Study on the Roles of Water in Solid Amine-Based Direct Air Capture of CO₂

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Abstract. Climate change triggered by the increasing amount of CO₂ released into the atmosphere has become a global priority. Direct Air Capture (DAC) of CO₂ has been regarded as one of the disruptive technologies to realize negative emission. Among the multiple strategies employed, adsorption on solid amines is a promising choice owing to its low energy requirements. Since the water vapor ubiquitously exists in ambient air, understanding the role it plays in DAC by the amine-functionalized solid sorbents is of vital importance. Due to the diversity in amine and support features, both promotion and deterioration of water impact on CO₂ adsorption were revealed. Herein we present a multifaceted review of the trends and innovations in DAC by solid amines under humid conditions. The effect of water was discussed over four groups of materials, based on the support categories, i.e., (a) mesoporous silica, (b) mesoporous alumina, (c) mesoporous carbon and other inorganic supports, and (d) cellulose and other organic supports.

1 Introduction

A series of problems caused by the continuous acceleration of global warming have aroused great concern of the whole society about anthropogenic CO₂ emissions, and promoted the development of carbon capture, utilization, and storage (CCUS) technologies. Controlling temperature rise below 1.5°C by the end of this century requires the participation of negative emission technologies, including direct air capture with the lowest land footprints and flexible deployments. The major differences between capture from concentration sources (e.g., flue gas or industrial exhaust gas) and ambient air lies in the CO₂ partial pressure. The widely-used technology of CO₂ absorption by alkanolamine solutions like monoethanolamine was proven as less effective because of 0.04% CO₂ in air and low liquid-gas ratio. The alkali metal hydroxide-based absorption, owing to its high affinity, low volatility, and process maturity, has been employed, whereas still suffers from high energy requirement in calcination under ~800°C [1].

Compared with absorption, adsorption does not require the high latent heat of solvent, and has certain advantages in reducing equipment corrosion and resistance to degradation. In particular, for air capture scenario with large gas volume and less pollutants, adsorption technology can effectively deal with tricky problems including amine volatilization and water loss. Researchers around the world have carried out extensive and in-depth studies in the field of adsorption-based air capture. In 2010, the first-ever application of solid amine sorbents in DAC was conduct by Sayari et al., showing superiority in capture capacities and energy consumption [2]. Relevant researches were booming in the last decade, with a variety of sorbents proposed which could basically categorized into class 1–3 (Fig. 1).

The class 1 sorbents are prepared by impregnation of porous supports with amine-containing polymers or small molecules including branched/linear poly(ethylenimine) (PEI), poly(propylenimine) (PPI), poly(allylamnine) (PAA), and tetraethylenepentamine (TEPA). Both inorganic supports, e.g., silica, alumina, activated carbon, and organic ones, e.g., cellulose, polystyrene (PS) are available. The class 2 sorbents are typically prepared by grafting amine-containing small molecules, mostly aminosilane, onto pre-formed supports. 3-aminopropyltrimethoxysilane (APTES or APS), 3-(2-Aminoethylamino)propyldimethoxymethyl silane (ED), and 3-[2-(2-Aminoethylamino)ethylamino]propyltrimethoxysilane (DT) are the most commonly used. Essential feature of the supports, silica and nanocellulose as the representatives, is the reactive OH groups on the surface. Therefore aminosilane can be attached to the surface via Si–O–Si linkages. High amine loadings can be easily achieved for class 1 sorbents, whereas the weak hydrogen bond involved incurs easily leaching of the amines. Owing to the Si–O–Si bonding, class 2 sorbents are more stable with moderate amine loadings. Class 3 sorbents are originated from the idea that combines the advantages of class 1 and 2 sorbents. By in situ polymerization of reactive amine monomers on and in the silica, polyamine structure can be covalently bonded to the surface [3].
Fig. 1. The chemical structure of the polyamines or amine monomers used in synthesizing class 1–3 sorbents.

![Chemical structures of polyamines and amine monomers](image)

Water ubiquitously exists in ambient air, e.g., the annual average relative humidity in China ranges from 40%–80%. Due to its unique chemical reactivity and physical properties, water shows complex effects on solid amine-based CO₂ capture, depending on the nature of sorbents and separation variables. It is important to clarify the roles of water plays in CO₂ reaction and diffusion, for the effective choice of sorbents and processes. Water effects in CO₂ capture were documented in a few papers. While there is no multifaceted report reviewing that how water influences the air capture performance for the whole types of solid amines. This review aims to fill the gap by discussing both the promotion and deterioration of water on CO₂ uptake, with emphasis on the underlying mechanism.

