CO₂ Capture via Adsorption in Amine-Functionalized Sorbents

Lalit A Darunte, Krista S. Walton, David S. Sholl and Christopher W. Jones

School of Chemical & Biomolecular Engineering, 311, Ferst Dr.

Georgia Institute of Technology, Atlanta, GA, 30332, USA

Fax: (+1) 404-894-2866 E-mail: cjones@chbe.gatech.edu

Abstract:

Amine functionalized solid adsorbents are promising materials for the capture of CO₂ because of their tunability and lower heat capacity compared to liquid amine solutions. This review focuses on recent advances in the use of solid-supported amines for CO₂ capture, with emphasis on amine functionalized metal organic framework (MOF) materials. The recently reported diamine functionalized Mg-DOBPDC MOF demonstrates intriguing performance for CO₂ capture, offering a unique adsorption mechanism with favorable energetics. Stable performance for CO₂ capture under humid conditions and easy regenerability of the adsorbent are critical to the realization of practical CO₂ adsorbents. Scalable regeneration methods such as temperature swing in a CO₂ purge stream and temperature swing via steam stripping are discussed. Emerging gas-solid contacting strategies for CO₂ capture with amine adsorbents are also discussed.

1. Introduction

The concentration of CO₂ in air has increased from ~270 ppm before the industrial revolution to close to 400 ppm today [1]. The Intergovernmental Panel on Climate Change (IPCC) has forecast an increase in global temperature of 1.8° C by 2100, largely as a result of anthropogenic CO₂ emissions [2]. About half of these CO₂ emissions are from distributed sources such as transportation, with the remainder coming from concentrated sources such as fossil fuel-based power plants [3]. Research on carbon capture has primarily focused on capturing CO₂ from large point sources. Consideration has also been given to capturing CO₂ directly from ambient air (direct air capture (DAC)) [4]. All CO₂ capture technologies come with an economic penalty, and as a result lower-cost capture methods are continuously sought. Aqueous amine based technologies, which are the benchmark capture technologies, suffer from a high-energy penalty [5,6] because of the energy required to heat water during the CO₂ recovery step, which typically forms 70% of the amine solution.

Supported amine materials are an attractive class of solid adsorbents that have potential advantages relative to liquid amines [7,8]. Porous solids have intrinsically lower heat capacities than water, so they can have lower parasitic energy demands than liquid absorbents. Supported amine materials are most often employed in temperature swing adsorption (TSA) processes or similar cyclic processes, where adsorption is conducted at low temperature and desorption is induced by heating the adsorbent. Here, we review recent advances with supported amine adsorbents for CO₂ capture. Supported amine materials are particularly effective for CO₂ capture at low CO₂ partial pressures, so this review will focus on materials for CO₂ capture from streams such as flue gas and ambient air. We place an emphasis on current trends in development of these materials for practical CO₂ capture, focusing on (i) CO₂ adsorption mechanisms, (ii) novel materials (MOFs), (iii) the effect of humidity on CO₂ capture, and (iv) regeneration and practical implementation of amine sorbent materials.

Much of the work on supported amines has used ordered mesoporous oxide supports as illustrated in Figure 1 because of their excellent stability. Alumina and metal organic frameworks (MOFs) are among the other support materials that are gaining attention for use in supporting amines [8,9]. These materials have been classified into three groups based on the nature of the interaction with the support and the preparation method [7,10]. In class 1 materials, polymeric amines such as poly(ethylene imine) (PEI), are impregnated into the support's pores and have relatively weak, non-covalent interactions with the support surface. In class 2 materials, molecular amines such as aminopropyl silane (APS) are bound to the support surface through covalent bonds. In class 3 materials, *in-situ* polymerization of an amine containing monomer is used to create polyamines with both covalent and non-covalent interactions with the surface (e.g. hyperbranched aminosilicas (HAS)).

Figure 1. Classification of supported amine materials, illustrated for a silica support [7]. The schematic shows supported amines (green) in the pores of a support. Reproduced with permission from the Royal Society of Chemistry.

