

# Chemisorption and regeneration of amine-based CO<sub>2</sub> sorbents in direct air capture



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## ABSTRACT

Sustainable Direct Air Capture (DAC) of CO<sub>2</sub> is a key issue in negative carbon technologies and is essential to return CO<sub>2</sub> concentrations to pre-industrial revolution levels. In DAC technology, amine-based solid chemisorbent materials have received great attention due to their low corrosivity, high adsorption capacity and cycling stability. This review summarizes the preparation methods and performance characteristics of current amine-modified sorbents, including the type of amine-based loading, the effect of porous support structure, amine-based MOFs and support-free polyamine sorbents. The adsorption capacity, adsorption kinetics, regeneration energy and cycling stability of these sorbents were compared in details. Meanwhile, the influencing factors of the chemisorption performance were also analyzed, including different amine groups, humidity, temperature and oxygen in air. In addition, regeneration technology directly affects the energy consumption and economic feasibility of the DAC system, but the current discussion and summary of this aspect is relatively rare. Therefore, this review evaluates four low-energy CO<sub>2</sub> sorbents regeneration routes and analyzes their technical and economic feasibility. Finally, this paper briefly outlines the future challenges and research interests in the development of industrialized DAC technology.

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## 1. Introduction

The accumulation of greenhouse gases is the main cause of global warming, and CO<sub>2</sub> is widely considered to be the most important part of global greenhouse gas emissions, accounting for more than 80% of global greenhouse gas emissions [1,2]. The large-scale deployment of carbon capture and storage (CCS) technologies are the most effective way to mitigate the greenhouse effect and can contribute to effective carbon reduction. Traditional CCS technology is implemented on point sources of CO<sub>2</sub> emissions, such as coal-fired or gas-fired power plants (i.e., point-source carbon capture (PSCC)), which can effectively reduce CO<sub>2</sub> emissions. But the latest report from Working Group III of the Intergovernmental Panel on Climate Change (IPCC) suggests that if the atmosphere is to be stabilized at twice pre-industrial levels (CO<sub>2</sub> concentrations of about 430–530 ppm), it will meet the “1.5 °C” target recommended

by the Intergovernmental Panel on Climate Change. It is not enough to significantly reduce carbon dioxide emissions into the atmosphere, but it is more necessary to develop negative carbon emission technology and actively remove carbon dioxide from the air [3]. Direct air capture (DAC) is one of the few potential negative emissions technologies (NETs), a concept first proposed by Lackner et al., in 1999 to mitigate climate change [4]. As one of the technologies in NETs, DAC technology has the potential to eliminate past emissions, can restore atmospheric CO<sub>2</sub> concentrations to optimum levels below 350 ppm, and reduce global temperatures to pre-industrial times [5].

The advantage of the DAC as a unit is that its location flexibility makes the technology location-independent and independent of centralized emission sources, which is important for compensating distributed, mobile CO<sub>2</sub> emissions and providing carbon leakage insurance [6,7]. Also in terms of commercialization, DAC technology is more likely to achieve large-scale global application rather than the current fixed-position application similar to PSCC. The practical application of any technology requires a trade-off between performance and cost, and achieving industrial production at the factory line level is key to reducing the cost of the technology.

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Producing small CO<sub>2</sub> DAC devices that are targeted to meet the needs of businesses or individuals can bring DAC technology to maturity sooner. As the core of DAC technology is the sorbents material, the production cost and regeneration cost of sorbents is the largest component of the technology cost, so it is very important to study the high adsorption capacity, high stability, and low cost of sorbents.

Sorbents for CO<sub>2</sub> capture applications include physical and chemical sorbents [8,9]. However, it is believed that the adsorption heat of physical sorbents is low [10]. Due to the extremely low CO<sub>2</sub> concentration (about 415 ppm at present) in the air capture process, the CO<sub>2</sub> concentration is about 300 times lower than that found in the typical coal-based flue gas, so the pure physical sorbents usually show poor adsorption performance at low CO<sub>2</sub> partial pressure, and the chemical sorbents have been proved to be more effective for the DAC process [11].

The chemisorption of CO<sub>2</sub> mainly includes alkali metal carbonates and amine-based sorbents. Due to the high CO<sub>2</sub> desorption and regeneration temperature (800–1000 °C), alkali metal carbonates have high energy consumption and cost in practical applications, limiting their large-scale application range. On the other hand, amine-based adsorbents have rich and adjustable surface and interface chemical properties, which can achieve better selectivity and rapid capture ability in the DAC applications. Through optimized material design, amine-based adsorption materials typically have lower unit energy consumption during the CO<sub>2</sub> adsorption and desorption cycle of DAC, thereby reducing the cost of large-scale use. Also, solid sorbents are usually easier to handle and have a high CO<sub>2</sub> capture capacity. Recent research on amine-based solid sorbents is increasing, so it is necessary to review these sorbents as a whole [12–14].

Therefore, this review will describe the progress of research on amine-based solid CO<sub>2</sub> sorbents, the impact of multiple influencing factors on the capture system, and a variety of advanced regeneration systems in which CO<sub>2</sub> capture sorbents are at the core of DAC technology. Fig. 1 shows a schematic diagram of solid sorbent-based DAC technology for CO<sub>2</sub> capture.

## 2. Synthesis of amine-based solid sorbents for DAC applications

### 2.1. Three classes of different amine loading method

By far, the most reported studies describing sorbents for DAC have focused on the use of solid support amine materials. In loaded amine materials, chemical reactions between CO<sub>2</sub> and amines form strong bonds that allow significant uptake even at low partial pressures of CO<sub>2</sub> [15]. As a result, the adsorption heat and selectivity for CO<sub>2</sub> is higher than that of physical sorbents. This property makes amine-based solid sorbents well suited for DAC. Amine-based sorbents were previously classified into three categories [10,16]: Class 1 sorbents, prepared by impregnating amines into the pores of the support [17–19]. However, most regeneration systems are still temperature swing regeneration in which the low molecular weight amines are easily degraded away [20]; Class 2 sorbents, prepared by chemically grafting amine functional groups onto the support surface to stabilize the sorbents during regeneration, and typically Class 1 sorbents have a higher capacity than Class 2 sorbents because of their higher amine content [21,22]; Class 3 sorbents, consisting of inorganic support and a chemically grafted polyamine component, which are prepared by *in situ* polymerizations of amine-based monomers [23–26]. The working capacity of these sorbents is higher than that of the class 2 amine sorbents because they contain more amines and they exhibit good regeneration in continuous operation due to the covalent linkage of the amines to the sorbents. The advantages of Class 3 sorbents are ease of synthesis, potential cost effectiveness, and stability over multiple cycles [26]. Fig. 2 shows a schematic diagram of these three types of sorbents.

### 2.2. Amine-based sorbents with different porous structure supports

When studying physical sorbents, CO<sub>2</sub> uptake can easily be related to structural properties. For example, pore size plays a major role in the adsorption performance of microporous sorbents

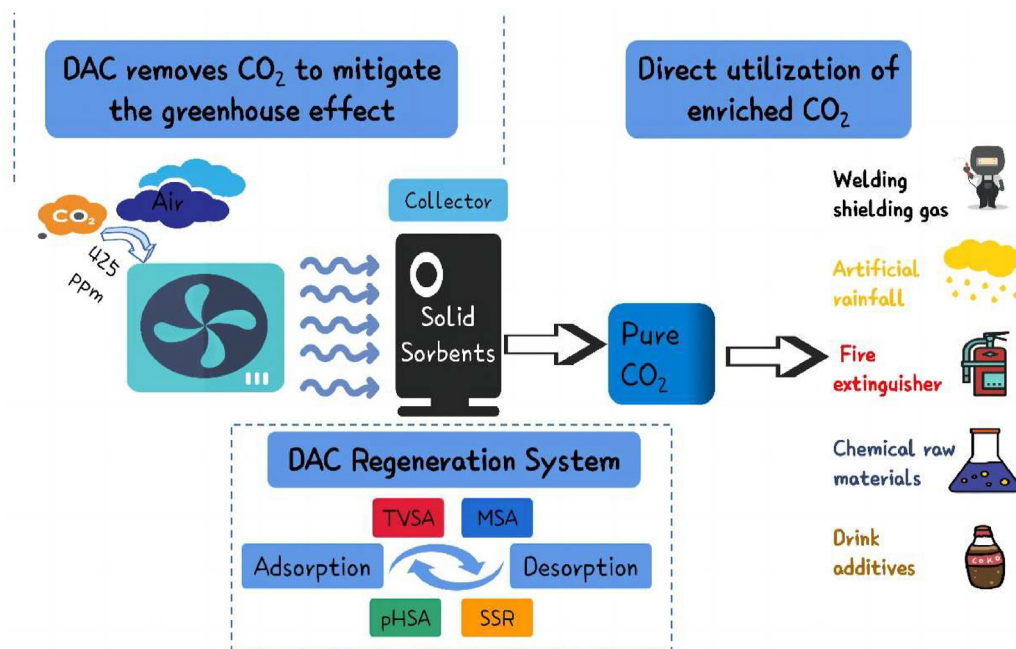


Fig. 1. Schematic diagram of solid sorbent-based DAC technology.

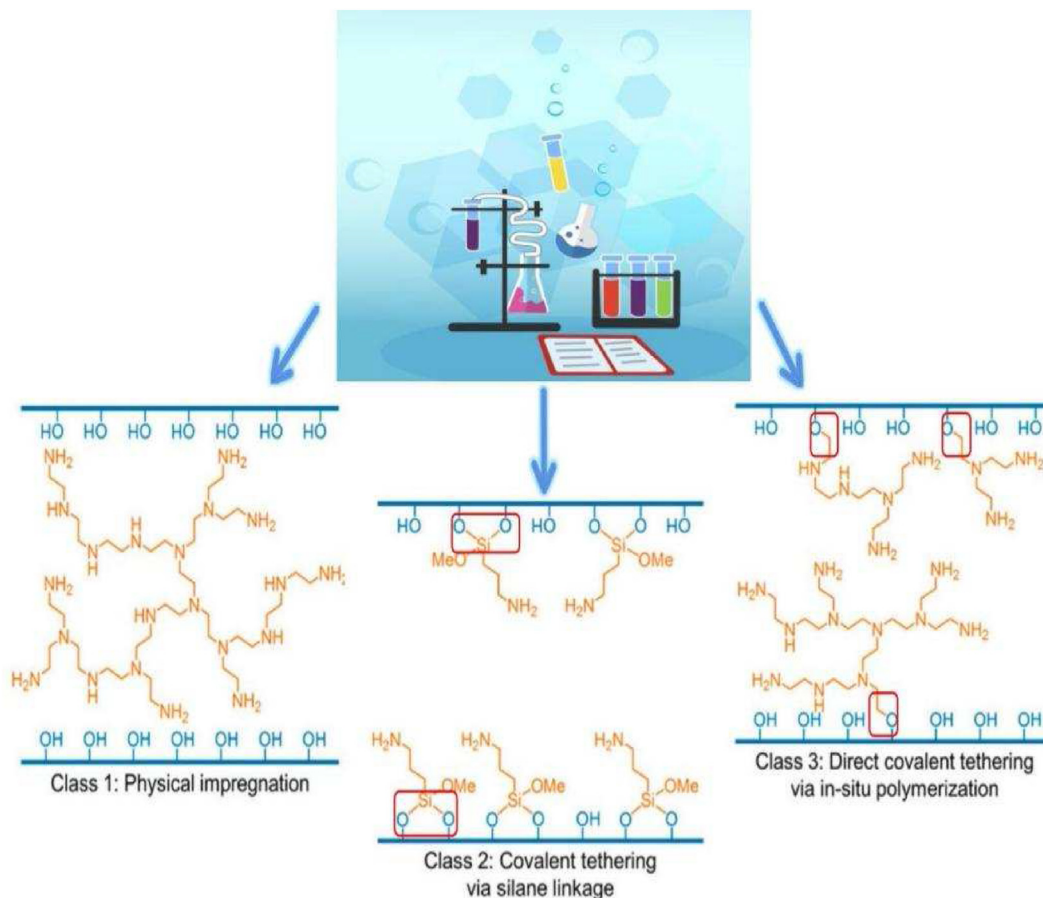


Fig. 2. Schematic diagram of three types of amine sorbents.