2 Roles of water in direct air capture: brief comments on the amine-CO₂-water interaction

The amine-CO₂-water interaction is vital to CO₂ adsorption by solid amines. Primary and secondary amines can react with CO₂ via the zwitterion mechanism. In the absence of water, two amine moieties and one CO₂ molecule are involved in the reaction, giving one ammonium carbamate. In the presence of water, the maximum molar ratio of CO₂:amine is 1:1, since water molecule serves as the additional free base instead of amine (Fig. 2a). Tertiary amine only reacts with CO₂ via water-assisting deprotonation, forming bicarbonate or carbonate species in the presence of water. The molar ratio of CO₂:amine is 1:1 (Fig. 2b). That mechanism is also applicable for primary and secondary amines in aqueous states, whereas routinely neglected for the solid amines considering the slow kinetics [4]. Enhanced CO₂ adsorption under humid conditions can be ascribed to the formation of bicarbonate or carbamate. The co-adsorbed water could also be detrimental as it blocks the access for CO₂ approaching amines. Besides, a few studies revealed that water has positive effect through reduced kinetics restrictions, either acting as a diffusive intermediate to transport CO₂ or increasing the mobility of amine chains via a plasticization effect [5].

3 Roles of water in direct air capture: the reaction and diffusion aspects

The studies on amine-CO₂-water interaction suggested that water could have a convolutional influence on direct air capture from reaction and diffusion aspects. To elucidate that, relevant researches were reviewed separately by the differences in supports. Key properties concerning DAC were explained as below: (I) adsorption capacity: the amount of CO₂ adsorbed. (II) amine efficiency: the mole of CO₂ captured per mole of amine functional group.

3.1. Mesoporous silica

Mesoporous silica is comprised of honeycomb-like structures with mesoporous channels that enables impregnating or tethering active groups onto internal surfaces. Questioning on how water influences the CO₂ adsorption emerged with the first proposal of PEI-impregnated mesoporous silica for flue gas CO₂ capture. Up to 50% increase in CO₂ capacity were achieved by introducing water content (0–15.5%) in the feed gas of CO₂ (12.6%–14.9%). Branched PEI reacted with CO₂ in the presence of water to form carbamate and bicarbonate species but not synchronously because of quicker CO₂ uptake than water. The CO₂ capacity enhancement was ascribed to the water-involved 1:1 stoichiometric adsorption, especially for the tertiary amine groups whose reactivity was endued by water [6].

![Mechanisms for reaction of amines with CO₂ and water](image)
The effect of moisture on the CO$_2$ adsorption was related to multiple parameters, including amine structure, amine loading, support hydrophilicity, CO$_2$/H$_2$O content, and temperature. The 10% CO$_2$ uptakes of functionalized silica with the same loading of linear or branched PEI were similar at dry condition, e.g., 1.36 and 1.45 mmol/g for linear and branched PEI, respectively at 25°C. While promoting function of water on CO$_2$ capacity was found more significant for the linear PEI than the branched one (195% v.s. 108%). Under ultra-high humidity, the branched PEI suffered from CO$_2$ capacity decrease, in contrast to its linear counterpart which remained being facilitated probably due to more hydrophobic nature [7].

Using PEI-impregnated CARiACT G10 silica, Monazam et al. reported a linear increase of 10% CO$_2$ uptake with humidity at 60°C. 85.6% increase was due to lower crosslinking degree of amine, and bicarbonate formation either from carbamate hydrolysis or direct reaction of PEI with CO$_2$. Humid CO$_2$ adsorption on the prehydrated sorbents followed a two-step mechanism, i.e., a rapid regime of chemisorption on surface and a slow regime of bulk diffusion within aminopolymer. The equilibrium time prolonged with increasing water content in the gas stream, as deeper penetration into PEI layer comes along with larger proportion of slow regimes [8].