2. Mechanism of CO₂ capture in supported amine materials

The most common mechanism for CO₂ capture in supported amines (Figure 2) involves the formation of a zwitterion through the interaction of CO₂ and an amine, followed by deprotonation of the zwitterion by a base to produce a carbamate [11-14]. The amine efficiency, defined as the ratio of moles of CO₂ captured to moles of nitrogen in the material, is a useful metric to quantify the effectiveness of adsorbents for CO₂ capture. In the zwitterionic mechanism, a second amine typically acts as the base to produce an ammonium carbamate, giving a theoretical maximum amine efficiency of 0.5. This suggests achieving a high density of amines in close proximity to each other can improve the amine efficiency. Under humid conditions, water or hydroxide ions can potentially act as the base, leading to theoretical amine efficiencies that approach 1. There is now experimental evidence [12••] that a second mechanism producing ammonium bicarbonate can occur under humid conditions, also with a theoretical amine efficiency of 1. At low CO₂ partial pressures, amine efficiencies lower than these theoretical maxima are typically expected, depending on the equilibrium between the gaseous CO₂ and the bound states (shape of the adsorption isotherm) as well as kinetic limitations.

Figure 2. A zwitterion is formed by interaction of CO₂ with an amine, which is further deprotonated in the presence of another base to produce an alkyl carbamate [7]. Reproduced with permission from the Royal Society of Chemistry.

3. Metal organic frameworks as supports for amine sorbents

Metal organic frameworks (MOFs) are hybrid materials consisting of metal ions or metal clusters bound together through organic linkers to create a multi-dimensional porous crystalline structure. Their high porosity and chemical diversity make MOFs highly attractive candidates for gas adsorption [15]. MIL-101, MIL-100 and UiO-66 are some of the MOFs that have shown excellent stability under extreme conditions of temperature, humidity and pH [16^{••}]. Although stability is a concern for some materials, MOFs have potential as materials for CO₂ capture [17], by showing high capacities associated with high surface areas [18,19] or via novel adsorption mechanisms [20^{••}].

3.1 MOFs built with amine functionalized ligands

Use of amine-functionalized ligands in the synthesis of MOFs is one approach to decorate MOF pores with amines. For example, An et al. [21] reported that Bio-MOF-11 with pores decorated with amine and adeninate groups could adsorb 1.30 mmol/g of CO₂ at 298 K and 0.15 bar CO₂ with a heat of adsorption of ~45 kJ/mol. Couck et al. [22] reported amine-functionalized MIL-53(Al) had significantly higher CO₂ adsorption capacities than the parent, amine-free MIL-53(Al). The material also demonstrated secondary gas uptake because of contraction of the framework, but at different pressures than conventional MIL-53(Al).

Use of amine linkers coupled with another pillaring ligand has been shown to enhance both CO₂ adsorption as well as CO₂ selectivity over nitrogen. Vaidyanathan et al. [23] used 3-amino-1,2,4-triazole ligands along with oxalic acid as pillaring linkers to create a narrow pore 3-D framework that adsorbed ~3 mmol/g CO₂ at 0.15 bar CO₂ and 273 K, but showed negligible N₂ adsorption because of its narrow pore-induced diffusion resistance. In other work, Halder et al. [24] reported two double catenated Cd-based frameworks with 2-amino, 1-4 benzenedicarboxylic acid (NH₂-BDC) and 1,2-bis-(4-pyridyl-methylene) hydrazine ligands. The rigid framework adsorbed ~1.2 mmol/g CO₂ at 0.15 bar CO₂ and 273 K.

MOFs constructed with amine functionalized ligands are generally less effective for CO₂ capture compared to post synthetically modified MOFs containing amines because of delocalization of the electron pair on the aromatic amine ligand. This is manifested by relatively lower heats of adsorption (~30-40 kJ/mol) [21,22,24] for CO₂ capture over these materials compared to heats of adsorption (~60–90 kJ/mol) for post synthetically modified MOFs with amine alkyl groups.

