when CO<sub>2</sub> is applied at 2 bars. While the rate of CO<sub>2</sub> uptake falls far short of what would be required for a potential practical application, the use of AAIL, which has an additional basic site in the amino acid side chain, expands the scavenging capacity of the IL, thereby increasing the local concentrations of the putative CO<sub>2</sub> source and theoretically increasing the rate of conversion of the captured CO<sub>2</sub> into products. In addition, the careful selection of the cations for the amino acid anion in the form of salt, ILs, or mixtures of different types of absorbents could serve as another strategy to modulate the CO<sub>2</sub> uptake rate and capacity. However, it is imperative to consider compatibility with the subsequent hydrogenation process. Additional properties of capturing agents to be assessed for reactive CO<sub>2</sub> capture include stability under the reducing conditions necessary for conversion chemistry and compatibility with the catalyst. Further investigation is necessary into issues such as sorbent integrity after hydrogenation and its interaction with the catalyst metal, which can reduce its efficiency.

Two of the catalysts applied in the AA-assisted CO<sub>2</sub> capture and hydrogenation, Ru-MACHO-BH **1** and the N-heterocyclic carbene-ligated iridium catalyst **7**, have been used directly for the hydrogenation of CO<sub>2</sub> captured from air in water. These catalysts have demonstrated tolerance to both oxygen and water at the reaction temperature of 155 °C and 120 °C, respectively. It is imperative that catalysts engineered for reactive CO<sub>2</sub> capture exhibit stability against oxygen and water, as these elements are also present in flue gases in varying amounts.<sup>128</sup> Additionally, flue gases contain other contaminants, such as NO<sub>x</sub> and SO<sub>x</sub>, against which catalysts must be evaluated to ensure a more realistic assessment. Ru-MACHO-BH **1** is a very robust catalyst; however, it is almost insoluble in water. Its use in combination with amino acid-based absorbents requires the addition of a miscible organic solvent to improve its efficiency. While this may be a limitation, the use of a water-insoluble organic solvent to solubilize the catalyst in a biphasic system can be advantageously exploited to confine and recycle the catalyst while facilitating product separation.

The lipophilicity of the catalyst can be further enhanced by modifying its ligand structure through the introduction of long alkyl chains, as demonstrated by Leitner and coworkers.<sup>129</sup> The same research group has synthesized a Ru-MACHO-BH complex tagged with linear C12 alkyl chains at the para position of the phosphorus-phenyl substituents and demonstrated its efficiency in catalyzing the aforementioned reaction. Disappointingly, in a biphasic *n*-decane/water system, while the overall TON for CO<sub>2</sub> conversion in the presence of *N,N'*-dimethylethane-1,2-diamine was close to that exhibited by the self-separating system, however, a significantly lower selectivity of approximately 50% for complete hydrogenation to methanol was observed, resulting in the accumulation of significant amounts of formamide at the reaction. This suggests that excess water hinders the reduction of captured CO<sub>2</sub> to methanol, as water is a by-product and an excessive amount could adversely impact the equilibrium position of such a conversion. The employment of water-lean solvents, such as ionic liquids, may offer a solution to this challenge.<sup>130</sup> In the sole instance of



CO<sub>2</sub> hydrogenation to formate in AAIL,<sup>23c</sup> the ionic liquid was dissolved in water to alleviate the rise in viscosity triggered by CO<sub>2</sub> absorption. Consequently, further research is necessary to reconcile these two conflicting requirements by exploring amino acid-based ionic liquids that are less viscous and by identifying suitable alternative solvents to water that would not affect the conversion of CO<sub>2</sub> to methanol. In this respect, the knowledge established in amino acid-based CO<sub>2</sub> capture systems could be revisited. In terms of catalysts, both noble and non-noble metals have been successfully applied to the reactive capture of CO<sub>2</sub> by conversion to formate.

With one exception, catalysts based on non-noble metals,<sup>104</sup> at least those recalled in this review and supported by pincer ligands, are less efficient for integrated CO<sub>2</sub> capture and hydrogenation to methanol because of the formation of highly stable metal formate adducts. These adducts require the use of additives to return them to the catalytic cycle in an active form. Replacement of noble metals by non-noble metals is urged by economic considerations and the limited availability of the former, although even manganese has been identified as a critical element due to its increased use.<sup>131</sup> It must be said that, at least for the MACHO-type catalysts, regardless of the metal, the ligand contributes significantly to the overall cost. Nevertheless, the cost of the metal and ligand may not be an issue if the catalyst can be retained and recycled.

Although this review deals with homogeneous catalysts, it is worth mentioning that heterogenization of homogeneous catalysts has been implemented for the sake of catalyst recovery and reuse, and although not directly applied to amino acid-based solvents, examples have been reported concerning the amine-based hydrogenation of CO<sub>2</sub> to either formate<sup>132</sup> or methanol,<sup>133</sup> which has been realized by anchoring iridium metal to a bidentate PN moiety within a suitably modified polyimine PEI. Alternatively, the hyper-crosslinking polymerization (HCP) technique has been used to prepare a single-site heterogenized version of Ir<sup>132b</sup> and Ru<sup>133</sup>-based molecular catalysts whose ligand carries a phenyl substituent. In the presence of triphenylmethane as copolymerizing arene monomer and formaldehyde dimethylacetal as crosslinking agent, aryl moieties of ligand units could be linked together by the Friedel-Crafts alkylation reaction using FeCl<sub>3</sub> as catalyst in 1,2-dichloroethane as solvent. Such HCP catalysts have shown activities superior to those of their homogeneous counterparts in CO<sub>2</sub> hydrogenation to formate<sup>132b</sup> and methanol,<sup>133</sup> combined with excellent recyclability. Interestingly, a similar heterogenization has also been applied to Ru-MACHO **1a**, and the heterogenized version has been applied to aqueous reforming to methanol,<sup>134</sup> with activity comparable to that of **1a** under otherwise identical conditions.<sup>135</sup> To the best of our knowledge, no application to amine-assisted hydrogenation of CO<sub>2</sub> with such a catalyst has yet been reported.