Zhang et al. investigated the CO$_2$/H$_2$O adsorption on linear and branched PEI functionalized silica (Fig. 3). The CO$_2$ capacity of linear PEI-loaded silica was improved by 2-fold at medium humidities. The enhancement was more pronounced at higher amine loadings (>44.5%) and lower temperature (<70°C), which implies that the major contribution of water lies in mass transfer. Water promotion nearly changed as CO$_2$ concentration lower from 10% to 1%, despite a little more competitive adsorption at high humidity [9]. In more dilute cases like 0.5%CO$_2$ in the feed gas, CO$_2$ uptake could still increase from 1.33 to 2.28 mmol/g by introducing 90%RH at 25°C [10].

Difference in CO$_2$ partial pressure between flue gas capture and DAC cases caused a significant reduction of CO$_2$/H$_2$O ratio, whereas positive effect of water did not seem to change. Sayari et al. examined the 400 ppm CO$_2$ uptake by PEI impregnated MCM-41 sorbent under a wide range of humidity (0–88%RH). CO$_2$ capacity steadily increased from 2.19 to 2.95 mmol/g. 35% increase in CO$_2$ capacity was associated with partial change from carbamate to bicarbonate formation. Plateau in enhancement arose when RH approaching 60%, and noticeable increase in CO$_2$ capacity did not occur at higher RHs [11]. Using PEI-functionalized cellulose acetate/silica fiber sorbent, in the presence of 385–395 ppm CO$_2$ with 85% RH at 35°C, Jones et al. reported 78% and 171% increases in breakthrough and pseudo-equilibrium capacities, respectively compared to dry condition. The more than doubled CO$_2$ capacity suggested the release of PEI reactivity, as water not only enhances the mobility and flexibility of molecular chain to expose more amine sites, but also facilitates carbonate species formation [12].

The hierarchical silica with bimodal meso/macroporosity was proposed as substrate to achieve a high PEI loading of 72.4%. Moisture (19%RH) increased the 400 ppm CO$_2$ uptake from 2.6 to 3.4 mmol/g at 30°C. It was suggested that water could enhance the aminopolymer chain mobility by weakening inter or intra-molecular hydrogen bonds and dipole−dipole interactions. Besides, bicarbonate formation in the moist air might not only increase the CO$_2$ capacity, but also facilitate mass transfer due to less aminopolymer chain cross-linking compared to carbamate formation [13]. Water-improved amine accessibility was also found in PEI impregnated MCFs. With 2% water content in feed gas, the highest enhancement factor was 1.53 at 33°C as CO$_2$ uptake increasing from 1.54 to 2.36 mmol/g. Temperature rise caused enhancement factor decline to 1.22 at 58°C [14]. Moisture higher than 3% appeared to be less effective and even detrimental to CO$_2$ adsorption, as it might present additional diffusion barrier to amines especially at high amine loadings [15].

Considering higher CO$_2$ affinity, the all primary amine-comprised PAA-impregnated MCF was proposed and achieved capacity of 0.86 mmol/g for 400 ppm CO$_2$, with amine loading of 7.24 mmol/g at 25°C [16]. A further increase of amine loading to 12.2 mmol/g, whereas resulted in negligible CO$_2$ uptake in dry air. That sorbent could be activated by moisture, as the dry and pre-humidified sample achieved CO$_2$ capacity of 11.8 and 12.6 mmol/g, respectively at 60%–70%RH. Densely loaded sorbents usually suffers from high diffusion resistance, and water might act as a plasticizer, loosening the polymer network, and allowing for penetration of CO$_2$ [17].

Owing to the co-existence of primary and secondary amine groups in TEPA and its structural simplicity, the mechanism of humid CO$_2$ adsorption on TEPA-immobilized silica was explored by in situ IR. CO$_2$ was adsorbed on the primary amine sites as ammonium carbamate, and on the more hydrophilic secondary amine sites as carbamic acid. Water adsorbed could displace the amine from the surface silanol groups to release the reactivity. Moreover, the formation of carbamic acid on
the secondary amine could be facilitated by proton transfer from ammonium ion to carbamate via neighboring water molecules, and thus the 1:1 stoichiometric reaction could contribute to CO₂ capacity increase in the presence of moisture [18].

Sorbents containing single amine types or sterical hindrance structure were studied with spectroscopic and molecule scale method deep into amine-CO₂-water interaction. For APS-based sorbents in dilute CO₂ capture. Carbamate species were the main product at dry and humid condition, as evidenced by in situ IR [18].

Besides, the forming of surface-bonded carbamate were far slower than free carbamate. In the presence of moisture, the bonded carbamate could hydrolysis to liberate the hydrogen-bonded amines, and thus contributed to higher moist CO₂ uptake than dry condition [19].