3.2 MOFs with post synthetic amine functionalization

Post-synthetic modification of MOF frameworks with alkyl amines is another approach to improve CO₂ capture in MOFs at low partial pressures of CO₂. Some as synthesized MOFs such as MIL-101 (Cr) and Mg-DOBPDG have solvents attached to metal centers that can be removed under vacuum and/or high temperature to create unsaturated metal sites. These open metal sites can then be functionalized with diamine molecules, one amine bound to an open metal site and the other end exposed in the pore to capture CO₂. Conventional CO₂ capture with amines proceeds through the formation of ammonium carbamate, and it is important to have amines located close to each other. Open metal sites can be post-synthetically modified with small amines such as ethylene diamine (ED), dimethyl ethylene diamine (DMEN), and larger polyamines such as PEI. The MIL-101(Cr) framework has been reported to have a high BET surface area ($\sim 2600 \text{ m}^2/\text{g}$ – $4500 \text{ m}^2/\text{g}$) and outstanding water stability [25]. The framework offers open metal sites that are generated by heating the framework under high vacuum at 423 K. Hwang et al. [26] first reported the post synthetic modification of MIL-101(Cr) with ED. Later, Jiang et al. [27[•]] functionalized MIL-101(Cr) with ED (Figure 3), diethylene triamine (DETA), and diaminodipropylamine (DADPA) and studied CO₂ adsorption over the amine functionalized MIL-101(Cr). They observed that DETA showed the highest CO₂ capacity (2 mmol/g) at 0.15 bar CO₂ and 298 K. Chen et al. [28] studied MIL-101(Cr) loaded with PEI using PEI-300, PEI-1800 and PEI-10000 and found that PEI-300, at higher loadings, demonstrated the highest CO₂ capacity (4.2 mmol/g) 0.15 bar CO₂ and 298 K.

Figure 3. Functionalization of open metal sites in MIL-101(Cr) with an alkyl amine [27[•]]. Reproduced from ref. 27 with permission from John Wiley and Sons.

UiO-66 is another water stable MOF framework with weakly acidic zirconium open metal sites after evacuation of guest molecules at high temperature. Zhang et al. [29] grafted deprotonated monoethanol amine (MEA) onto the UiO-66 framework and obtained CO₂ capacities of 0.8 mmol/g at 0.15 bar CO₂ and 298 K.

Mg-DOBDC has been demonstrated to have the highest CO₂ capacity (6.1 mmol/g) at 298 K and 0.15 bar CO₂ among MOFs because of its strongly acidic open metal sites that effectively bind CO₂ [30]. The presence of open metal sites also makes the MOF susceptible to degradation in the presence of moisture [31]. Kizzie et al. [31] reported that Mg-MOF-74 lost close to 80% of its CO₂ adsorption

capacity upon exposure to 70% relative humidity. However, functionalization of the open metal sites by primary amines can enhance the water stability of MOFs and simultaneously allow for superior CO₂ capacities. Choi et al. [32] reported functionalization of Mg-DOBDC with ED and noted CO₂ capacities of 1.5 mmol/g at a CO₂ concentration of 400 ppm. Andirov et al. [33[•]] exposed ED functionalized Mg-DOBDC and the parent Mg-DOBDC to an accelerated steam testing. ED-Mg-DOBDC showed negligible loss in porosity and CO₂ capacity with some loss in the BET surface area. However, there are no studies to date that analyze CO₂ capture of ED-Mg-DOBDC after steam exposure over many cyclic adsorption-desorption cycles.

Figure 4. Functionalization of open metal sites of Mg-DOBPDC with diamines created a unique performance for CO₂ capture. Reprinted from ref 34 with permission from the American Chemical Society.

Recently McDonald et al. [34] expanded the terephthalic acid ligand to create M-4,4'-dioxido-3,3'-biphenyldicarboxylate (M-DOBPDC, M= Mg, Mn, Ni, Fe, Co and Zn) MOF materials (Figure 4) [34]. This MOF has one dimensional hexagonal pores like M-BOBDC that are 1.8 nm wide. Functionalization of the open metal sites with diamines such as N, N'-dimethyl ethylene diamine (MMEN) has equipped the framework with a unique performance for the CO₂ capture. The CO₂ adsorption isotherms show a step change as a function of the CO₂ partial pressure [34]. Mmen-Mg-DOBPDC adsorbed ~ 3 mmol/g CO₂ at air capture conditions (400 ppm) which is the highest among the current MOFs available for air capture conditions. The material also has very high amine efficiencies at low partial pressures of CO₂, which is uncommon in traditional adsorbents. The step change pressure in the CO₂ adsorption isotherm changes as a function of temperature and metal [20^{••}]. This has created an opportunity to achieve temperature swing adsorption with a relatively small temperature change [20^{••},34]. Diamines such as ED, MMEN and DMEN have been used for functionalization of Mg-DOBPDC, resulting in subtle changes in the capacities and step initiation pressures of the MOFs [34,35]. The step initiation pressure is also a function of the metal, with the order Co>Zn>Fe>Mn>Mg [20^{••}]. Mmen-Ni-DOBPDC does not demonstrate a step change in CO₂ adsorption because of the strong bonding energy between the Ni and the amine, which prevents CO₂ insertion into the metal-amine bonds.