[27,28]. However, for chemical sorbents, the contribution of the pore size structure to the adsorption is much smaller, and the chemical reaction dominates the adsorption. The support of choice in this case is usually a mesoporous or microporous structured material, and they are often used to provide a suitable loading space for the amine active site so that CO<sub>2</sub> can chemically react with the amine site in the material. The most common supports in amine-based sorbents are inorganic oxides, e.g., silica and alumina. In addition to that, there are other porous materials such as nanofibrillar cellulose, carbon-based materials, porous polymers, layered double hydroxide, and MOFs as supports in combination with various types of amino compounds, and the resulting composites have their unique advantages for applications in the DAC field.

### 2.2.1. Amine-based sorbents with silicon/aluminium oxide supports

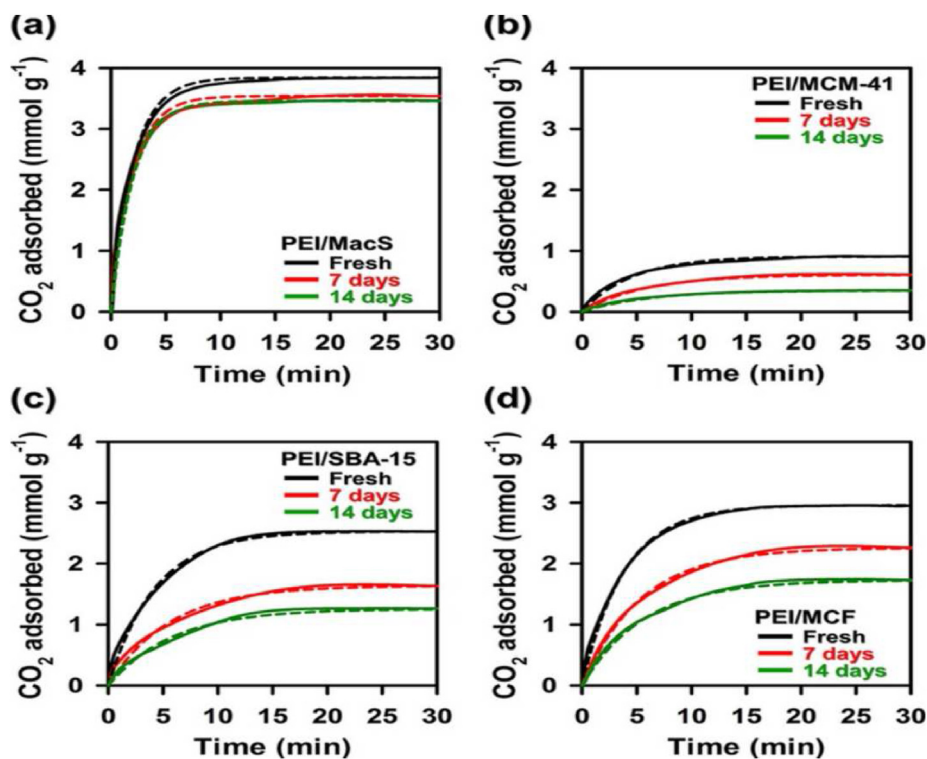
Silicon dioxide or alumina is a high specific surface area material with mesopores or macropores and is often used as a support for amine-based sorbents. The advantages of inorganic oxide amine-based sorbents include relatively low cost of precursors, simple preparation process, and potentially high amine loading. The mesoporous silica is particularly attractive support due to its specific surface properties, such as specific surface area and structure [29–32].

Due to several disadvantages inherent in silicate supports, for example, silica undergoes significant structural changes and loses its ability to trap carbon dioxide when exposed to water vapor [33]. Researchers have developed alumina supports that overcome these shortcomings [32,34,35]. Drage et al. [36] found that under drying

conditions above 135 °C, CO<sub>2</sub> reacts with two amine groups in a urea synthesis reaction that is difficult to reverse. Ultimately, this process leads to the irreversible decomposition of PEI to urea, which limits the stability of amine-based CO<sub>2</sub> sorbents. Sorbents regenerated with water vapor (at temperatures below 110 °C) can avoid this irreversible decomposition [37], but cannot completely prevent the formation of urea [38]. Exhaust gases from industrial processes are typically around this temperature, steam regeneration or vapor extraction is a convenient method of thermal regeneration. Steam also avoids drying conditions by adding water rather than removing it, and it eliminates the significant energy loss associated with evaporation of water adsorbed on the material during exposure to open air. Unfortunately, porous silica, such as MCM-41, Santa Barbara amorphous (SBA-15), and mesoporous foam (MCF), is reported to be unstable in water vapor [39], especially in the presence of hydroxide, which can lead to the collapse of the silica pores and associated CO<sub>2</sub> adsorption capacity is lost (Fig. 3). Due to the crystalline nature and lower hydrophilicity of alumina supports, they are more resistant to structural changes and degradation during water vapor regeneration [34]. The regeneration capacity of mesoporous alumina-loaded PEI composites and PEI-impregnated SBA-15 sorbent under water vapor extraction conditions were compared. After accelerated treatment with water vapor at 105 °C for 24 h, it lost 25.2% of its CO<sub>2</sub> adsorption capacity, while the silica-based sorbent lost 81.3% under similar conditions.

### 2.2.2. Amine-based sorbents with nanofibrillar cellulose supports

Gebald et al. [40] discovered amine-based nanofibrillar cellulose (NFC) sorbents for CO<sub>2</sub> capture from air. NFC is a richly natural



**Fig. 3.** CO<sub>2</sub> adsorption profiles of the fresh sorbents and those steam-treated for 7 and 14 days. (a) PEI/Macroporous silica, (b) PEI/MCM-41, (c) PEI/SBA-15, and (d) PEI/MCF. The solid lines indicate the measured CO<sub>2</sub> adsorption profiles of the sorbents, and the dashed lines indicate the fitting curves obtained using the pseudo-first-order kinetic equation [39]. Copyright 2017, Wiley.

material consisting of cellulose fiber aggregates rich in surface hydroxyl groups that can covalently anchor chemical functions to the cellulose backbone [41]. The NFC sorbents were synthesized by an environmentally friendly method using NFC and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane as raw materials. The adsorption amount was 1.39 mmol/g at a CO<sub>2</sub> concentration of 506 ppm in air (temperature of 25 °C and relative humidity of 40%). The desorption temperature was 90 °C. After 100 consecutive adsorption cycle tests, the adsorption capacity decreased by less than 5%, demonstrating good cycle stability [42]. More data are still needed to demonstrate the practical value of these materials. The lower cycle adsorption life is a great challenge for the economic viability of most sorbents. Ng et al. [43] investigated the coadsorption kinetics of CO<sub>2</sub> and H<sub>2</sub>O in a differential bed composed of amine-functionalized NFC CO<sub>2</sub> sorbents under DAC conditions. The temporal adsorption distribution of the sorbents in the absence of external heat and mass transfer intrusion was determined based on the mass balance of the constant volume gas phase, as shown in Fig. 4 [43].

### 2.2.3. Amine-based sorbents with carbon-based materials supports

The greatest advantage of carbon-based sorbents is their low cost and wide availability of raw materials. Porous carbon sorbents can be used as excellent CO<sub>2</sub> physical sorbents in their own right, as well as being good supports for amine-based solid sorbents [44–46].

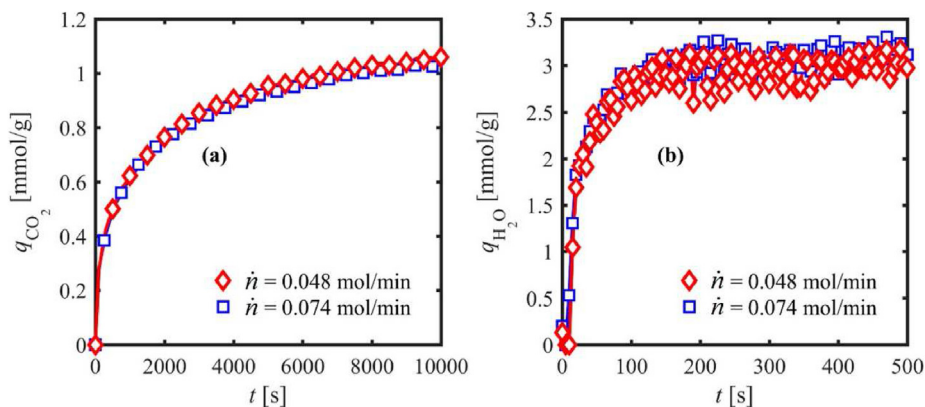
Wang et al. [47] studied a PEI-impregnated sorbents with mesoporous carbon (MC) as support. This study showed the sorbents' ability to absorb CO<sub>2</sub> and the loss of PEI. The authors report that the MC framework can accommodate a large amount of PEI while maintaining a large number of residual channels that allow CO<sub>2</sub> diffusion into the internal pores. In 2017, Gadipelli et al. [48] reported an extremely effective CO<sub>2</sub> sorbent consisting of highly

hierarchical mesoporous and macroporous graphene oxide networks impregnated with triethylenetetramine (TETA). Keller et al. [46] investigated the CO<sub>2</sub> capture performance of PEI-loaded multi-walled carbon microtubes. At a CO<sub>2</sub> concentration of 350 ppm, the CO<sub>2</sub> uptake of microtubules loaded with 10% PEI was 1.07 mmol/g (Fig. 5). The sorbent developed by Cuesta et al. [49] was a carbon black co-activated with potassium carbonate and a nitrogen-containing copolymer, which was impregnated with immobilized bovine carbonic anhydrase, and the adsorption system had the capacity to capture 1 kg of CO<sub>2</sub> in a cycle of less than 4 h. These sorbents, which use porous carbon as a support, are often widely available and have the potential for large-scale applications at low cost.

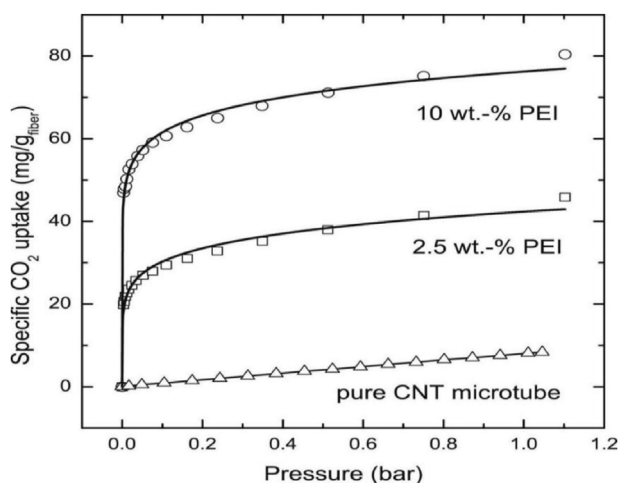
### 2.2.4. Amine-based sorbents with porous polymers supports

The kinetics of the sorbents is an important factor in the evaluation of the sorbents. Porous polymers usually have good kinetic properties for CO<sub>2</sub> diffusion, and loading different types of amino compounds into the porous polymer support can significantly improve the overall kinetics of the sorbents, and also help to improve the long-term cycling stability of the sorbents. Of course, there is inevitably a sacrifice in the overall CO<sub>2</sub> adsorption capacity of the material with the polymeric support, but this is acceptable compared to the stability and higher adsorption kinetics benefits of the porous polymeric support [50–52].

A PEI impregnated resin for capturing CO<sub>2</sub> from air with high loading capacity was reported by Chen et al. [53] This sorbent HP20/PEI-50 is made from the non-polar resin HP20 by wet impregnation [54]. Compared to other resins, HP20 shows better adsorption capacity for CO<sub>2</sub> adsorption. HP20/PEI-50 has a capacity of 2.26 mmol/g of CO<sub>2</sub> adsorption from 400 ppm at 25 °C, where the 43–68 nm mesopores may facilitate the diffusion of CO<sub>2</sub> [53]. Guo et al. [55] presented a kilogram-scale experiment to evaluate a



**Fig. 4.** Effect of gas flow rate on the (a) CO<sub>2</sub> and (b) H<sub>2</sub>O uptake profiles obtained with 30 mg of the sorbent under  $T_{\text{ads}} = 30\text{ }^{\circ}\text{C}$ ,  $x_{\text{CO}_2,0} = 1000\text{ ppm}$ , and  $\text{RH}_{\text{ads},0} = 50\%$ . Larger fluctuations seen in Fig. 4b are attributed to the inherently larger noise in  $x_{\text{H}_2\text{O}}$  measured with the IRGA [43]. Copyright (2018) American Chemical Society.



