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## New chemistry for enhanced carbon capture: beyond ammonium carbamates

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Carbon capture and sequestration is necessary to tackle one of the biggest problems facing society: global climate change resulting from anthropogenic carbon dioxide (CO<sub>2</sub>) emissions. Despite this pressing need, we still rely on century-old technology—aqueous amine scrubbers—to selectively remove CO<sub>2</sub> from emission streams. Amine scrubbers are effective due to their exquisite chemoselectivity towards CO<sub>2</sub> to form ammonium carbamates and (bi)carbonates, but suffer from several unavoidable limitations. In this perspective, we highlight the need for CO<sub>2</sub> capture *via* new chemistry that goes beyond the traditional formation of ammonium carbamates. In particular, we demonstrate how ionic liquid and metal–organic framework sorbents can give rise to capture products that are not favourable for aqueous amines, including carbamic acids, carbamate–carbamic acid adducts, metal bicarbonates, alkyl carbonates, and carbonic acids. These new CO<sub>2</sub> binding modes may offer advantages including higher sorption capacities and lower regeneration energies, though additional research is needed to fully explore their utility for practical applications. Overall, we outline the unique challenges and opportunities involved in engineering new CO<sub>2</sub> capture chemistry into next-generation technologies.

### Introduction

Rising atmospheric levels of carbon dioxide (CO<sub>2</sub>) are the major contributor to global climate change, with annual emissions approaching 40 billion tonnes.<sup>1</sup> Nearly two-thirds of anthropogenic CO<sub>2</sub> emissions result from the combustion of fossil fuels, including coal and natural gas, for the global production of electricity.<sup>1</sup> In addition, CO<sub>2</sub> emissions are an inevitable by-product of other industrial processes, including the production of cement, steel, and natural gas.<sup>1</sup> As a result, new technologies are needed to mitigate emissions from these industrial point sources during the gradual transition to cleaner fuels and building materials. One such proposed technology is carbon capture and sequestration or utilization, in which CO<sub>2</sub> is selectively removed from low-concentration emission streams (4–15% CO<sub>2</sub>) prior to its permanent storage underground or conversion into more valuable products.<sup>2</sup>

Building upon technology developed in the 1930s to purify crude natural gas, many have shown that aqueous amine scrubbers are currently the most technology-ready sorbents for CO<sub>2</sub> capture from flue emissions on large scale (Fig. 1a).<sup>3</sup> Aqueous amine scrubbers are effective because amines react selectively with CO<sub>2</sub> to produce carbamic acid intermediates, which rapidly react with a second equivalent of amine to

produce ammonium carbamates; under aqueous conditions, ammonium carbamates and carbamic acids can further react with water to produce ammonium (bi)carbonates.<sup>4</sup> The captured CO<sub>2</sub> is then desorbed using heat and/or vacuum (temperature and/or vacuum swing), thereby regenerating free amines. Over the last ninety years, there has been significant optimisation of the amine structure to maximize working capacities (*i.e.* the usable amount of CO<sub>2</sub> captured in an actual process) while minimising regeneration energies (*i.e.* the total energy input needed to heat the material and desorb CO<sub>2</sub>).<sup>5</sup> However, aqueous amine scrubbers are still faced with several challenges, including: (1) low capacities (<3 mol CO<sub>2</sub> per kg solution or <15 wt%) due to dilution of the corrosive amines with water;<sup>6</sup> (2) poor oxidative stability of amines towards O<sub>2</sub>; and (3) degradation in the presence of contaminants such as SO<sub>2</sub>, which reacts with amines similarly to CO<sub>2</sub>.<sup>7</sup> In addition, one aspect of aqueous amine scrubbers has remained largely constant: the products of their reaction with CO<sub>2</sub>.<sup>8</sup> This restriction generally leads to high regeneration energies (≥2.4 MJ kg<sup>-1</sup> CO<sub>2</sub>) and CO<sub>2</sub> desorption temperatures (>100 °C), greatly increasing the cost of carbon capture from flue emissions.<sup>9–11</sup>

### Amine-based materials for CO<sub>2</sub> capture

One promising avenue to overcome the challenges associated with CO<sub>2</sub> capture by aqueous amine scrubbers is to employ other types of sorbents, such as porous solids or ionic liquids