Existence of carbamic acid products were suspected in studies decades ago, although it was until the usage of FT-IR spectra, the mechanism of CO₂/H₂O sorption on APS-modified silica considering the amine coverage was revealed. Moisture was found always advantageous to CO₂ adsorption, while became less effective as amine coverage decreases, especially at ultralow pressure. The only product species detected were carbamates for sorbents with high amine loading, under both dry and humid conditions. Facilitated CO₂ adsorption by moisture was related to the reduced kinetic restrictions. Only at long time scale and low amine loading were the bicarbonate suspected, suggesting the poor kinetics of its formation and less contribution to the capacity [20].

Table 1. Amine impregnated or grafted silicas for DAC under dry and humid conditions.

<table>
<thead>
<tr>
<th>Support</th>
<th>Amine</th>
<th>Variables</th>
<th>CO₂ capacity (mmol/g)</th>
<th>H₂O enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>PEI</td>
<td>40%PEI, 25°C, 0%RH</td>
<td>2.19</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40%PEI, 25°C, 88%RH</td>
<td>2.95</td>
<td>1.35</td>
</tr>
<tr>
<td>Fumed silica PEI</td>
<td>33%PEI, 25°C, 0%RH</td>
<td>1.18</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>33%PEI, 25°C, 67%RH</td>
<td>1.77</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50%PEI, 25°C, 0%RH</td>
<td>1.71</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50%PEI, 25°C, 67%RH</td>
<td>1.41</td>
<td>0.83</td>
</tr>
<tr>
<td>Silica PEI</td>
<td>72%PEI, 30°C, 0%RH</td>
<td>2.60</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>72%PEI, 30°C, 19%RH</td>
<td>3.40</td>
<td>1.31</td>
</tr>
<tr>
<td>CA silicate fiber PEI</td>
<td>42%PEI, 35°C, 0%RH</td>
<td>0.59</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>42%PEI, 35°C, 85%RH</td>
<td>1.60</td>
<td>2.71</td>
</tr>
<tr>
<td>SBA-15 Ph-ED</td>
<td>35°C, 0%RH</td>
<td>0.78</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>35°C, 30%RH</td>
<td>1.42</td>
<td>1.81</td>
</tr>
<tr>
<td>SBA-15 APS</td>
<td>25°C, 0%RH</td>
<td>0.09</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°C, 80%RH</td>
<td>0.13</td>
<td>1.44</td>
</tr>
<tr>
<td>SBA-15 DT</td>
<td>25°C, 0%RH</td>
<td>0.77</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°C, 60%RH</td>
<td>1.10</td>
<td>1.42</td>
</tr>
<tr>
<td>Silica gel APS</td>
<td>25°C, 0%RH</td>
<td>0.08</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°C, 60%RH</td>
<td>0.17</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°C, 80%RH</td>
<td>0.17</td>
<td>2.26</td>
</tr>
<tr>
<td>MCM-41 DT</td>
<td>25°C, 0%RH</td>
<td>0.90</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25°C, 64%RH</td>
<td>1.40</td>
<td>1.56</td>
</tr>
</tbody>
</table>

In stark contrast to primary or secondary amine, tertiary amine itself was considered as non-reactive in dry CO₂ since it could not be deprotonated. Therefore formation of bicarbonate is the exclusive route for tertiary amine. Small IR peaks (1645, 1360 cm⁻¹) related to bicarbonate was found when tertiary amine grafted SBA-15 reacts with dry CO₂ due to the residual physisorbed water. Studies showed that the bicarbonate product was usually missed by the conventional ¹³C CPMAS, while Bloch decay could detect a single narrow resonance assigned to bicarbonate for tertiary amine-modified SBA-15 [21].

Lee et al. studied the CO₂ chemisorption of sterically hindered amines (a primary or secondary amine with a secondary or tertiary α-carbon) modified silicas in the presence of water. In situ FTIR revealed that both the sterically hindered and unhindered amines could form carbonate or carbamic acid under dry condition, despite weaker chemisorbed species of the hindered one. Under humid condition, the sterically hindered amines are prone to form bicarbonate, as unfavorable steric interaction between the COO⁻ group and the methyl/methylene substituents on the α-carbon attributing to the carbamate’s poor stability. The preferential formation of bicarbonate might also due in part to kinetic factors, since CO₂ diffusion to the amine sites could be blocked by steric hindrance on the α-carbon (carbamate or carbamic routes),
and the nitrogen was more likely protonated by water (bicarbonate route). When compared to the solution of which ionic species could be stabilized through solvation or hydrogen bond, the extent of bicarbonate formation on solid amines was much lower [25].