**Fig. 5.** Sorption isotherms at room temperature for pure as well as loaded microtubes with 2.5 and 10 wt% PEI in the impregnation solution [46]. The lines represent the fits of the Freundlich-model for the amine-functionalized microtubes. Copyright (2018), with permission from Elsevier.

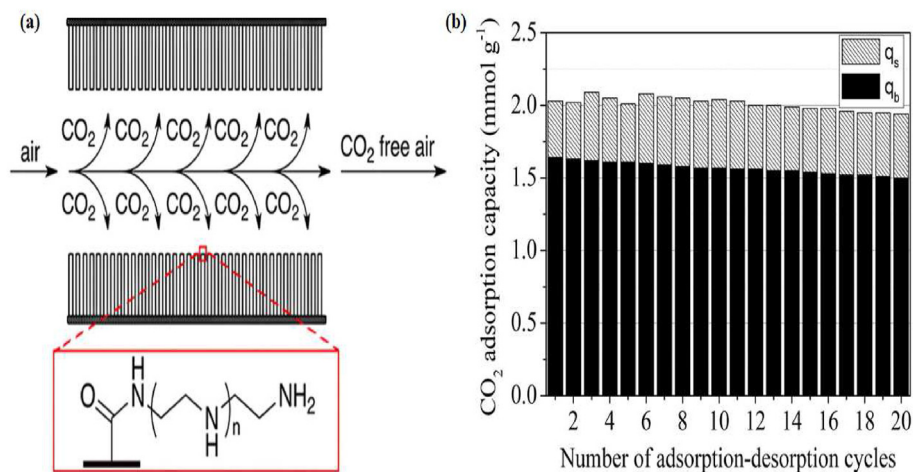
novel metal-organic framework (MOF) and polyacrylate (PA) composite, NbOFFIVE-1-Ni@PA, for the prospect of trace CO<sub>2</sub> capture. At 400 ppm CO<sub>2</sub> and 298 K, NbOFFIVE-1-Ni loaded with 45.8 wt% PA has a higher CO<sub>2</sub> uptake rate (ca. 1.44 mmol/g) than pure NbOFFIVE-1-Ni, indicating that the adsorption efficiency of NbOFFIVE-1-Ni is improved by 2.42 times. Rim's group [50] developed a hybrid CO<sub>2</sub> capture material solvent impregnated polymers (SiPs) based on a simple, scalable encapsulation technique to improve CO<sub>2</sub> capture kinetics in high-viscosity dilute aqueous solvents. Liquid nanoparticle organic hybrid materials functionalized with polyethyleneimine (NOHM-I-PEI) were encapsulated into the shell material and UV-cured to produce NOHMs-loaded uniformly permeable solid sorbent (NPEI-SiPs). The CO<sub>2</sub> capture kinetics of NPEI-SiPs has significantly improved by a factor of 50 compared to that of pure NOHM-I-PEI due to the large increase in NOHMS-CO<sub>2</sub> interfacial surface area provided by the SIP design [50]. Tan's group [56] prepared polyacrylonitrile (PAN) hollow fibers by wet spinning method and loaded TEPA on PAN support for CO<sub>2</sub> capture in low concentration sources. The CO<sub>2</sub> adsorption capacity of 2.03 mmol/g was achieved using TEPA@PAN hollow fibers for direct CO<sub>2</sub> adsorption from the atmosphere (25 °C, 470 ppm, RH 25%). The used TEPA@PAN hollow fibers can be

regenerated by a temperature change process after carbon dioxide adsorption. Twenty adsorption-desorption cycle tests were performed and no significant decrease in CO<sub>2</sub> adsorption capacity was observed. The breakthrough adsorption capacity ( $q_b$ ) is 1.64 mmol/g, 80.7% of the equilibrium adsorption capacity ( $q_s$ ) (2.03 mmol/g) [56]. The schematic diagram of the sorbent with cyclic stability is shown in Fig. 6.

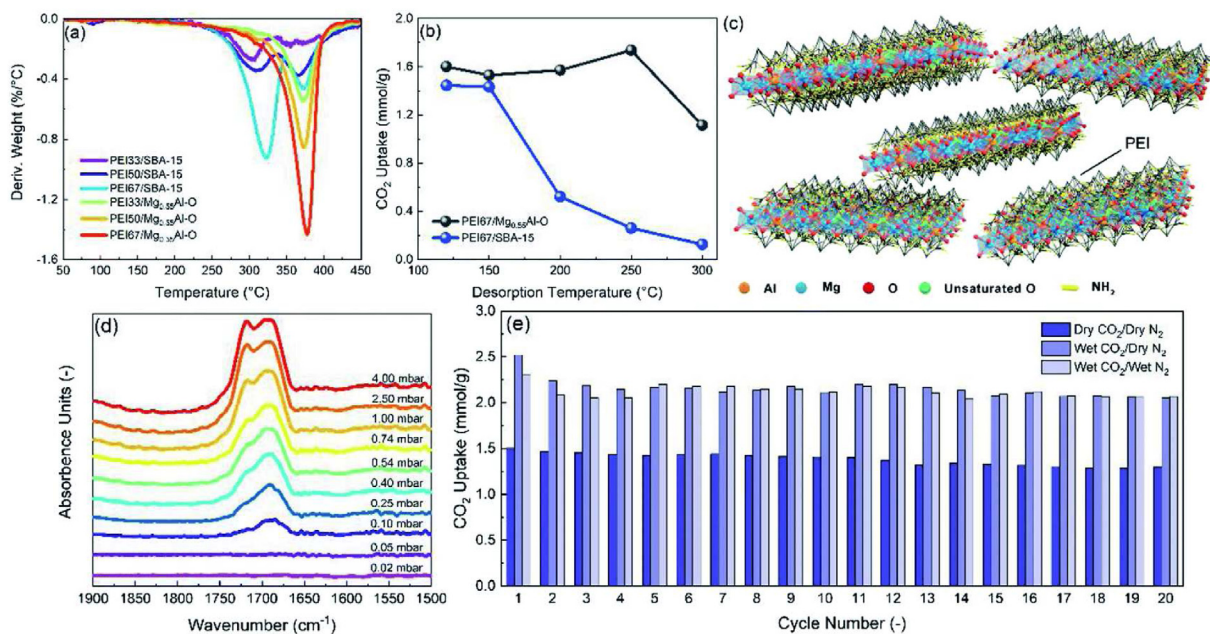
#### 2.2.5. Amine-based sorbents with layered double hydroxide supports

Layered double hydroxide (LDH) nanosheets are a popular class of supports recently studied for loading amine groups, which outperform the common silica supports in terms of CO<sub>2</sub> adsorption capacity, adsorption kinetics, and cycling stability. The good adsorption performance of these sorbents is derived from their rich slit-like mesopores, large surface area, and wide pore distribution. This excellent nanostructure leads to a homogeneous distribution of impregnated amines.

Zhu et al. [57] reported a new class of sorbents for CO<sub>2</sub> DAC, which was prepared by loading branched PEI into mixed metal oxides (MMO) derived from Mg–Al–CO<sub>3</sub> LDH, as shown in Fig. 7. The sorbents exhibited excellent large adsorption capacity, fast kinetics, and high stability. At 25 °C and 400 ppm CO<sub>2</sub>, Mg<sub>0.55</sub>Al–O MMO impregnated with 67 wt % PEI achieved a total CO<sub>2</sub> adsorption capacity of 2.27 mmol/g and a fast adsorption rate of 1.1 mmol/g · h within 90 min. Recently, a new DAC material with an enhanced charge transfer effect was synthesized by the same method by the group of Wang et al. [58] by loading TEPA on defect-rich Mg<sub>0.55</sub>Al–O MMOs. The best Mg<sub>0.55</sub>Al–O-TEPA67% showed the highest CO<sub>2</sub> uptake (3.0 mmol/g) and good regeneration, maintaining 90% of the initial adsorption capacity after 80 adsorption/desorption cycles [58]. A comprehensive and systematic study of the stabilization mechanism of MMOs-supported solid amine sorbents was conducted by Wang et al. [58]. The stronger binding between the Mg<sub>0.55</sub>Al–O support and the solid amine is caused by the abundant oxygen defects on the MMO, and thus the sorbent has the highest adsorption and excellent cycling stability. LDH supports can also be prepared as amine-functionalized sorbents by amine grafting. Zhu et al. [59] functionalized amine-grafted Mg–Al–CO<sub>3</sub> LDH nanosheets for efficient and rapid capture of airborne CO<sub>2</sub> [59]. The CO<sub>2</sub> uptake reaches 70% of the maximum capacity within 30 min, twice as fast as the supported polyamines. The highly dispersed LDH nanosheets exhibit excellent thermal, hydrothermal, and chemical stability with negligible performance degradation after 50 adsorption-desorption cycles [59].



**Fig. 6.** (a) Proposed amine-grafted hollow fiber CO<sub>2</sub> sorbent. (b) Cyclic CO<sub>2</sub> adsorption-desorption performance of TEPA@PAN hollow fiber [56]. Copyright (2022), with permission from Elsevier.



**Fig. 7.** Stability of poly(ethylenimine) (PEI)-impregnated samples under direct air capture conditions: (a) thermal stability from 50 to 450 °C at a heating rate of 5 °C min<sup>-1</sup> under an N<sub>2</sub> flow, (b) CO<sub>2</sub> uptake in 2 h at 400 ppm CO<sub>2</sub> and 25 °C after desorption at different temperatures, (c) schematic diagram of the PEI/MMO structure, (d) *in situ* infrared spectroscopy spectra for the CO<sub>2</sub> adsorption of PEI67%/Mg<sub>0.55</sub>Al-O at 25 °C, and (e) cyclic stability of PEI67%/Mg<sub>0.55</sub>Al-O with 2 h of adsorption at 25 °C followed by 1 h of desorption at 120 °C [57]. Copyright(2020), with permission from the Royal Society of Chemistry.

### 2.3. Amine-modified MOFs as sorbents in DAC

Stable and porous MOFs have received considerable attention from researchers since they were first synthesized in the 1990s. MOFs consist of organic ligands and metal centers with porosity, flexible topology, tunable pore size, and tunable surface chemistry [60], and based on these qualities, MOFs are considered materials with established potential in the field of CO<sub>2</sub> capture [61]. Compared to zeolites and amine conventional porous materials, such as grafted porous silica, MOFs exhibit higher capacities at lower CO<sub>2</sub> partial pressures and lower heats of adsorption. However, the CO<sub>2</sub> capture performance of MOF for DAC still needs to be improved. Based on the MOFs material design approaches

proposed by Liu et al. [62], Ozkan et al. [63] classified MOFs for CO<sub>2</sub> capture into the following three materials: MOFs with open metal sites (OMSs), hybrid ultra-microporous materials (HUMs), and MOFs with amine-functionalized sites (AFSSs). Among them, OMSs and HUMs for CO<sub>2</sub> capture are based on physical adsorption mechanisms and are suitable for scenarios with higher CO<sub>2</sub> concentration adsorption. Therefore, the following section will focus on the research progress of AFSSs in the field of CO<sub>2</sub> DAC.

To improve the ability of MOFs to capture ultra-low concentration CO<sub>2</sub>, modification of MOFs with amino groups is an effective strategy to achieve better CO<sub>2</sub> adsorption and separation [64]. There are two ways to anchor amine functional groups into the pores of MOFs. One strategy is to introduce amine units on the MOFs and

anchor the amines to the open metal centers through strong bonds between the positively charged N atoms and the unsaturated open metal cations [55,65]. Another strategy is to attach the amine group to the organic ligands [66]. Examples of two strategies for modifying MOFs with amino groups are given in Fig. 8.