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Fig. 1 Classes of amine-based materials for CO<sub>2</sub> capture. (a) Traditional amine chemistry for CO<sub>2</sub> absorption via the formation of ammonium carbamates under dry conditions and ammonium bicarbonates under humid conditions.<sup>3</sup> (b) Amine-functionalised porous silicas, where amines are either impregnated into or covalently attached to silica supports.<sup>12</sup> (c) Amine-functionalised ionic liquids.<sup>13</sup> (d) Post-synthetically amine-functionalised zeolites.<sup>14</sup> (e) Post-synthetically amine-functionalised metal-organic frameworks.<sup>15</sup>

(ILs). Porous materials such as silicas, carbons, zeolites, metal-organic frameworks (MOFs), porous organic polymers (POPs), and covalent-organic frameworks (COFs), have the potential advantages of higher thermal stabilities and lower heat capacities compared to aqueous amine scrubbers.<sup>16–21</sup> Likewise, ILs are low-melting ionic salts that offer advantages over aqueous amines including non-volatility (preventing release into the atmosphere) and structural tunability. Although hydrophobic porous solids such as silicon-rich zeolites and carbons are capable of scrubbing CO<sub>2</sub> from high-concentration streams (*e.g.* crude biogas),<sup>22</sup> many of these materials cannot remove CO<sub>2</sub> from humid low-concentration streams such as flue gas emissions.<sup>23</sup> This limitation arises because CO<sub>2</sub> and water directly compete for the same physisorption sites in these sorbents. An additional general challenge for porous solid adsorbents that remains to be addressed is their poor thermal conductivity, which complicates adsorbent heating and cooling during adsorption/desorption cycling.

A powerful approach to overcome the poor selectivities of typical sorbents towards CO<sub>2</sub> under humid conditions is to leverage the favourable reactivity of aqueous amine scrubbers in the form of amine-functionalised sorbents (Fig. 1).<sup>24,25</sup> Beginning with the first report of amine-functionalised silicas in 1992 (Fig. 1b),<sup>12,24</sup> a range of amine-functionalized solid adsorbents, including zeolites (Fig. 1d),<sup>14</sup> MOFs (Fig. 1e),<sup>15,19</sup> and carbons<sup>26</sup> have been prepared. Researchers have demonstrated that amine-functionalised porous solids possess the high CO<sub>2</sub> selectivities native to aqueous amines while generally evidencing improved thermal and chemical stabilities. For example, confining amines within a porous support largely eliminates oxidation pathways that are catalyzed by leached

metal ions from the absorption columns.<sup>7,27</sup> Similarly, ionic liquids (ILs) can also be functionalised with amine groups to achieve high CO<sub>2</sub> capacities and selectivities without the need for dilution with water (Fig. 1c).<sup>28,29</sup> Numerous *in situ* spectroscopic studies using solution- and solid-state nuclear magnetic resonance (SSNMR) and infrared (IR) spectroscopy combined with theoretical calculations suggest that in most cases amine-functionalised materials produce similar sorption products as aqueous amine scrubbers, namely, ammonium carbamates under dry conditions<sup>13,30,31</sup> and, as confirmed recently, ammonium bicarbonates under humid conditions.<sup>32</sup> As such, the majority of these materials still require high temperatures (>120 °C) to fully desorb CO<sub>2</sub>, resulting in high regeneration penalties.<sup>33</sup> In addition, amine-functionalised silicas suffer from oxidative degradation by distinct bimolecular pathways,<sup>34</sup> as well as the irreversible formation of ureas under dry conditions.<sup>35</sup> Overcoming these fundamental limitations is critical to enabling the widespread adoption of carbon capture technologies.

## New CO<sub>2</sub> chemisorption pathways in solution and the solid state

An underexplored approach to overcome the fundamental limitations of amine-based materials is not to focus on the development of new materials, but on new chemisorptive pathways for selective carbon dioxide capture. For example, the formation of carbamic acids by CO<sub>2</sub> capture at amine sites is potentially desirable because it involves reaction with CO<sub>2</sub> at only a single amine site, increasing the CO<sub>2</sub> : amine sorption



