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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 (CO₂) emissions. Despite this pressing need, we still rely on century-old technology—aqueous amine scrubbers—to selectively remove CO₂ from emission streams. Amine scrubbers are effective due to their exquisite chemoselectivity towards CO₂ to form ammonium carbamates and (bi)carbonates, but suffer from several unavoidable limitations. In this perspective, we highlight the need for CO₂ 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 CO₂ 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 CO₂ capture chemistry into next-generation technologies.

Introduction

Rising atmospheric levels of carbon dioxide (CO₂) are the major contributor to global climate change, with annual emissions approaching 40 billion tonnes.¹ Nearly two-thirds of anthropogenic CO₂ emissions result from the combustion of fossil fuels, including coal and natural gas, for the global production of electricity.¹ In addition, CO₂ emissions are an inevitable by-product of other industrial processes, including the production of cement, steel, and natural gas.¹ 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 CO₂ is selectively removed from low-concentration emission streams (4–15% CO₂) prior to its permanent storage underground or conversion into more valuable products.²

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 CO₂ capture from flue emissions on large scale (Fig. 1a).³ Aqueous amine scrubbers are effective because amines react selectively with CO₂ 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.⁴ The captured CO₂ 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 CO₂ captured in an actual process) while minimising regeneration energies (*i.e.* the total energy input needed to heat the material and desorb CO₂).⁵ However, aqueous amine scrubbers are still faced with several challenges, including: (1) low capacities (<3 mol CO₂ per kg solution or <15 wt%) due to dilution of the corrosive amines with water;⁶ (2) poor oxidative stability of amines towards O₂; and (3) degradation in the presence of contaminants such as SO₂, which reacts with amines similarly to CO₂.⁷ In addition, one aspect of aqueous amine scrubbers has remained largely constant: the products of their reaction with CO₂.⁸ This restriction generally leads to high regeneration energies (≥2.4 MJ kg⁻¹ CO₂) and CO₂ desorption temperatures (>100 °C), greatly increasing the cost of carbon capture from flue emissions.^{9–11}

Amine-based materials for CO₂ capture

One promising avenue to overcome the challenges associated with CO₂ 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 CO₂ capture. (a) Traditional amine chemistry for CO₂ absorption via the formation of ammonium carbamates under dry conditions and ammonium (bi)carbonates under humid conditions.³ (b) Amine-functionalised porous silicas, where amines are either impregnated into or covalently attached to silica supports.¹² (c) Amine-functionalised ionic liquids.¹³ (d) Post-synthetically amine-functionalised zeolites.¹⁴ (e) Post-synthetically amine-functionalised metal-organic frameworks.¹⁵

(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.^{16–21} 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 CO₂ from high-concentration streams (*e.g.* crude biogas),²² many of these materials cannot remove CO₂ from humid low-concentration streams such as flue gas emissions.²³ This limitation arises because CO₂ 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 CO₂ under humid conditions is to leverage the favourable reactivity of aqueous amine scrubbers in the form of amine-functionalised sorbents (Fig. 1).^{24,25} Beginning with the first report of amine-functionalised silicas in 1992 (Fig. 1b),^{12,24} a range of amine-functionalized solid adsorbents, including zeolites (Fig. 1d),¹⁴ MOFs (Fig. 1e),^{15,19} and carbons²⁶ have been prepared. Researchers have demonstrated that amine-functionalised porous solids possess the high CO₂ 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.^{7,27} Similarly, ionic liquids (ILs) can also be functionalised with amine groups to achieve high CO₂ capacities and selectivities without the need for dilution with water (Fig. 1c).^{28,29} 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^{13,30,31} and, as confirmed recently, ammonium bicarbonates under humid conditions.³² As such, the majority of these materials still require high temperatures (>120 °C) to fully desorb CO₂, resulting in high regeneration penalties.³³ In addition, amine-functionalised silicas suffer from oxidative degradation by distinct bimolecular pathways,³⁴ as well as the irreversible formation of ureas under dry conditions.³⁵ Overcoming these fundamental limitations is critical to enabling the widespread adoption of carbon capture technologies.