Jones et al. [67] successfully synthesized the post-amine functionalization of Mg-MOF-74 (i.e.  $Mg_2(\text{Dobdc})$ ) by modifying OMS with ethylenediamine (ED). Mg-MOF-74 had only 0.88 mmol/g of  $\text{CO}_2$  uptake under DAC and was difficult to regenerate. In addition to Mg-MOF-74, they also explored its derivative  $Mg_2(\text{Dobpdc})$  by applying post-synthetic modifications with ED functional groups. Compared with Mg-MOF-74,  $Mg_2(\text{Dobpdc})$  has a larger pore size and pore channels, providing more sites for amine functional groups [68]. After insertion of the primary amine ED on the Lewis acid center, carbamic acid is generated instead of carbamate when  $\text{CO}_2$  is absorbed onto the free amine of ED. Under DAC conditions, other amine functional groups, such as *N,N'*-dimethylethylenediamine (MMEN) are also tethered to the unsaturated metal center of  $Mg_2(\text{Dobpdc})$  to absorb  $\text{CO}_2$  [69]. Although the ED and MMEN groups of the modified MOF exhibit good  $\text{CO}_2$  uptake, their maximum capacity is limited by their length and size, which results in strong intermolecular hydrogen bonding between two adjacent amine groups. Hydrazine ( $\text{N}_2\text{H}_4$ ) is the smallest and shortest diamine with similar basicity to the aforementioned amine groups [65].  $Mg_2(\text{Dobpdc})$  was chosen for the modification of ED and MMEN because it has larger pores and channels for longer and larger amine groups; since  $\text{N}_2\text{H}_4$  is shorter, it was decided to modify  $Mg_2(\text{Dobdc})$  with smaller pores. Chen and coworkers [65] synthesized  $Mg_2(\text{Dobdc})(\text{N}_2\text{H}_4)_{1.8}$ , and detected ultra-high concentrations of free amine groups during  $\text{CO}_2$  adsorption (6.01 mmol/g) and reversible carbamic acid, which led to a  $\text{CO}_2$  uptake record (3.89 mmol/g) that far exceeded the previous capacity under DAC conditions.

Another approach is attaching amine groups to organic ligands. For example, Chand et al. [70] prepared amine-functional microporous MOFs based on the combination of V-type carboxylic acid ligands with azo-functionalized *N,N'* spacers. The  $\text{CO}_2/\text{N}_2$  selectivity of this molecular sieve was 106.7 and 43.7 at 273 and 298 K, respectively. Ishitani et al. [66] investigated two complexes  $\text{fac-Mn}(\text{X}_2\text{bpy})(\text{CO})_3(\text{OCH}_2\text{CH}_2\text{N}_2)$  and  $\text{fac-Re}(\text{X}_2\text{bpy})(\text{CO})_3(\text{OCH}_2\text{CH}_2\text{NR}_2)$  ( $\text{X}_2\text{bpy} = 4,4'\text{-X}_2\text{-2,2\text{'-bipyridine}}$  and  $\text{R} = \text{-CH}_2\text{CH}_2\text{OH}$  for  $\text{CO}_2$  capture. Both of these complexes are effective in capturing  $\text{CO}_2$  in Ar containing only 1%  $\text{CO}_2$  and converting it to  $\text{fac-M}(\text{X}_2\text{bpy})(\text{-CO})_3(\text{OC}(\text{O})\text{OCH}_2\text{CH}_2\text{NR}_2)$  ( $\text{M} = \text{Mn}$  and  $\text{Re}$ ). These  $\text{CO}_2$  capture reactions are reversible with separation constants  $>1000$ .

#### 2.4. Polyamine sorbents without supports

Amine-functionalized solid sorbents are one of the most promising alternatives to the conventional technology for  $\text{CO}_2$

capture. However, their widespread application in industry is unfulfilled due to their expensive cost and complex fabrication, which depends on a porous support. One advantage of unsupported sorbents over loaded amine-based sorbents is their lighter mass, which is a great advantage both for  $\text{CO}_2$  adsorption capacity and energy consumption during regeneration. In general, there are two ways to synthesize cross-linked polyamine solid sorbents. One method is the reaction of selected monomers to form porous polymers with amine groups. The formation of porous polymers with amine groups by specific monomer reactions was first proposed by Wang et al. [71] They formed porous polyamine particles by the precipitation polymerization of *N*-methyl-*N*-vinylformamide and  $\text{di}[2\text{-(N-vinylformamide)ethyl}]$ . Kumar et al. [30] developed polyamine fractions for loaded sorbents by reacting ethylenediamine and malondiamine with 1,3,5-tris(bromomethyl)benzene and hexa(bromomethyl)benzene in 2020.

Another method of synthesizing cross-linked polyamines is by reacting existing polyamines with cross-linking units. Varying the relative amounts of reactants controls the degree of crosslinking and thus the abundance of primary and secondary amines, which affects the properties of the material. This technique has yielded a new and diverse range of support-free materials that can be considered a new polyamine-based sorbent [72]. The reaction of polyamines with aldehyde groups was utilized by Hwang et al. [73] in cross-linking PEI ( $M_w$  25 000) with glutaraldehyde, and by Thompson et al. [74] in cross-linking PEI ( $M_w$  600) with polyaldehyde phosphorus dendrimers. Xu et al. [75] used epichlorohydrin to form unsupported PEI ( $M_w$  25 000 Da) hydrogel beads. The beads have an increased surface area compared to liquid PEI, thus increasing  $\text{CO}_2$  uptake. In addition, they have excellent thermal stability, thus avoiding the problem of solvent loss encountered with conventional amines. Diepoxy crosslinkers are an effective part of the synthesis of such  $\text{CO}_2$  sorbents. Andreoli et al. [76] studied a series of materials synthesized by crosslinking PEI ( $M_w$  25 000 Da) with epoxy resins, bisphenol-A diglycidyl ether (DER), while Jones et al. [77] used poly(ethylene glycol) diglycidyl ether and crosslinked PEI ( $M_w$  750 000) by the ice-plastic method Da). The synthesis process is provided in Fig. 9 [77].

With the above discussion of DAC materials for  $\text{CO}_2$ , we show in Table 1 about the solid  $\text{CO}_2$  capture materials for DAC technology.

### 3. Influencing factors of chemisorption of $\text{CO}_2$ sorbents

The  $\text{CO}_2$  sorbents for DAC differ from other sorbents used in the rest applications in that its selectivity for  $\text{CO}_2$  is not considered since this type of sorbents is usually based on chemisorption. Considering that some sorbents may be used in an open-air environment, the effect of oxygen in the air on their cycling stability must be considered in addition to some criteria for evaluating  $\text{CO}_2$  sorbents, such as adsorption capacity, kinetics, cycling stability,

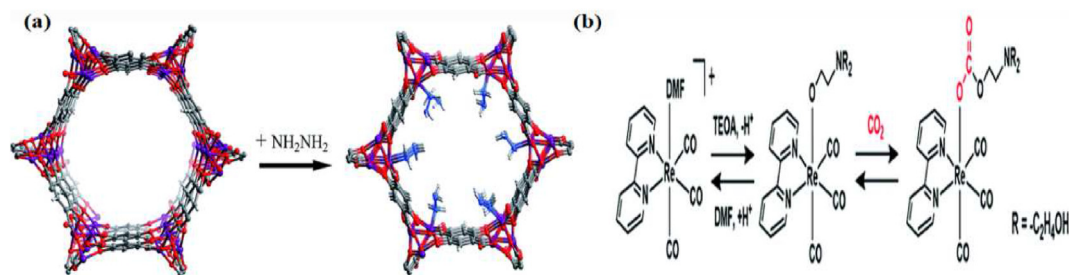


Fig. 8. (a) Comparison of the structures of  $[Mg_2(\text{dobdc})]$  (drawn from the reported crystal structure) and  $[Mg_2(\text{dobdc})(\text{N}_2\text{H}_4)_2]$  (simulated from PDFt) [65]. Reproduced from ref. 79 with permission from the Royal Society of Chemistry. (b) Ligand substitution and  $\text{CO}_2$  capture reactions of the Re(i) complex [66]. Copyright (2016 and 2019), with permission from the Royal Society of Chemistry.

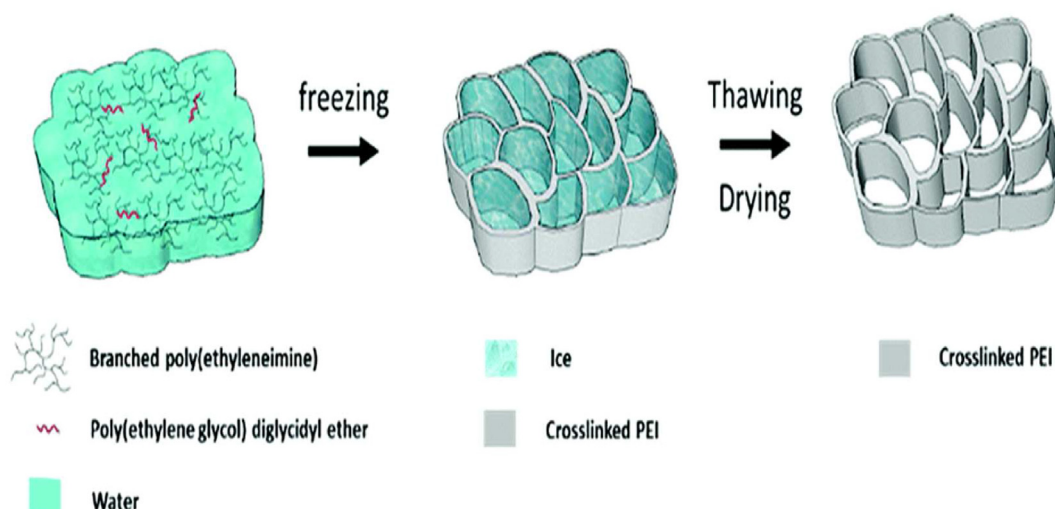


Fig. 9. Schematic synthesis of the self-supported PEI sorbents [77]. Copyright (2019), with permission from the Royal Society of Chemistry.