ratio to 1 : 1.<sup>36</sup> Indeed, unlocking 1 : 1 reaction stoichiometries in general should produce higher gravimetric and volumetric sorption capacities by enabling a higher density of reactive sites within a given volume. Additionally, mechanisms beyond ammonium carbamate formation have been shown to lead to lower CO<sub>2</sub> desorption temperatures in some cases (see below). Importantly, each combination of CO<sub>2</sub> partial pressure (*P*) and temperature (*T*) for a given separation (e.g. 400 ppm, 25 °C for capture directly from the atmosphere) leads to an ideal differential free energy of sorption ( $-\Delta G$ ) for that separation (e.g.  $-19 \text{ kJ mol}^{-1}$  for direct air capture), which is critical to maximising sorption capacities while minimising regeneration energies.<sup>41</sup> New chemisorption pathways should enable more dramatic tuning of the differential enthalpies ( $-\Delta H$ ) and entropies ( $-\Delta S$ ) of sorption to achieve these optimal values. Last, moving away from amines entirely could lead to adsorbents with improved oxidative stabilities, a recurring challenge associated with amine-based materials, although more work is required to characterize the oxidative stability of promising sorbents.<sup>42</sup> Here, we highlight examples of new CO<sub>2</sub> adsorption pathways beyond ammonium carbamates that may ultimately lead to enhanced CO<sub>2</sub> capture.

The unique, highly-charged environment within ILs makes them an ideal setting to unlock new CO<sub>2</sub> reactivity. For example,

although carbamic acids are normally disfavoured outside of polar aprotic solvents (e.g. dimethyl sulphoxide),<sup>36,43</sup> Schneider, Brennecke, and coworkers found that installing amines onto the anions of amino acid-derived ILs favours CO<sub>2</sub> capture *via* the formation of carbamic acids stabilized by hydrogen-bonding (Fig. 2a).<sup>37</sup> This change in mechanism doubled the molar absorption capacity of these ILs compared to those bearing amine-functionalized cations, which operate by the traditional ammonium carbamate mechanism.<sup>13</sup> In addition, the strong binding of CO<sub>2</sub> within a proline-derived IL ( $-\Delta H_{\text{abs}} = 80 \text{ kJ mol}^{-1}$ ) led to nearly complete saturation at low pressures of CO<sub>2</sub> (<0.1 bar at 25 °C). Therefore, this switch in chemisorption products demonstrates that the local environment of an amine is a crucial design element for controlling its reactivity towards CO<sub>2</sub>.<sup>44</sup>

Following these initial studies, even more unconventional CO<sub>2</sub> absorption pathways began to emerge in ILs. Building upon previous reports,<sup>45</sup> Li, Dai, and coworkers demonstrated that amines can be completely bypassed by capturing CO<sub>2</sub> in ILs bearing alkoxide or phenoxide anions and organic superbases-derived cations, which reversibly capture CO<sub>2</sub> *via* alkylcarbonate formation (Fig. 2b).<sup>38</sup> Similar to carbamic acids (Fig. 2a), this chemistry gives rise to a 1 : 1 reaction stoichiometry and thus higher gravimetric capacities (up to 20 wt%) compared to



Fig. 2 New CO<sub>2</sub> absorption mechanisms in solution. (a) Proposed formation of carbamic acid in ILs with amine-functionalised anions.<sup>37</sup> (b) Proposed absorption mechanism by phenoxide and alkoxide ILs.<sup>38</sup> (c) Proposed mechanism for electrochemical CO<sub>2</sub> capture by 1,4-naphthoquinone.<sup>39</sup> (d) Proposed absorption mechanism for an IL with an aspartate dianion.<sup>40</sup> In all cases, the corresponding cations are omitted for clarity.



traditional IL sorbents (<10 wt%). Importantly, alkoxide-based ILs also possess low viscosities and rapid absorption kinetics (saturation in less than 5 minutes at room temperature), overcoming common challenges that plague traditional amine-functionalized ILs.<sup>38</sup> Subsequently, Kim and coworkers demonstrated that similar reactivity at oxygen could be achieved in water-lean alcoholamines bearing sterically-hindered amines and that the resulting ammonium alkylcarbonates desorb CO<sub>2</sub> more readily than ammonium carbamates.<sup>50</sup>

Another route to generate oxyanion nucleophiles for rapid CO<sub>2</sub> capture *via* carbonate formation is by the electrochemical reduction of quinones, as demonstrated by Hatton and others (Fig. 2c).<sup>39</sup> Promising results with electrochemically-reduced quinones have been observed in the presence of water and oxygen, although some loss in capacity was observed due to re-oxidation of the nucleophile by oxygen.<sup>51</sup> This electrochemical approach has subsequently been expanded to other nucleophiles, such as reduced sulphides, suggesting it may be a general strategy to expand the scope of nucleophiles for CO<sub>2</sub> capture.<sup>52</sup> An advantage of this approach is that electrochemical regeneration of the quinone (electrochemical swing adsorption) leads to energy savings over traditional temperature or pressure swing processes.