New CO₂ 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 CO₂ capture at amine sites is potentially desirable because it involves reaction with CO₂ at only a single amine site, increasing the CO₂ : amine sorption





Fig. 3 New CO₂ adsorption mechanisms unlocked in MOFs. (a) Proposed formation of carbonic acids in CD-MOF-2 (CD = cyclodextrin).⁴⁶ (b) Crystallographically confirmed formation of carbamic acid pairs in dmpn-Zn₂(dobpdc) (dmpn = 2,2-dimethyl-1,3-diaminopropane; dobpdc⁴⁻ = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate).⁴⁷ (c) Proposed formation of mixed carbamic acids and ammonium carbamates in dmpn-Mg₂(dobpdc).⁴⁸ (d) Proposed formation of metal bicarbonates in Zn(ZnOH)₄(bibta)₃ (bibta²⁻ = 5,5'-bibenzotriazolate).⁴⁹ 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).⁴⁸ 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 CO₂ in a temperature-swing adsorption process to <100 °C, potentially enabling adsorbent regeneration with low-grade steam.⁴⁷ These thermodynamic parameters enable

adsorbent regeneration with an estimated energy of 2.5 MJ kg^{-1} CO₂, comparable to the best-in-class aqueous amine scrubbers such as Mitsubishi KS-1 ($2.4 \text{ MJ kg}^{-1} \text{ CO}_2$).^{10,64} 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 CO₂/N₂ selectivity (880) under the conditions relevant for CO₂ capture from coal flue emissions (150 mbar CO₂, 750 mbar N₂, 40 °C).⁶⁵



Materials Challenges



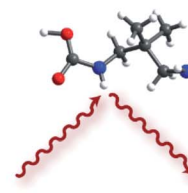
- Fast sorption kinetics.
- High capacity for competitive adsorption.
- Improved stability (H₂O, O₂, SO₂ etc.).
- Improved thermal management.

Computational Challenges



- Treat competitive sorption.
- Screen for new chemisorption modes.
- Predict thermodynamics and kinetics.
- Identify new classes of materials.

Characterisation Challenges



- Elucidate new sorption mechanisms.
- Characterise sorption in situ.
- Study realistic conditions.
- Probe kinetic, thermodynamic products.

Fig. 4 Grand challenges for next-generation sorbents for CO₂ capture.

hydrophobic adsorbophores to maximize the adsorption of CO₂ under humid conditions. However, the capacities and CO₂/N₂ selectivities reported for best-in-class physisorbents are typically lower than those reported for chemisorptive materials. Similar computational screens to predict chemisorption—for example, using a higher level of theory to account for bond-breaking and -forming processes—remain rare but have the potential to be transformative.^{63,80} Similarly, calculations that can predict chemisorption thermodynamics under realistic mixed gas conditions should lead to promising materials for real-world applications.⁷⁹ Due to the complex processes inherent to chemisorption, an additional challenge for computational analyses is to predict transition states relevant to sorption kinetics. A promising strategy to address these computational challenges may be to use machine learning to guide the search for new chemisorbent materials.⁸¹

In order to elucidate and ultimately build upon new CO₂ capture chemistry, advanced characterisation methods are also needed. These methods serve to both validate and discover new chemisorption products when unexpected sorption properties arise. Recent years have seen significant advances in the characterisation of CO₂ capture pathways through *in situ* spectroscopic and X-ray diffraction experiments.^{30,32,47,48} These experiments must now be adapted to study conditions that more closely mimic envisaged industrial applications and, in particular, must address mixed gas conditions rather than pure CO₂.^{32,48} Furthermore, experiments must not be restricted to studying static/equilibrium conditions and should probe the dynamic conditions associated with practical sorption processes.

Conclusions

New CO₂ sorption pathways such as those recently uncovered in appropriately-functionalised ILs and MOFs may offer improved performance for CO₂ capture compared to traditional sorbents, including higher capacities and lower regeneration costs. Many of these binding modes do not readily occur in aqueous solution and instead arise from the unique opportunity to precisely install chemical functional groups with a controlled spatial

arrangement and carefully tuned local environment. For many of these prospective sorbents, more work is needed to assess their sorption kinetics, selectivities, stabilities, and thermal conductivities. This mechanistically-focused line of sorbent discovery is still in its infancy, and a new generation of computational, analytical, and synthetic chemistry is needed to design transformative materials – and sorption mechanisms – for reducing anthropogenic CO₂ emissions.

Conflicts of interest

The authors declare the following competing interest: P. J. M. is listed as an inventor on several patents related to the preparation of metal-organic frameworks for CO₂ capture.

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