**Table 1**  
Comparison of CO<sub>2</sub> capture capacity of amine-based solid materials.

Amine modifier (Load content wt%)	Supports	Type	Adsorption conditions	Desorption conditions	Adsorption capacity (Dry   Wet(RH%)) (mmol/g)		Cycle stability	Refs.
Ph-3-ED (60%)	SBA-15	Impregnation	400 ppm CO <sub>2</sub> /He at 35 °C	He at 90 °C	1.43	2.90 (30%)	Almost no loss after 25 cycles	[30]
linear PPI (50%)	SBA-15	Impregnation	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 35 °C	N <sub>2</sub> at 110 °C	1.25	–	Almost no loss after 50 cycles	[78]
NOHM-I-PEI (49%)	TEGO Rad 2650	Impregnation	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 120 °C	1.05	1.66 (80%)	About 2.6% loss after 20 cycles	[50]
PEI (40%)	γ-alumina	Impregnation	400 ppm CO <sub>2</sub> /Ar at room Temperature	Ar at 110 °C	1.33	–	Almost no loss after 3 cycles	[34]
PEI (66%)	MCF Silica	Impregnation	420 ppm CO <sub>2</sub> /N <sub>2</sub> at 33 °C	N <sub>2</sub> at 100 °C	1.52	2.36 (41%)	–	[17]
PEI (55%)	MC	Impregnation	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 110 °C	2.25	2.58 (80%)	About 3% loss after 10 cycles	[47]
PEI (50%)	HP-20	Impregnation	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 100 °C	2.26	–	Almost no loss after 5 cycles	[53]
PEI (67%)	MMO	Impregnation	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 120 °C	2.27	–	About 2.7% loss after 10 cycles	[57]
TEPA (67%)	MMO	Impregnation	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 100 °C	3.00	–	About 9.4% loss after 20 cycles	[58]
TEPA (50%)	MMSN	Impregnation	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 100 °C	3.68	4.75 (–)	Almost no loss after 6 cycles	[79]
APS	MCF	Graft	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	He at 120 °C	0.30	–	–	[80]
DT (10%)	SBA-15	Graft	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 110 °C	0.64	–	–	[21]
TRI	MCM-41	Graft	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 150 °C	0.98	–	–	[81]
DETA	PPNs	Graft	400 ppm CO <sub>2</sub> , 78.96% N <sub>2</sub> , and 21% O <sub>2</sub> at 22 °C	–	1.04	–	–	[82]
TRI	LDH	Graft	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 120 °C	1.05	1.44 (–)	About 14% loss after 20 cycles	[59]
AEAPDMS	NFC	Graft	506	Ar at 90 °C	–	1.39 (40%)	Almost no loss after 20 cycles	[40]
TEPA	PAN	Graft	470 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 110 °C	1.70	2.03 (25%)	Almost no loss after 20 cycles	[56]
ED	Mg-MOF-74	Graft	400 ppm CO <sub>2</sub> /Ar at 25 °C	Ar at 110 °C	1.51	–	Almost no loss after 4 cycles	[67]
ED	Mg-MOF-74	Graft	390 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	Vacuum at 120 °C	2.83	–	About 4% loss after 20 cycles	[69]
Hydrazine	Mg-MOF-74	Graft	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 130 °C	3.89	–	Almost no loss after 5 cycles	[65]
PL	SBA-15	Hyperbranching	400 ppm CO <sub>2</sub> /Ar at 25 °C	Ar at 110 °C	0.60	–	Almost no loss after 3 cycles	[24]
AEAPTMS	SBA-15	Hyperbranching	400 ppm CO <sub>2</sub> /Ar at 25 °C	Ar at 110 °C	0.35	1.72 (–)	Almost no loss after 4 cycles	[26]
linear polyethylene amine	mesoporous silica foam	Hyperbranching	400 ppm CO <sub>2</sub> /N <sub>2</sub> at 25 °C	N <sub>2</sub> at 100 °C	0.74	1.50 (65%)	Almost no loss after 10 cycles	[83]

**Note:** RT-Room Temperature; RH-Relative Humidity; PEI-Polyethyleneimine; PPI-Polypropyleneimine; NOHM-I-PEI-Liquid-like nanoparticle organic hybrid materials functionalized with polyethyleneimine; TRI-Triamine; APS-Aminopropyl Organosilanes; DT-Diethylenetriamine Alkoxysilane; DETA-Diethylenetriamine; AEAPDMS-N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane; ED-Ethylene Diamine; AEAPTMS-N-(3-(trimethoxysilyl)propyl)ethane-1,2-diamine; MC-Mesoporous Carbon; LDH-Layered Double Hydroxide; NFC-Nanofibrillated Cellulose; TEGO Rad 2650-Silicone Acrylate; TEPA-Tetraethylenepentamine; PL-Poly(L-lysine); PPNs-Porous polymer networks; PAN-Polyacrylonitrile.



regeneration energy consumption, etc. The following section describes the influence of various factors on sorbents' performance in terms of amine modifier, temperature, humidity, and oxygen.

### 3.1. Amine modifier

The internal factors affecting the CO<sub>2</sub> adsorption performance of amine-based solid sorbents are mainly the amine loading and the textural properties of the support material with the amine loading being particularly critical. However, high amine loading does not imply higher adsorption capacity, as too much loading can cause the pores of the support to be easily clogged with thick agglomerates, hindering the diffusion of CO<sub>2</sub> [84]. Therefore, it is extremely critical to select a suitable load amine with high dispersion. Moreover, the addition of appropriate additives to enhance the specific properties of the material can also improve the overall adsorption performance of the material.

#### 3.1.1. Effect of morphology and structure of loaded amines

Amine compounds have been used for loading or direct synthesis of CO<sub>2</sub> sorbents, including amine polymers Polyethyleneimine (PEI), Polypropyleneimine (PPI), etc. There are other common amine loadings, such as tetraethylenepentamine (TEPA), triethylenetetramine (TETA), diethylenetriamine (DETA), triamine (TRI), etc. Among them, PEI is the most common type of loading in amine-functionalized solid sorbents and contains amine groups attached by vinyl groups (CH<sub>2</sub>–CH<sub>2</sub>). The morphology of PEI in silica has a strong influence on the capture efficiency and saturation rate. Holewinski et al. [85] found that PEI first forms a thin conformal polymer coating on the porous silica walls. As an additional polymer aggregate, it forms a plug that is aligned with the pore axis. They post-synthetically modified the surface of SBA-15 material with hexamethyldisilazane (HMDS) to convert hydrophilic silanols to hydrophobic trimethylsilyl. This is expected to increase CO<sub>2</sub> capacity and uptake by changing the attractive interaction of the surface with PEI to a repulsive interaction, thereby releasing the previously bound amine. The schematic diagram of the sorbents morphology and the sorbents amine efficiency before and after HDMS treatment are shown in Fig. 10 [85].

PEI with very high molecular weight (up to 750 000 number-average molecular weights (M<sub>n</sub>)) are stable in a high temperature vacuum environment when capturing CO<sub>2</sub>, but these structures are not conducive to CO<sub>2</sub> diffusion and efflux in the matrix. High molecular weight PEI can lead to pore blockage [85]. Goeppert et al. [86] reported a class of easily prepared sorbents that can efficiently capture CO<sub>2</sub> from the atmosphere at temperatures ranging from room temperature to 100 °C. The loaded PEIs, particularly low molecular weight (LMW, M<sub>w</sub> 800) and high molecular weight (HMW, M<sub>w</sub> 25000), exhibited excellent CO<sub>2</sub> uptake capacities of 2.6–3.8 mmol/g and 2.0–3.2 mmol/g, respectively. It was also shown that specific linear PEIs (M<sub>w</sub> 400) have good adsorption capacity, but their stability is problematic. PEI degrades oxidatively at high temperatures, leading to a loss of CO<sub>2</sub> capture capacity. Thus, although HMW has a lower adsorption capacity, they have a higher potential in CO<sub>2</sub> capture materials due to their better stability [86]. To solve the stability problem, Choi et al. [87] proposed a new Class 1 sorbent consisting of PEI loaded on porous silica that can capture CO<sub>2</sub> from ultra-dilute gas streams (e.g., air). Pang et al. [88] demonstrated the use of small molecule polypropylene imine (PPI) in a linear form and silica as a sorbents for CO<sub>2</sub> capture from air. For DAC, PPI is more effective than PEI-based sorbents because PPI has a longer sorbent operating life due to greater oxidative degradation than PEI.

#### 3.1.2. Effect of loading amine content and additives

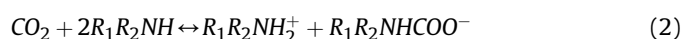
The content of the loaded amine and some additives have a great influence on the adsorption performance of the material. Sanz

et al. [21] prepared amine-silica composites by tethering diethylenetriamine alkoxy silane (DT) on SBA-15 pore walls using a grafting technique to obtain a series of materials with increased DT content. The CO<sub>2</sub> adsorption effects of the two gases (simulated air and pure CO<sub>2</sub> gas stream) were compared and it was found that the CO<sub>2</sub> adsorption capacity in the simulated air became closer to that in the pure CO<sub>2</sub> atmosphere as the DT content in the amine-silica composite increased [21]. Maresz et al. [89] reported that on layered porous silica with surface areas of 275 and 344 m<sup>2</sup>/g, CO<sub>2</sub> adsorption capacity decreased with increasing PEI loading (at 75 °C of pure CO<sub>2</sub>). Using a larger surface area support of 651 m<sup>2</sup>/g, adsorption capacity improved with increasing polyamine loading, with 60 wt % of PEI sorbents adsorbed up to 4.16 mmol CO<sub>2</sub>/g. As shown in Fig. 11. The authors calculated that the low surface area material has a double PEI layer and therefore hinders the diffusion of CO<sub>2</sub>. Keller et al. [90] investigated the CO<sub>2</sub> capture performance of PEI-loaded multi-walled carbon microtubes and observed that the specific surface area of PEI-loaded microtubes decreased from 203.6 to 4.7 m<sup>2</sup>/g as the PEI content increased from 0 to 30% (mass fraction). For the low PEI fraction in the impregnated solution, the high specific surface area and porosity of the microtubes remained constant, the CO<sub>2</sub> uptake improved with increasing PEI fraction. When the loading of PEI continued to increase to more than 20%, the adsorption of CO<sub>2</sub> decreased [90]. The reason is that too much PEI may lead to pore clogging of the support and subsequently affect the CO<sub>2</sub> adsorption capacity.

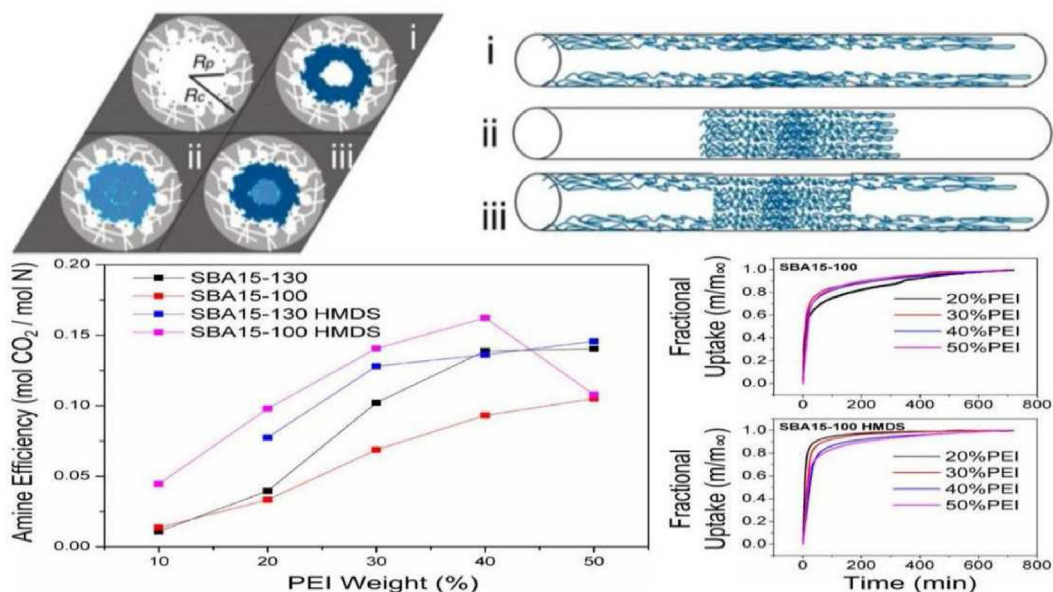
The low amine efficiency of the widely studied amine sorbents today is a key factor preventing their practical application under dry conditions. Wang et al. [47] investigated a PEI-impregnated sorbent with an MC support and enhanced the CO<sub>2</sub> kinetics of the sorbents by adding specific additives (surfactants), such as span 80. The diffusion additive transforms the PEI membrane from a homogeneous solid block into a double interpenetrating polymer network. The loosely filled surfactant channels support high CO<sub>2</sub> diffusion rates [91]. This channel network alleviates the kinetic barriers to CO<sub>2</sub> diffusion within the PEI membrane. The performance of surfactant-promoted sorbents may be influenced by the self-assembled structure of the surfactant in the PEI, the interaction between the surfactant and PEI, and the CO<sub>2</sub> affinity of the surfactant [91].