Figure 5. Novel mechanism of CO₂ capture in mmen-Mg-DOBPDC [20^{••}]. Reprinted from ref 20 with permission from the Nature Publishing Group.

Figure 6. CO₂ adsorption as a function of temperature in Mg-DOBPDC. Reprinted from ref. 20 with permission from the Nature Publishing Group.

McDonald et al. [20^{••}] proposed a novel CO₂ adsorption mechanism whereby ammonium carbamate formation occurs via reversible insertion into the metal-amine bond, with propagation of the effect along the pore length (Figure 5). This mechanism has been reported to result in the unique CO₂ adsorption isotherm shape (Figure 6) observed for these materials. The CO₂ adsorption isotherms reveal a phase shifting behavior that is a function of the temperature and metal in the framework. Use of in-situ-FTIR, structural models and refinement against PXRD and NEXAFS [36[•]] data all support the formation

of the insertion structure along with an increase in the metal-nitrogen spacing. Calorimetric [37] and density functional theory (DFT) studies [38] further support the novel mechanism from an energetics perspective. This important family of materials will undoubtedly be explored in great detail in the future.

4. CO₂ capture under humid conditions

Humidity has been reported to have a significant impact on CO₂ capture with solid adsorbents. Humidity can influence CO₂ adsorption through both kinetic and thermodynamic factors and often precise identification of the controlling factor is difficult. Water has been shown to both enhance and hurt CO₂ adsorption, depending on the adsorbent and conditions used. Among kinetic factors, in conventional oxide-supported amine adsorbents water can alter the accessibility of amines by improving or impeding CO₂ transport through amine layers [14[•]]. Goeppert et al. [39] investigated the effect of humidity on CO₂ capture from air for PEI-impregnated fumed silica. They observed that CO₂ capture under humid conditions is enhanced at lower PEI loadings and decreased at higher PEI loadings, effects attributed to a water-induced changes in the accessibility of amines. In other studies, Mebane et al. [14[•]] hypothesized that humidity improves the accessibility of amines for CO₂ interaction.

Water can act as a base to create more alkyl carbamates or alkyl ammonium bicarbonate [12^{••},40,41]. Ammonium bicarbonates are formed at slower rate compared to more commonly observed alkyl ammonium carbonates. This makes it difficult to detect bicarbonate species through spectroscopic techniques using short adsorption and desorption times [12^{••},14]. As discussed in section 2, bicarbonate formation can significantly improve amine efficiency as one amine can theoretically capture one CO₂ molecule. Serna-Guerrero et al. studied the effect of different relative humidities on pore expanded MCM-41 functionalized with 3-aminopropylsilyl groups (APS-MCM-41) and observed that capillary condensation of water improved CO₂ adsorption using 5% CO₂ in N₂ [40]. They observed further amine efficiency improvement when the samples were prehydrated before CO₂ adsorption, suggesting the possibility of bicarbonate formation. Didas et al. [12^{••}] studied the effect of water on the amine efficiency for direct air capture conditions for different surface coverages of primary amines for APS-SBA-15 materials and observed that the maximum efficiency improvement was observed for low loadings of amines, representing sub monolayer amine coverage. They probed the nature of the adsorbed species through *in-situ* FTIR spectroscopy and elucidated the formation of ammonium bicarbonate at longer times for low APS loading materials. Formation of ammonium bicarbonate was not observed for high APS loading materials for the time duration of the experiments. This was the first demonstration of formation of bicarbonate in humid studies for supported amine materials.

In MOFs, Mason et al. [42] analyzed the mmen-Mg-DOBPDC system for CO₂ adsorption in the presence of water, CO₂ and N₂ and noted slightly increased CO₂ capture in the presence of water. The metal-amine carbamate insertion was still observed in the presence of water, which was confirmed through *in-situ* FTIR spectra. Mmen-Ni-DOBPDC, which does not show carbamate insertion in the presence of CO₂, showed a considerable increase in the CO₂ capture in the presence of moisture, possibly due to bicarbonate formation or the formation of more alkyl ammonium carbamate species.

For many MOFs [31,43], researchers have reported losses in crystallinity and BET surface area after exposure to humid conditions. Functionalization with amines is expected to improve the stability under humid conditions for MOFs with open metal sites. For amine sorbents, urea formation under dry conditions reduces the sorbent capacity but its formation under humid conditions is strongly suppressed [44], thus enhancing the stability of the adsorbent.