Recent work has revealed that CO<sub>2</sub> capacities approaching a remarkable 2 : 1 reaction stoichiometry can be accessed in ILs, representing a four-fold increase compared to the traditional ammonium carbamate mechanism (Fig. 2d).<sup>40</sup> Specifically, Wang and coworkers found that an ionic liquid with an aspartate dianion was able to reversibly bind 1.96 mol CO<sub>2</sub> per mol IL at 30 °C and 1 atmosphere CO<sub>2</sub>, which was hypothesised to occur *via* two subsequent reactions at a single amine site to form both a carbamate (calculated  $\Delta E_{\text{abs}} = -69 \text{ kJ mol}^{-1}$ ) and a carbamic acid (calculated  $\Delta E_{\text{abs}} = -54 \text{ kJ mol}^{-1}$ ).<sup>40</sup> This proposed absorption pathway was supported by <sup>13</sup>C NMR measurements as well as density functional theory (DFT) calculations, with the latter ruling out reaction of CO<sub>2</sub> at the carboxylate groups as proposed for related ILs.<sup>53</sup> A similar 2 : 1 absorption mode was also evidenced in an earlier organic chemistry study. The observation of a triplet in solution <sup>15</sup>N NMR studies of selected primary amines in the presence of <sup>13</sup>CO<sub>2</sub> and a base confirmed the reaction of 2 CO<sub>2</sub> molecules with a single amine group at -30 °C.<sup>53</sup> The high capacity offered by this absorption mode makes it a very attractive target for CO<sub>2</sub> capture applications.

Although ILs and water-lean solvents represent a unique platform for the discovery of new CO<sub>2</sub> capture products, they are not without their own challenges. For example, the absorption capacities of most ILs are relatively low (<20 wt%) compared to amine-functionalized solids.<sup>13,28</sup> In addition, the viscosities of ionic liquids are relatively high and tend to increase upon CO<sub>2</sub> adsorption (in some cases up to 200-fold), which represents a significant process challenge.<sup>28,54</sup> While molecular engineering allows access to CO<sub>2</sub>-loaded ILs with viscosities as low as 650 mPa s,<sup>55</sup> these values are still significantly higher than CO<sub>2</sub>-loaded 30% aqueous monoethanolamine solution (4 mPa s).<sup>56</sup> Last, the CO<sub>2</sub>/N<sub>2</sub> absorption selectivities, kinetics, desorption conditions, and long-term cycling stabilities of ILs remain

poorly characterized in many cases. Addressing these challenges is critical to advancing the commercial viability of IL-based sorbents.

An emerging alternative approach is to engineer new CO<sub>2</sub> capture mechanisms within the controlled pore environments of crystalline porous materials, such as MOFs. The arrangement of functional groups in an ordered fashion within the pores of MOFs presents a potential opportunity for unlocking new CO<sub>2</sub> capture chemistry.

One of the earliest demonstrations of CO<sub>2</sub> chemisorption in MOF adsorbents involved CD-MOFs (Fig. 3a; CD =  $\gamma$ -cyclodextrin).<sup>46,57</sup> These MOFs demonstrate strong adsorption of CO<sub>2</sub> at low partial pressures (<2 mbar), leading to excellent CO<sub>2</sub>/CH<sub>4</sub> selectivity (estimated to be >3000) in this regime.<sup>46</sup> Using SSNMR measurements, the authors proposed the formation of carbonic acids or alkylcarbonates; however, the exact chemisorption pathway in this material remains unclear. Nonetheless, the strong bonding of CO<sub>2</sub> in CD-MOF-2 (>1 mmol CO<sub>2</sub> per g MOF adsorbed at 10 mbar and 30 °C) makes this a promising potential material for flue gas capture applications. Analysis of the thermodynamics of CO<sub>2</sub> chemisorption in this material by calorimetry revealed a moderate enthalpy of adsorption at intermediate loadings ( $-\Delta H_{\text{ads}} = 65 \text{ kJ mol}^{-1}$ ), enabling easier desorption of CO<sub>2</sub> from the strong-binding sites compared to amines.<sup>58,59</sup> However, the poor water stability of these MOFs necessitates the translation of this chemisorption mechanism to more stable materials for practical applications.<sup>46</sup>