### 3.2. Humidity

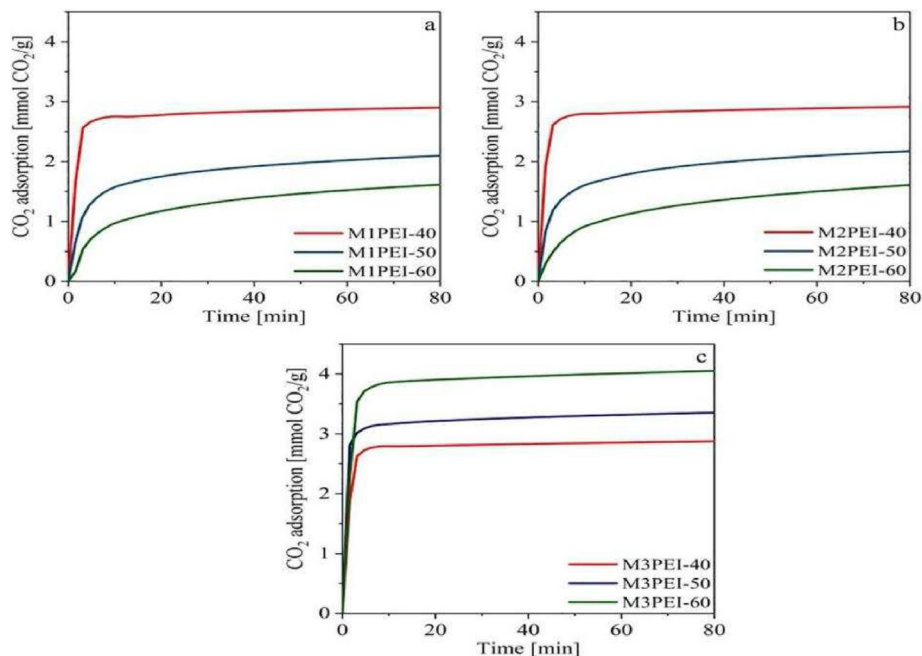
Water was shown to have a significant effect on the sorption capacity and kinetic uptake of CO<sub>2</sub> in many studies in which amine-based sorbents were exposed to water [48,75,76]. According to Caplow and Danckwerts, the mechanism of CO<sub>2</sub>-amine reaction under anhydrous conditions requires one CO<sub>2</sub> molecule and two primary amine fractions (reaction equation (1)) or two secondary amine fractions (reaction equation (2)) to obtain ammonium carbamate [92]. Therefore, the maximum CO<sub>2</sub>/N ratio that can be obtained by a chemical reaction with an amine sorbent under these conditions is 0.5 mol/mol N. The molar ratio CO<sub>2</sub>/N is usually considered the amine efficiency.



The reaction to produce ammonium carbonate or bicarbonate (depending on pH) was observed when water was present (reaction equation (3)). Moreover, this reaction is the only possibility reported for a strong chemical interaction between CO<sub>2</sub> and tertiary amines (reaction equation (4)), since these groups do not react in the absence of water or other proton groups (e.g. alcohols) [93], although the latter are described much less frequently. Derived

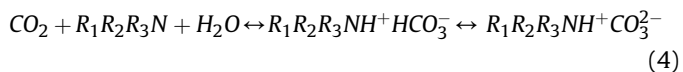
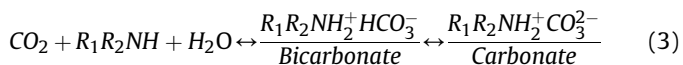


**Fig. 10.** Sorbents morphology and various PEI filling themes: i) conformal polymer coatings, ii) single, localized polymer plugs, iii) polymer fillings yielding a hybrid structure of plugs and conformal coatings (top). Amine efficiency for untreated and HDMS capped PEI/SBA-15 composites (lower left). CO<sub>2</sub> uptake over time for PEI/SBA15–100 materials before and after HDMS capping (lower right) [85]. Copyright (2020), with permission from the American Chemical Society.



**Fig. 11.** CO<sub>2</sub> desorption vs. time for M1-based sorbents: (a) M1PEI, (b) M1A1, (c) M1A2 series [89]. Copyright (2020), with permission from Elsevier.

from the above reactions, the maximum CO<sub>2</sub>/N ratio obtainable by chemical reaction under humid conditions is 1.0 mol CO<sub>2</sub>/mol N, which is twice as high as under the corresponding anhydrous conditions.



A recent work by Mahinpey et al. can corroborate the aforementioned effect of water on amine-based sorbents. To evaluate the effect of moisture on CO<sub>2</sub> capture performance, groundbreaking experiments were performed using 400 ppm CO<sub>2</sub> at different relative humidities (0–65%). As shown in Fig. 12, the adsorption capacity of CO<sub>2</sub> increased with increasing humidity, doubling at 65% RH, which can be attributed to the reaction mechanism of CO<sub>2</sub> with amines under dry and humid conditions [83]. The effect of moisture on the CO<sub>2</sub> capture behavior of materials is complex, and given that water vapor is a ubiquitous component of air and virtually all CO<sub>2</sub>-rich industrial gas streams, understanding its

effect on CO<sub>2</sub> adsorption is critical. Due to the great diversity of sorbents, water plays many different roles, from a serious inhibitor of CO<sub>2</sub> adsorption to an excellent promoter. In DAC, the effect of water in the air on the capture system is complex, and co-adsorbed water may either hinder the capture of CO<sub>2</sub> by the system or act as a positive factor to facilitate it. In Amine-based sorbents, water is even necessary for their long-term stability. The recent review by Kolle et al. [94] provides a detailed discussion of the impact of water on CO<sub>2</sub> adsorption. Under dry conditions, co-adsorbed water may increase the heat demand for sorbent regeneration by several times [95], although water-related energy losses can be minimized through heat recovery [95]. Another negative effect of humidity may be to make the sorbent degraded, which may occur, for example, in some MOFs [96]. On the other hand, due to the altered reaction mechanism between CO<sub>2</sub> and amine groups, the presence of water promotes the reaction of the system towards the production of carbonates and bicarbonates, increasing the sorption capacity of CO<sub>2</sub>. Meanwhile, in promoting the formation of the bicarbonate ion, water may suppress the formation of ionic cross-linking between alkylammonium carbamate entities, which has been suggested to form a surface diffusion barrier to CO<sub>2</sub> [84]. Besides, it was proposed that water could act as a diffusion intermediate, acting as a free radical to stabilize the zwitterion during urethane formation, replacing the second amine and thus aiding adsorption [97]. This adsorption enhancement was also demonstrated in the presence of methanol, which may also act as a diffusion intermediate in the same manner as water [98].

The effect of water on amine-based sorbents is obvious, considering from the point of view of reaction mechanism, the presence of water improves the efficiency of amine adsorption on CO<sub>2</sub>, and then from the point of view of desorption, the adsorption on water increases the energy penalty of the whole desorption regeneration process. If only the CO<sub>2</sub> adsorption process is considered, then the study for water must be considered in conjunction with the specific sorbents, such as the adsorption mechanism of the sorbents, the stability to water, and the competitive adsorption of H<sub>2</sub>O and CO<sub>2</sub>.

However, if CO<sub>2</sub> capture and conversion are combined and an integrated CO<sub>2</sub> capture and reduction device is designed, then the desorption regeneration aspect of the sorbents will be eliminated and only the CO<sub>2</sub> adsorption enhancement brought by water on the material can be considered.

### 3.3. Temperature

The external temperature has a strong influence on CO<sub>2</sub> adsorption. In general, adsorption can be roughly divided into two

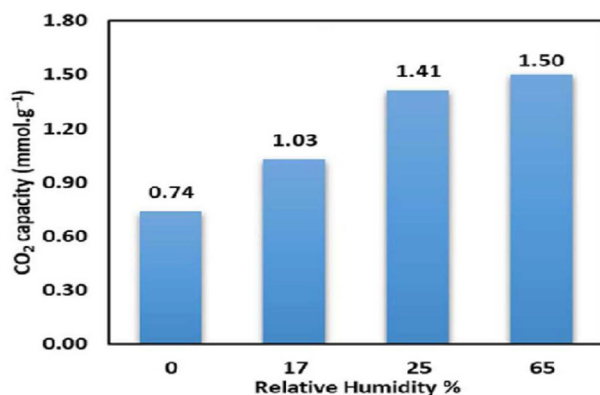


Fig. 12. Effect of relative humidity on CO<sub>2</sub> capacity [83]. Copyright (2022), with permission from Elsevier.

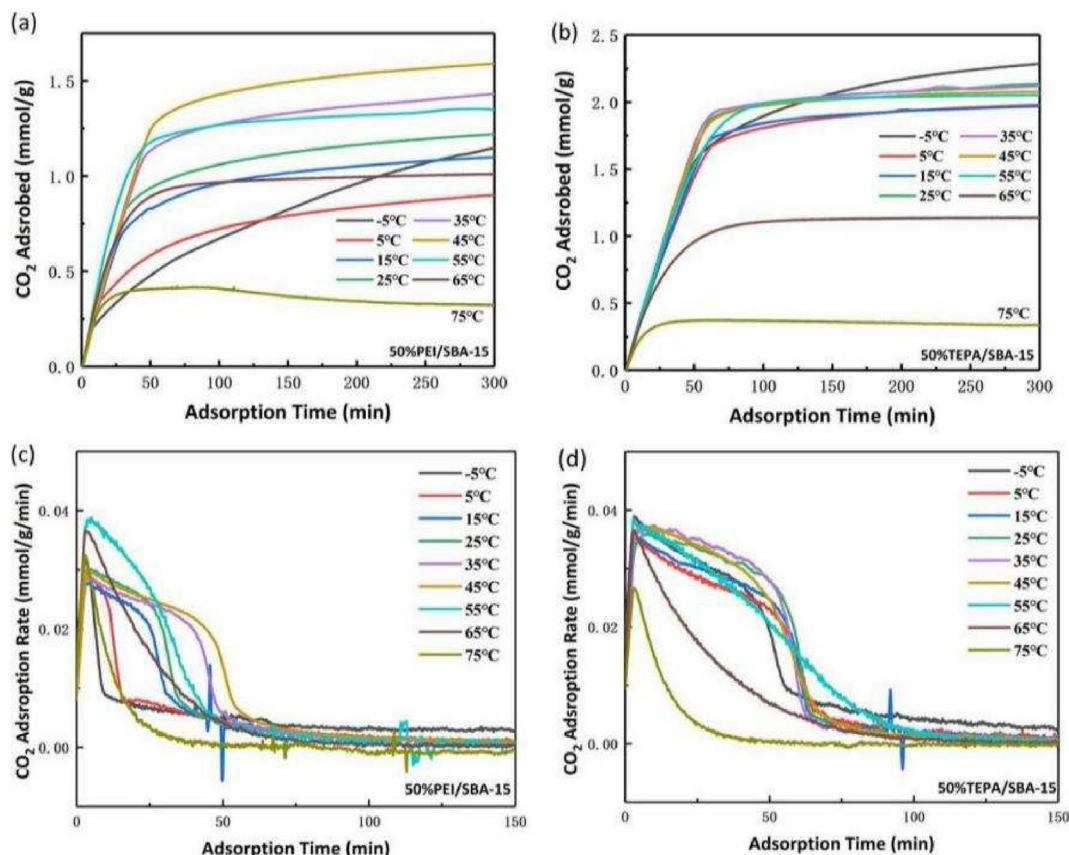
stages, the first stage is a chemical reaction-controlled process, where CO<sub>2</sub> can react rapidly with the affinity sites on the amine surface. This stage is characterized by a fast reaction and a large adsorption volume, which occupies the majority of the adsorption volume of the whole adsorption process. The second stage is a diffusion-controlled process, where CO<sub>2</sub> needs to overcome the accumulation of the ionic species ammonium carbamate layer generated by the CO<sub>2</sub> adsorption reaction on the surface and the diffusion barriers caused by cation-anion interactions. The reaction rate of this process is slow and the whole adsorption process slowly approaches adsorption saturation during this period. Although adsorption is an exothermic reaction, this does not mean that lowering the adsorption temperature will enhance its adsorption capacity. The thermodynamics in itself would favor lower temperature conditions, CO<sub>2</sub> adsorption is heavily influenced by adsorption kinetics, which controls the diffusion process - as well as thermodynamics. The adsorption kinetics enhances with increasing temperature, while the adsorption thermodynamics is exactly the opposite. Therefore choosing the appropriate adsorption temperature is a weighing between the kinetic and thermodynamic optimum temperatures [84].