## 7. Conclusions and outlook

The preceding discourse delineated advancements and unresolved challenges in the domain of reactive CO<sub>2</sub> capture

employing amino acid-based solvents. These challenges encompass sluggish absorption kinetics, constrained capacity, reliance on CO<sub>2</sub> sources and partial pressure, substantial catalyst expense, product selectivity, and concerns pertaining to catalyst recyclability. The surmounting of these limitations is imperative to enhance the overall performance of amino acid-based reactive CO<sub>2</sub> capture systems and facilitate their large-scale implementation. In light of the aforementioned discussion, the authors propose the following research directions to address these critical challenges and enhance the long-term prospects of reactive CO<sub>2</sub> capture technologies:

- It is imperative to investigate further scalable and inexpensive systems for reactive CO<sub>2</sub> capture.
- Furthermore, there is a need to develop more efficient solvents for reactive CO<sub>2</sub> capture, *e.g.* amino acid-based ones, able to operate under low CO<sub>2</sub> pressure and to withstand hydrogenation conditions.
- Additionally, there is a need to develop more efficient, active, stable, and selective catalysts that are tolerant to O<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub>.
- There is a need to develop strategies to facilitate product separation and efficiently recycle the sorbent and catalyst.
- Finally, techno-economic and life cycle assessment of CO<sub>2</sub> capture and hydrogenation should be performed on a regular basis, preferentially, as Leitner and coworkers suggested, for all the stages, from “cradle-to-grave”.<sup>136</sup> Despite the potential of reactive CO<sub>2</sub> capture to circumvent the CO<sub>2</sub> desorption and compression steps, the separation of the product may require an additional energy input. Therefore, the development of technologies to efficiently recover the final upgraded product from the absorbent medium with minimal energy expenditure is necessary. Additionally, a comparison of the total energy consumption and cost of integrated and non-integrated CO<sub>2</sub> capture and hydrogenation is recommended, as Bardow and coworkers demonstrated, if the CO<sub>2</sub> source is too diluted, the integration may indeed increase the capital investment compared to the non-integrated process.<sup>137</sup>

In conclusion, amine- and amino acid-based reactive CO<sub>2</sub> capture represents a promising and central system for CO<sub>2</sub> utilization and valorization. We believe that this review can serve as a valuable guide for researchers in this field in their efforts to respond to the ongoing search for effective strategies to reduce CO<sub>2</sub> emissions and achieve sustainability.

## List of acronyms

|         |                                                 |
|---------|-------------------------------------------------|
| MEA     | Monoethanolamine                                |
| DEA     | Diethanolamine                                  |
| MDEA    | <i>N</i> -Methyl diethanolamine                 |
| DETA    | Diethylenetriamine                              |
| NaADS   | Sodium aliphatic diamine sulphonate             |
| LOHC    | Liquid organic hydrogen carriers                |
| RuBisCO | Ribulose-1,5-bisphosphate-carboxylase/oxygenase |
| AAILs   | Amino acid based ionic liquids                  |
| GLY     | Glycine                                         |



|                      |                                    |
|----------------------|------------------------------------|
| TAU                  | Taurine                            |
| BALA                 | $\beta$ -Alanine                   |
| VAL                  | Valine                             |
| LEU                  | Leucine                            |
| ALA                  | Alanine                            |
| AABA                 | Aminobutyric acid                  |
| NMGLY                | Sarcosine                          |
| SER                  | Serine                             |
| AMALA                | $\alpha$ -Methyl alanine           |
| PHE                  | Phenylalanine                      |
| CYS                  | Cysteine                           |
| PRO                  | Proline                            |
| GABA                 | $\gamma$ -Aminobutyric acid        |
| HYPRO                | Hydroxyproline                     |
| PGA                  | Pyroglutamic acid                  |
| ASN                  | Asparagine                         |
| GLN                  | Glutamine                          |
| GLU                  | Glutamic acid                      |
| DIGLY                | Diglycine                          |
| ARG                  | Arginine                           |
| ILE                  | Isoleucine                         |
| MET                  | Methionine                         |
| PZ                   | Piperazine                         |
| EGME                 | 2-Methoxyethanol                   |
| EGEE                 | 2-Ethoxyethanol                    |
| DMF                  | <i>N,N</i> -Dimethylformamide      |
| NMP                  | <i>N</i> -Methyl-2-pyrrolidone     |
| BMIM                 | Butyl methyl imidazolium           |
| N66614               | Trihexyl(tetradecyl) ammonium      |
| P66614               | Trihexyl(tetradecyl) phosphonium   |
| C <sub>2</sub> OHmim | Hydroxyethyl methyl imidazole      |
| PEHA                 | Pentaethylenehexamine              |
| TMG                  | Tetramethylguanidine               |
| DABCO                | 1,4-Diazabicyclo[2.2.2]octane      |
| DBU                  | 1,8-Diazabicyclo[5.4.0]undec-7-ene |
| TBA                  | Tetrabutyl ammonium                |
| MIBC                 | 4-Methyl-2-pentanol                |
| CHO                  | Choline                            |

## Author contributions

Y. P. and E. A.: writing – original draft. M. B. and H. J.: conceptualization, writing – review & editing.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Conflicts of interest

There are no conflicts to declare.

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