Possible reactions involved in CO2 chemisorption on amine functionalized mesoporous silica under dry (Eq. 1–10) and humid cases (Eq.11–20) are listed as below. R1NH2, R1R2NH, and R1R2R3N denote primary, second, and tertiary amines, respectively.

\[
\begin{align*}
2R_1NH_2 + CO_2 & \rightarrow R_1NH_3^+ + R_1NHCOO^- & (1) \\
2Si-OR_1NH_2 + CO_2 & \rightarrow Si-OR_1NH_3^+ + Si-OR_1NHCOO^- & (2) \\
Si-OR_1NH_3^+ + CO_2 + Si-OH & \rightarrow Si-OR_1NHCOO^- \cdot Si + H_2O & (3) \\
Si-OR_1NH_2 + CO_2 + Si-OH & \rightarrow Si-OR_1NHCOOH \cdots OH-Si & (4) \\
Si-OR_1NH_2 + CO_2 & \rightarrow Si-OR_1NHCOOH & (5) \\
2R_1NH_2 + CO_2 & \rightarrow R_1NH_3^+ + R_1NHCOO^- & (6) \\
2Si-OR_1R_2NH + CO_2 & \rightarrow Si-OR_1R_2NCOO^- & (7) \\
Si-OR_1NH_3^+ + CO_2 + Si-OH & \rightarrow Si-OR_1NHCOOH \cdots Si + H_2O & (8) \\
Si-OR_1R_2NH + CO_2 + Si-OH & \rightarrow Si-OR_1R_2NHCOOH & (9) \\
Si-OR_1NH_2 + CO_2 + H_2O & \rightarrow Si-OR_1NHCOOH \cdots Si + H_2O & (10) \\
R_1NH_2 + CO_2 + H_2O & \rightarrow R_1NH_3^+ + HCO_3^- & (11) \\
R_1NH_2 + CO_2 + H_2O & \rightarrow R_1NHCOOH + H_2O & (12) \\
Si-OR_1NH_2 + CO_2 + H_2O & \rightarrow Si-OR_1NHCOOH \cdots Si & (13) \\
Si-OR_1NH_2 + CO_2 + H_2O & \rightarrow Si-OR_1NHCOOH \cdots Si + H_2O & (14) \\
R_1NH_2 + CO_2 + H_2O & \rightarrow R_1NH_3^+ + HCO_3^- & (15) \\
R_1NH_2 + CO_2 + H_2O & \rightarrow R_1NHCOOH + H_2O & (16) \\
Si-OR_1NH_2 + CO_2 + H_2O & \rightarrow Si-OR_1NHCOOH \cdots Si & (17) \\
Si-OR_1NH_2 + CO_2 + H_2O & \rightarrow Si-OR_1NHCOOH \cdots Si + H_2O & (18) \\
R_1R_2R_3N + CO_2 + H_2O & \rightarrow R_1R_2R_3NH^+ + HCO_3^- & (19) \\
Si-OR_1R_2R_3N + CO_2 + H_2O & \rightarrow Si-OR_1R_2R_3NHCOOH \cdots Si & (20)
\end{align*}
\]

3.2 Mesoporous silica

Alumina supports are more stable than silica when exposed to steam, therefore amine functionalized alumina was preferred when steam was used in regeneration. Studies of water-related issue focus on the stability as DAC sorbents treated with steam.. PEI impregnated alumina and silica underwent 24h steam treatment at 105°C, and alumina supported material turned out to be much more stable with 74.8% of its CO2 capacity at 400 ppm retained, in contrast to 18.7% for silica supported one. The discrepancy was related to mild structural change of PEI impregnated alumina and drastic collapse of mesostructured of silica, although the supports have comparable stability exposed to steam [26]. The oxidation stability of alumina supported amine sorbents in the presence of moisture was investigated by Bali et al. When treated with humid flow of 21% oxygen at 110°C for 20 h, the 10% CO2 capacity of PEI impregnated silica drastically decreased by 70% from 1.87 to 0.56 mmol/g, whereas only 7.5% reduction to 1.73 mmol/g relative to fresh sample was found in PAA impregnated silica [27].