Understanding the CO<sub>2</sub> capture performance of DAC materials in real-world environments is important to optimize the performance of DAC processes. Miao et al. [99] investigated the effect of operating temperature on the performance of DAC with mesoporous silica loaded with polyurethane. They found that below 15 °C, the CO<sub>2</sub> adsorption selectivity of TEPA-loaded mesoporous silica decreases with reduction adsorption temperature. The adsorption kinetics, long-term stability, and the optimal desorption temperature of 90–120 °C were also parametrically investigated. The results show that the mesoporous silica loaded with TEPA at 50 wt % polyamine loading exhibits an excellent capture capacity of 2.30 mmol CO<sub>2</sub>/g over a wide range of adsorption temperatures under simulated air conditions. The relevant data plots are shown in Fig. 13 [99]. The effect of temperature on CO<sub>2</sub> chemisorption is easy to understand. The optimal CO<sub>2</sub> adsorption temperature for an adsorbent varies from material to material and can be found through a simple series of CO<sub>2</sub> adsorption tests at different temperatures.

### 3.4. Oxygen in air

Oxygen makes up approximately 21% of the air, and oxidative degradation is a common problem to consider for amino sorbents under DAC conditions. One way to improve oxidative stability is to avoid the use of secondary amines altogether. PAA has a linear hydrocarbon backbone and side-chain primary amines; the polymer has a basic nitrogen content of 24% by weight. In 2011, Chai-kittisilp et al. [100] demonstrated PAA as an effective alternative to the class 1 polyamine sorbents PEI. Later, Bali et al. [101] directly compared the oxidative degradation of mesoporous g-alumina-loaded PAA and PEI (M<sub>w</sub> 800) under direct air trapping conditions and found that PAA was much more stable to oxidation than PEI. The CO<sub>2</sub> capacity of the PEI sorbent decreased by 70.1% and 33.4% at 110 °C and 70 °C, respectively, compared to 10.9% and 7.0% for the PAA sorbent after treatment with 21% O<sub>2</sub>/N<sub>2</sub> wet flow and adsorption in 10% CO<sub>2</sub>/He. The decrease in the adsorption performance of the PEI sorbents treated at 110 °C was associated with the formation of amide or imine species upon oxidation. An adsorption band at 1693 cm<sup>-1</sup> was observed in the infrared spectrum and a strong adsorption band at 1691 cm<sup>-1</sup> was observed in the Fourier transform Raman spectrum, both of which indicate the stretching frequency of C=O [101].

Although secondary amines tend to oxidize more readily, they have lower adsorption heat so it is advantageous to maintain their



**Fig. 13.** Comparison of the capacity of (a) 50% PEI/SBA-15 and (b) 50% TEPA/SBA-15, The CO<sub>2</sub> adsorption rate of (c) 50% PEI/SBA-15 and (d) 50% TEPA/SBA-15 [99]. Copyright (2021), with permission from Elsevier.

functionality to reduce the energy input for desorption [18]. Pan et al. [88] demonstrated that the length of the alkyl chain between amines has a significant effect on oxidative stability, with longer linkage groups associated with greater stability. To investigate this, the CO<sub>2</sub> uptake performance of pre-oxidized mesoporous silica-loaded polypropyleneimine and polyethylenediamine linear polyamines containing primary and secondary amines was compared with their unoxidized equivalents. Compared to TETA, the tripropyltetramine (TPTA) sorbent had only two carbons between the amines and showed a small decrease in the adsorption capacity of CO<sub>2</sub>. The TPTA sorbents showed a 20% decrease in amine efficiency, while the TETA sorbent showed a 90% loss in amine efficiency. The authors speculate that the conditions used during the oxidation process may have led to the oxygen-assisted thermal rearrangement of the amine separated by the ethylene linker [88].

According to many current studies on sorbents for DAC, there are few reports that investigate the effect of oxygen on the sorbent, yet the effect of oxygen on the sorbents is critical and directly related to the cycle life of the sorbents for atmospheric applications. The oxidative stability of the sorbent in DAC applications should be considered as important as parameters such as adsorption capacity, cycling stability, heat of adsorption, and regeneration temperature.

#### 4. Regeneration cycle in DAC system

In the DAC step, CO<sub>2</sub> is first bound to the sorbent and then desorbed into a concentrated stream, while the sorbent is regenerated by one or more chemical reactions for further circulation [102]. Obviously, the thermodynamic and kinetic processes of the desorption reaction are very important for practical cycling

applications. Depending on the sorbent regeneration methods, DAC technologies can be divided into the following categories: traditional sorbent regeneration methods include the following mechanisms: temperature swing adsorption (TSA), pressure swing adsorption (PSA), temperature vacuum swing adsorption (TVSA), and the regeneration of the remaining sorbent techniques are relatively new mechanisms, including moisture swing adsorption (MSA), pH swing adsorption (pHSA) and salt solution regeneration (SSR).

##### 4.1. Temperature vacuum swing adsorption (TVSA)

TSA, TVSA and PSA are the main process models for CO<sub>2</sub> capture based on adsorption technology. Among them, it has been shown through simulation studies that PSA is impractical because it requires unreasonably high vacuum levels during the desorption phase [103]. TSA uses elevated temperatures to desorb CO<sub>2</sub>, but the purity of the CO<sub>2</sub> desorbed during TSA is usually limited, with one report suggesting a limit of about 20% [104]. Therefore, the most widely studied system configuration for solid sorbent DAC is TVSA. As described by Sinha et al. [105] a typical TVSA process has five steps in the adsorption-desorption cycle and the flow diagram of the TVSA process is shown in Fig. 14.

The TVSA process is a complex process with many parameters that need to be adjusted to achieve optimal operating conditions. Sinha et al. [105] discussed the effect of adjusting the airflow rate in the adsorption step, the steam flow rate in the desorption step, and the duration of these two steps on the energy consumption and economic performance of the overall DAC system. Zhu et al. [106] studied the design of the steam-assisted TVSA process and

investigated the effect of air velocity during adsorption, steam velocity during desorption, duration of adsorption and desorption, and temperature and pressure during the desorption phase on the process performance. The authors observed a trade-off between daily CO<sub>2</sub> productivity and energy consumption per unit of CO<sub>2</sub> capture. Wilson et al. [107] investigated the DAC using TVSA with pumice zeolite and the effects of desorption temperature, gas space velocity during adsorption, and bed length. They concluded that increasing the desorption temperature improved the thermal energy required, but reduced the electrical energy per ton of CO<sub>2</sub> captured. Capture and isolation of CO<sub>2</sub> by DAC is a power and heat-consuming process [108,109]. For regeneration of the sorbent in the TVSA DAC, low temperatures (80–120 °C) are sufficient, so waste heat, heat pumps, or electric heaters can be used. Approximately 5–7.5 GJ of heat is required for each ton of CO<sub>2</sub> captured [108].

#### 4.2. Moisture swing adsorption (MSA)

The concept of MSA was first proposed and experimentally evaluated as a CO<sub>2</sub> sorbent regeneration system by Wang et al. [110]. The scheme is well suited for capturing CO<sub>2</sub> directly from the air. Amine-based anion exchange resins dispersed in polypropylene plates are prepared in an alkaline form and are capable of capturing CO<sub>2</sub> in the air when dry and releasing it when wet. This is a moisture-induced cycle and is a new way to regenerate CO<sub>2</sub> absorbers - the evaporation of water effectively provides the free energy to drive the cycle. Therefore, MSA is applied to specific moisture-sensitive sorbent materials to capture carbon dioxide from the air by controlling the amount of water (moisture) in contact with the air.

MSA technology has a series of advantages over conventional TSA systems: regeneration of the sorbent in the MSA system is achieved by humidity oscillation rather than energy, and there is no energy loss associated with water co-sorption as in conventional adsorption techniques. Furthermore, MSA systems do not require cooling and heating units, thus saving energy input for the adsorption system. In addition, the greatest advantage of the MSA system is that it is very flexible in terms of equipment placement

and can be supplemented with thermal swing and vacuum units to optimize the system.

Recently, Shi et al. [7] revealed the optimization of sorbents for CO<sub>2</sub> capture from the air by investigating different parameters of different porous materials: choosing materials with small pore sizes is a feasible strategy to capture more CO<sub>2</sub> than large pore sizes under the same humidity conditions; adjusting the particle size of silica and reducing the cation distance on its surface can increase its CO<sub>2</sub> capacity; at relatively high humidity. The use of hydrophobic carbon black as a support material instead of hydrophilic polystyrene can improve the efficiency of moisture-driven CO<sub>2</sub> capture systems.

The working mechanism is elucidated: when the environment is dry, the CO<sub>2</sub> adsorption system energetically prefers bicarbonate and hydroxide ions over carbonate ions, and the resulting high content of hydroxide ions is more favorable for CO<sub>2</sub> adsorption [7]. The reaction pathway of adsorption-desorption is shown in Fig. 15. The adsorption/desorption of CO<sub>2</sub> can be represented by a series of reactions: dissociation of water, formation of bicarbonate, adsorption of CO<sub>2</sub> on hydroxide, and release of CO<sub>2</sub> and H<sub>2</sub>O from bicarbonate. Yang et al. [111] studied moisture swing adsorption using nuclear magnetic resonance spectroscopy. In agreement with the theory, they stated that CO<sub>2</sub> is adsorbed as HCO<sub>3</sub><sup>-</sup>. They claim that at high humidity conditions, HCO<sub>3</sub><sup>-</sup> is replaced by hydrated OH<sup>-</sup> and the absorbed CO<sub>2</sub> is released. Since most of their data are well below the freezing point of water, it is unclear whether this explanation is inconsistent with the one given above. More experiments are needed to elucidate the relationship between these measurements and the previous analysis. Yang et al. [111] explain how OH<sup>-</sup> ions are stable in the presence of CO<sub>2</sub>, since environments with increased water availability typically behave more like aqueous solutions, with hydroxide ions strongly bound to CO<sub>2</sub>.

#### 4.3. pH swing adsorption (pHSA)

The pHSA system for specific sorbent materials that are sensitive to pH changes. There are very few studies on the regeneration system of pHSA adsorbed CO<sub>2</sub>, especially for low concentration CO<sub>2</sub>

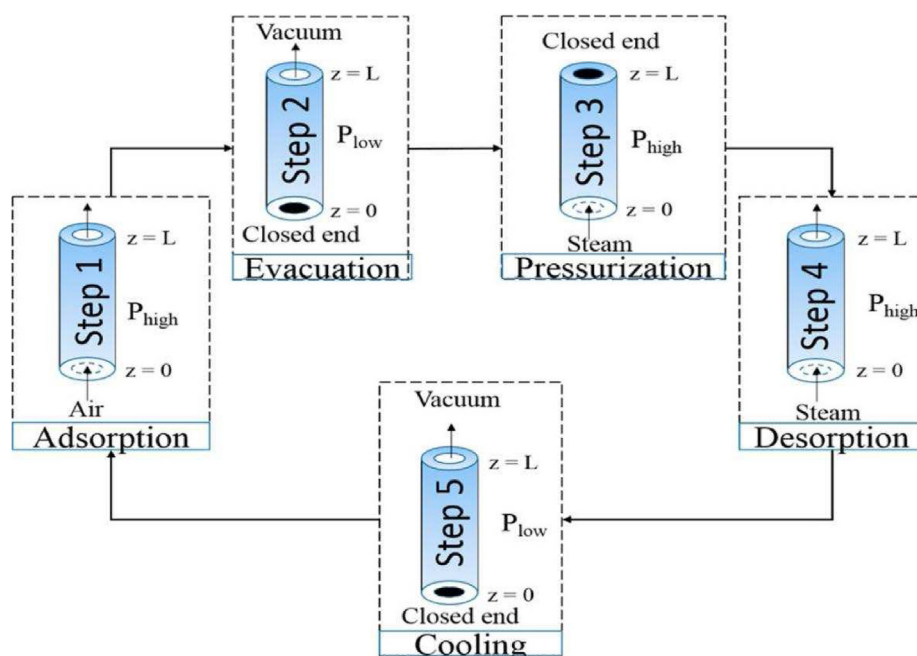


Fig. 14. Overview of the steps involved in the TVSA model for DAC [105]. Copyright (2017), with permission from the American Chemical Society.