5. Regeneration and Process Development

Higher heats of adsorption in supported amine adsorbents compared to conventional physisorbents create favorable thermodynamics for higher capacity at very low partial pressures of CO₂, such as those found in ambient air. Higher heats of adsorption also lead to higher energy required to desorb CO₂ during adsorbent regeneration. Recovery can be achieved through pressure swing adsorption (PSA) or temperature swing adsorption (TSA). In pressure swing adsorption (PSA), the pressure change of the large volumes of gas associated with dilute gas streams may make PSA too energy intensive for cost effective carbon capture and sequestration. Also, the complete desorption of CO₂ is typically not achieved at room temperature with amine materials[45] because of chemisorbed nature of the CO₂, thereby necessitating an increase in the temperature.

Use of inert sweep gases for TSA is common in laboratory studies but is cost prohibitive in an industrial setting, as the output is a diluted CO₂ gas stream. To this end, two more practical approaches have been studied to achieve temperature swing (i) use of a pure CO₂ purge stream at elevated temperature to obtain a concentrated stream of CO₂, and (ii) use of steam for CO₂ desorption [10]. Degradation of amines through formation of urea linkages has been observed at high temperature in presence of pure CO₂ [46,47]. Sayari et al. [48,49] systematically studied the stability of different amine types and observed that primary amines deactivate by forming ureas with relative ease compared to the secondary amines and proposed isocyanate intermediate and ammonium carbamate pathways for the deactivation of amine [48]. Their studies also reported that urea-induced deactivation was not observed in humid CO₂. DFT calculations by Didas et al. [50] supported the isocyanate pathway as energetically favorable. Also, as noted previously, MM-DOBPDC (MM = Mg, Mn, Zn, Co and Fe) are promising materials because regeneration is possible with a small change in the temperature compared to traditional amine materials. This presents an opportunity to use CO₂ for desorption at much lower temperatures, with the possibility of urea induced amine deactivation significantly lower.

With steam stripping, steam provides the impetus for CO₂ desorption via both a concentration and temperature driving force and a highly enriched stream of CO₂ can be achieved at the outlet after condensation of steam. Steam stripping has also been reported to provide faster desorption kinetics [10,51]. However, the effect of the steam on the stability of the adsorbent materials is a critical factor, as water soluble PEI can in some cases leach out or reorganization of the amine materials on the support may occur [51]. Chaikittisilp et al. [52] reported that mesoporous γ -alumina supported PEI materials are more stable than mesoporous SBA-15 supported PEI materials under 24- hour accelerated steam testing and retained more than 80% of the initial CO₂ adsorption for 0.1 bar CO₂ in N₂. In further studies, Sakwa-Novak et al. [53] reported PEI leaching as the primary reason for loss in capacity for 24-hour accelerated steam testing but observed little PEI leaching up to 12 h or in extended short duration cycles. Also, it was shown that structural changes in γ -alumina through bohemite formation during the steam exposure did not have a significant impact on CO₂ adsorption for air capture conditions.

For process design, a variety of gas-solid contacting configurations have been studied. These include conventional fixed beds, which are commonly employed for lab scale studies, but are not viable for practical CO₂ capture at large scales. Among the recently studied novel contactor configurations employed for amine adsorbents, hollow fibers for flue gas capture have been described by Lively et al. [54,55], monoliths for air capture by Eisenberger [56] and fluidized beds by Zhang et al. [57] Kulkarni et al. [58] analyzed a hypothetical monolith based supported amine CO₂ capture technology and determined that parasitic heat costs associated with the heat capacity of the monoliths were a key cost factor and they suggested the use of thin-walled monoliths. They also suggested that having a high equilibrium CO₂ capacity adsorbent was needed to achieve minimal energetic costs per unit CO₂ captured. In the future, an increased emphasis on co-developing sorbents and contactors is needed, as development of adsorbents

that cannot be suitably deployed in a practical contactor will not lead to new, effective CO₂ separation technologies.

Summary

In this article, we have reviewed recent advances in amine-functionalized oxide and MOF materials for CO₂ separation from dilute gas mixtures, such as flue gas and ambient air. Porous oxide supported PEI materials are among current state of the art materials for CO₂ capture, with new MOF supported amine materials based on MM-DOBPDC showing the potential for substantial improvements in CO₂ capacity as well as CO₂ separation energetics. Better understanding of CO₂ capture under humid conditions is still needed, along with increased focus on adsorbent and process development together, such that system level design can be substantially advanced.

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