3.3 Mesoporous carbon and other inorganic supports

Mesoporous carbon functionalized with PEI was employed in dilute and ultra-dilute CO2 capture, the CO2 capacity gains due to 80%RH for 5000 ppm and 400 ppm CO2 were 21.3% and 14.7%, respectively. Less profound improvement at 400 ppm was ascribed to the abated CO2/H2O selectivity [28]. By loading 67% branched PEI onto Mg-Al-CO3 layered double hydroxides (LDHs), the sorbent with abundant mesopores and broad pore size distribution could have adsorption capacity of 1.16 mmol/g, at 25°C under 400 ppm CO2. Up to 50% increase of CO2 uptake by the PEI-impregnated LDHs were found with humidified CO2 stream, higher than the similar LDHs grafted with TRI (36.7%). The change of product to ammonium carbonates and the LDHs’ prevention of amine access blockages contributed to the water-facilitated CO2 adsorption. In contrast to a 14% loss of CO2 capacity after 20 cycles under dry condition, the amine modified LDHs were stabilized when regenerated using hummid nitrogen purge [29].

3.4 Cellulose and other organic supports

The employment of nanofibrillated cellulose (NFC) as support in amine-based CO2 sorbent was suggested by Steinfeld et al. The 400 ppm CO2 capacity of APS-grafted NFC varied from 0.36 to 0.65 mmol/g for temperature range of 10–30°C and relative humidity range of 20%–80%, with evident promotion of water on CO2 capacities revealed. Compared to water adsorption, both the capacity and kinetics of CO2 adsorption were much lower, indicating rate controlling mechanism determined by diffusion and surface reaction with amine moieties [30]. Mutual interactions between CO2 and water during co-adsorption on APS-grafted NFC were investigated. The 10% and 400 ppm CO2 capacity increased from 2.26 and 1.11 mmol/g to 2.54 and 2.13 mmol/g, respectively, in the presence of 2.55 kPa water vapor (90%RH) at 23°C. The more significant role water plays under low partial pressure of CO2 was presumably ascribed to differed diffusion resistances. Besides, the water capacities were merely affected by the presence of 45 Pa CO2, as abundant adsorption sites for water, e.g., silanol group, free cellulose hydroxyl group, existed apart from amine-associated sites [31].

The 40% PEI-immobilized poly(methyl methacrylate) (PMMA) sorbents exhibited uptake of 2.50 mmol/g in pure CO2 stream at 40°C, and further increased to 3.60 mmol/g as 2% water vapor (25.5%RH) involved [32]. In ultra-dilute case, the saturation capacity for 400 ppm CO2
of 50% PEI-loaded macroporous PMMA resins was 1.96 mmol/g. Relative humidity of 10% enhanced the CO2 capacity by 61.2% while excess humidity could have a negative influence. The inverted-V trend of CO2 uptake response to humidity was similar under elevated CO2 concentration, e.g., 5000 ppm, with the optimal RH and enhancement factor shifting to 40% and 75.6%, respectively. Compared to cellulose, a stronger competitive adsorption on PMMA-based sorbents was found where CO2 and water share the same adsorption sites [33].

4 Conclusions

Water ubiquitously exists in the ambient air. Understanding the role water plays in solid amine-based CO2 capture was important for developing DAC materials and processes. The CO2 adsorption is generally facilitated by water, making solid amines one of the most promising DAC sorbents under real conditions. In the presence of moisture, CO2 reacton with solid amines containing primary or secondary amine groups could shift from carbamate (CO2:N=0.5) to bicarbonate formation (CO2:N=1), resulting higher capacities. Moreover, “inactive” tertiary amines could only react with CO2 in humid conditions. The enhance CO2 diffusion was also revealed as water could increase the mobility of aminopolymer chain and acting as a diffusive intermediate. The negative influence of water usually emerged at high humidity, and it may stem from competitive CO2/H2O adsorption or the blockage of CO2 access to amines.

Having obtained the water effect on direct air capture under complex variables including amine/support structure, amine loading, CO2/H2O content, and temperature, choices of sorbent, either from reaction or diffusion perspectives, are easier to be made. It also sheds light on the development of novel materials based on the underlying amine-CO2-water mechanism. Another water-related issue which does not addressed in this review, i.e., the energy penalty of moisture removal in regeneration, is also important in large-scale demployment of DAC and can be further discussed.

References