Carbamic acids have long been invoked as intermediates and products upon CO<sub>2</sub> capture in amine scrubbers,<sup>4</sup> amine-functionalized silicas<sup>30,60</sup> and amine-functionalized MOFs,<sup>61,62</sup> as suggested by NMR and IR spectroscopies. For example, Ho and coworkers found that hydrazine-functionalized variants of the MOF Mg<sub>2</sub>(dobdc) (dobdc<sup>4-</sup> = 2,5-dioxido-1,4-benzenedicarboxylate) exhibit incredibly strong and selective binding of CO<sub>2</sub> (3.89 mmol g<sup>-1</sup> at 25 °C and 0.4 mbar of CO<sub>2</sub>), which they ascribe to highly favourable carbamic acid formation ( $-\Delta H_{\text{ads}} = 90 \text{ kJ mol}^{-1}$ ) within the framework pores.<sup>62</sup> However, until recently there remained little crystallographic evidence for this elusive adsorption product in the solid state. Long and coworkers identified variants of the MOF M<sub>2</sub>(dobpdc) (dobpdc<sup>4-</sup> = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) functionalised with the diamine 2,2-dimethyl-1,3-diaminopropane (dmpn) as promising adsorbents for post-combustion CO<sub>2</sub> capture owing to their exceptional hydrothermal and oxidative stability (Fig. 3b and c).<sup>47,48</sup> Exposure of single crystals of dmpn-Zn<sub>2</sub>(dobpdc) to 1 bar of CO<sub>2</sub> induced the formation of carbamic acid pairs bridging two adjacent amine sites in the framework, as confirmed by SCXRD and SSNMR (Fig. 3b).<sup>47,48</sup> In this structure, the normally disfavoured formation of carbamic acids is facilitated by well-defined hydrogen-bonding interactions, corroborated by the presence of strong <sup>1</sup>H<sub>(COOH)...<sup>13</sup>C correlations in 2-dimensional SSNMR experiments. Notably, carbamic acid pairs were actually predicted computationally in related frameworks before they were observed experimentally.<sup>63</sup></sub>

Building upon this work, the same group demonstrated that dmpn-Mg<sub>2</sub>(dobpdc) chemisorbs CO<sub>2</sub> by another distinct





Fig. 3 New CO<sub>2</sub> adsorption mechanisms unlocked in MOFs. (a) Proposed formation of carbonic acids in CD-MOF-2 (CD = cyclodextrin).<sup>46</sup> (b) Crystallographically confirmed formation of carbamic acid pairs in dmpn-Zn<sub>2</sub>(dobpdc) (dmpn = 2,2-dimethyl-1,3-diaminopropane; dobpdc<sup>4-</sup> = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate).<sup>47</sup> (c) Proposed formation of mixed carbamic acids and ammonium carbamates in dmpn-Mg<sub>2</sub>(dobpdc).<sup>48</sup> (d) Proposed formation of metal bicarbonates in Zn(ZnOH)<sub>4</sub>(bibta)<sub>3</sub> (bibta<sup>2-</sup> = 5,5'-bibenzotriazolate).<sup>49</sup> Gray, white, red, black, dark blue, sky blue, and green spheres correspond to carbon, hydrogen, oxygen, rubidium, nitrogen, zinc, and magnesium, respectively.

pathway: the formation of both ammonium carbamates and carbamic acids (Fig. 3c).<sup>48</sup> In-depth DFT calculations and 2-dimensional SSNMR experiments support the formation of ammonium carbamate chains that interact with carbamic acids *via* hydrogen-bonding in this material. The advantage of this mechanism lies in its high enthalpy of adsorption ( $\Delta H_{\text{ads}} = -74 \text{ kJ mol}^{-1}$ ) coupled with a large entropic penalty ( $-\Delta S_{\text{ads}} = 204 \text{ J mol}^{-1} \text{ K}^{-1}$ ), which reduces the temperature required to desorb CO<sub>2</sub> in a temperature-swing adsorption process to <100 °C, potentially enabling adsorbent regeneration with low-grade steam.<sup>47</sup> These thermodynamic parameters enable

adsorbent regeneration with an estimated energy of  $2.5 \text{ MJ kg}^{-1}$  CO<sub>2</sub>, comparable to the best-in-class aqueous amine scrubbers such as Mitsubishi KS-1 ( $2.4 \text{ MJ kg}^{-1} \text{ CO}_2$ ).<sup>10,64</sup> Therefore, this finding highlights the potential to overcome thermodynamic trade-offs of carbon capture processes by tuning the adsorption pathway. In addition, this adsorption mode leads to faster adsorption kinetics than ammonium carbamate formation in related materials and a high non-competitive CO<sub>2</sub>/N<sub>2</sub> selectivity (880) under the conditions relevant for CO<sub>2</sub> capture from coal flue emissions (150 mbar CO<sub>2</sub>, 750 mbar N<sub>2</sub>, 40 °C).<sup>65</sup>