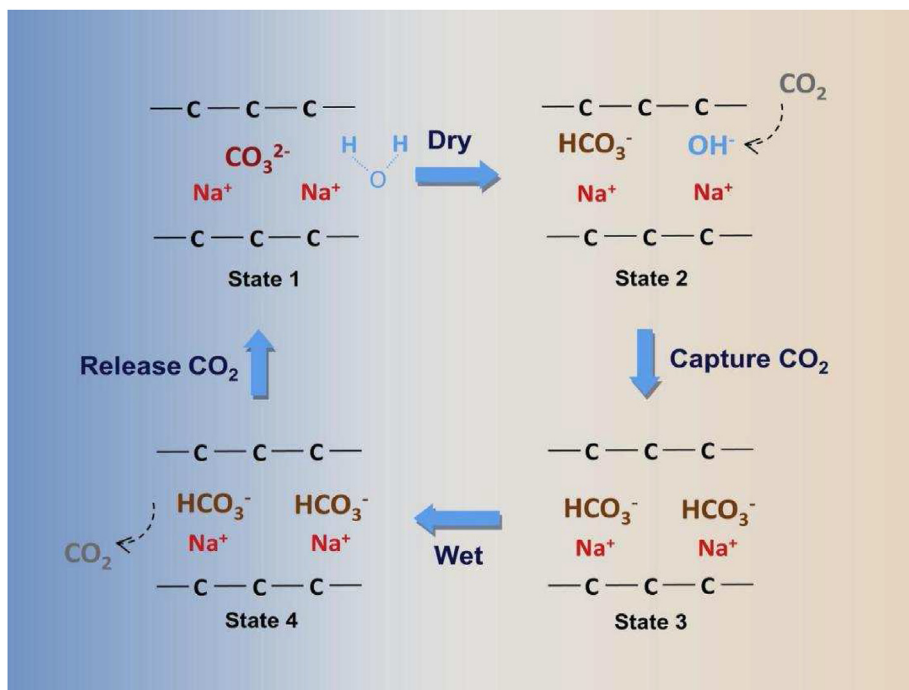


Fig. 15. Moisture-swing sorbent for  $\text{CO}_2$  capture from ambient air [112]. Copyright (2020), with permission from Elsevier.

conditions. Cuesta et al. [49] proposed a pHSA system for functionalized carbon black sorbent through chemical activation, nitrogen enrichment, and biocatalyst immobilization. The lead sorbent developed is a carbon black that is co-activated with potassium carbonate and a nitrogen-containing copolymer and impregnated with immobilized BCA (bovine carbonic anhydrase biocatalyst). It is inspired by the natural conversion of carbon dioxide by carbonic anhydrase biocatalyst found in mammalian red blood cells. This natural enzyme has an aqueous ligand that can be deprotonated and acts as a Lewis base, reacting with  $\text{CO}_2$  to produce a bicarbonate ligand. This ligand rearranges and enters the solution, returning the ligand to the aqueous ligand, and deprotonation is attributed to the ability of this enzyme to readily transfer protons [113]. Studies have shown that BCA sorbents have higher adsorption capacity and more successful pH swing than non-biocatalyst sorbents (Fig. 16).

The study system also combines the advantages of TSA and MSA solid sorbent systems. pHSA systems allow for faster and more complete carbon dioxide capture from the gas stream. The results show that the pHSA sorbents outperform both the TSA sorbent and the MSA sorbents. These properties of the pHSA demonstrate the potential ability to reduce the energy consumption and operating costs associated with carbon capture, which is a necessary condition for the global implementation of the technology.

#### 4.4. Salt solution regeneration (SSR)

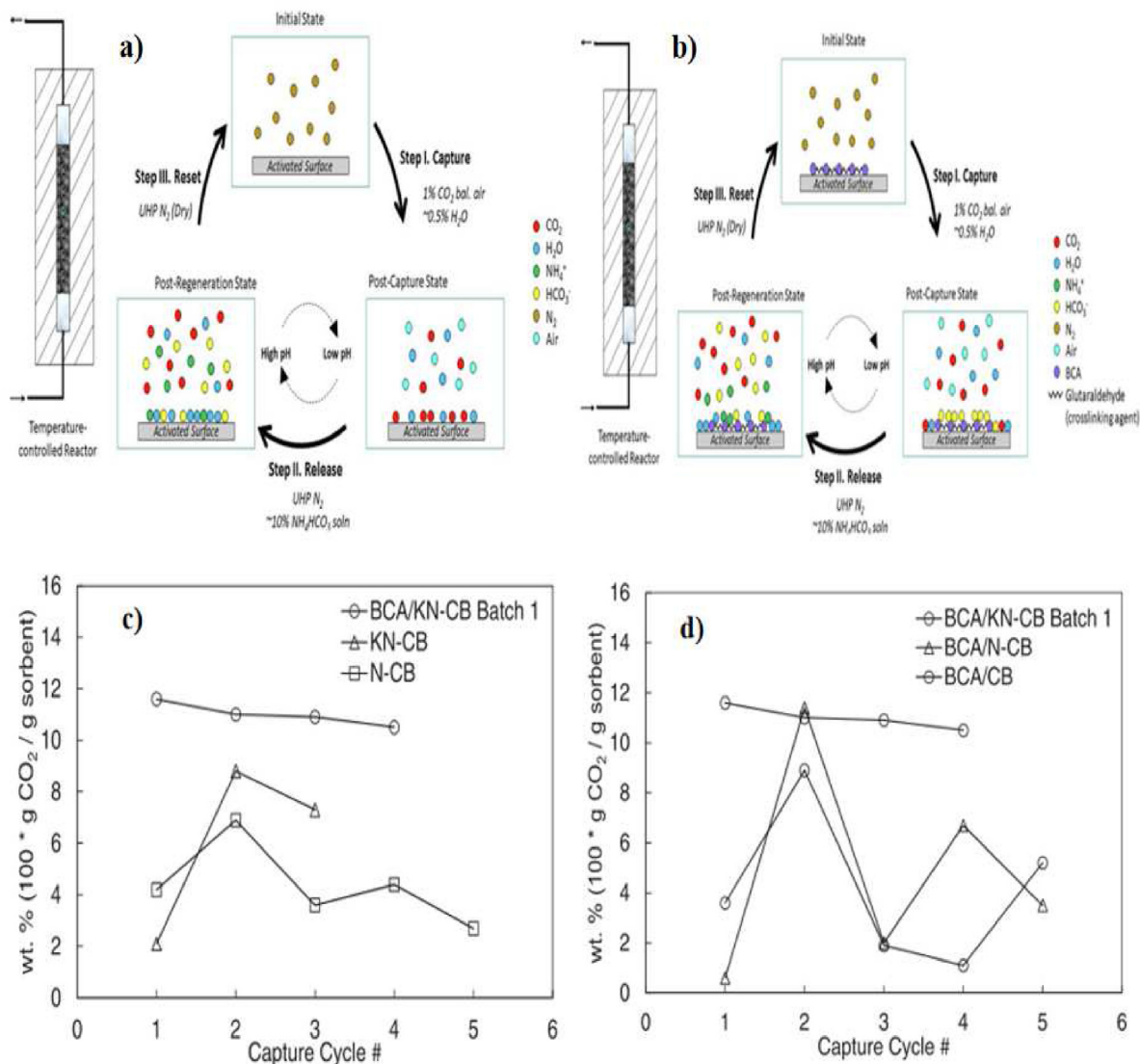
Recently SenGupta et al. developed a new  $\text{CO}_2$  capture regeneration system for DAC, which avoids the energy penalty incurred by the desorption process with high temperature or other physical factors by using salt solution or seawater as regenerant and the desorbed  $\text{CO}_2$  is simultaneously isolated to a harmless, chemically stable alkalinity ( $\text{NaHCO}_3$ ) [114]. The sorbent they used was a Lewis acid-base (LAB) interaction-derived polyamine-Cu(II) complex heterogeneous sorbent, which allowed the sorbent to capture more than 5.0 mmol/g of  $\text{CO}_2$ , almost two to three times more than most

DAC sorbents reported so far. By studying the  $\text{CO}_2$  capture process of the material, they found that the sorbent is essentially a high-capacity anion exchanger, since the  $\text{CO}_2$  capture capacity of the material is not affected by the inlet gas concentration (whether the  $\text{CO}_2$  concentration is 400 ppm, 10% or 50%). At the same time, the regeneration durability of this system has been proven, and there is no significant decrease in adsorption capacity after ten seawater regeneration cycles. The key to this system is the use of a polyamine-Cu(II) complex hybrid sorbent in which the Cu(II) coordination is partially satisfied by the nitrogen donor (N-donor) atoms in the polymer phase, while the carbonate and water satisfy their two positive charges and the remaining coordination number. The concept of  $\text{CO}_2$  adsorption by this complex is given in Fig. 17.

This study shows that simple salt solutions, including seawater, can be used as an effective regenerant; the adsorbed  $\text{CO}_2$  is converted to alkalinity or  $\text{NaHCO}_3$ , and no additional heat is required at this stage. Since it is environmentally safe and acceptable to increase the concentration of  $\text{NaHCO}_3$  at the same salinity level, the used regenerant can be safely returned to the sea, an infinite sink for the captured  $\text{CO}_2$ . Such a sequestration technology would also eliminate the energy required to pressurize and liquefy the  $\text{CO}_2$  prior to deep well injection. Geographic locations near the ocean that do not have geological storage or have difficulty transporting  $\text{CO}_2$  may find this approach attractive. Japan falls into this category because it has no geologic storage on land, and geologic storage to inject  $\text{CO}_2$  beneath the seabed is relatively expensive [115].

Table 2 summarizes the working characteristics of several types of regeneration systems based on  $\text{CO}_2$  DAC technology.

The above discussion shows that TSA is still the most widely researched and most likely to be used in production regeneration systems today, while other regeneration systems have their own significant disadvantages that are difficult to overcome. The MSA systems have low  $\text{CO}_2$  capture efficiency and dependence on humidity, especially the requirement that the source of humidity must be high purity water, which greatly limits their practical application. pHSA systems are still essentially electrochemical



**Fig. 16.** The comprehensive pHSA cycle illustration with a) an activated sorbent and b) biocatalyst-immobilized activated sorbent. c) pHSA performance trends of sorbents in step-wise synthesis compositions. d) pHSA performance trends from potassium and nitrogen additions with BCA [49]. Copyright (2020), with permission from Elsevier.

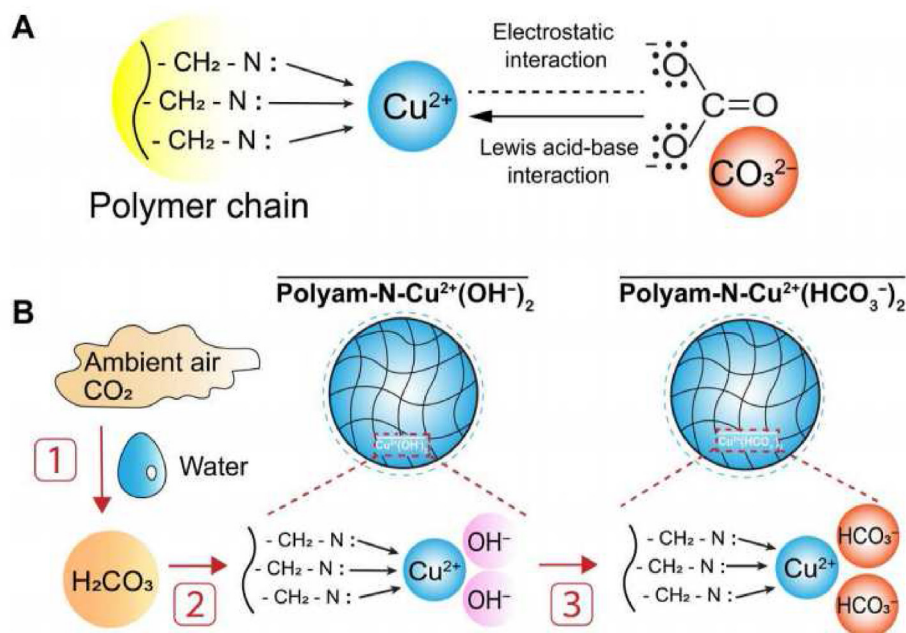
capture systems. The pHSA system is still a special form of CO<sub>2</sub> capture, and the biggest obstacle to its application is the special pH-responsive catalyst, such as the BCA mentioned above, whose expensive cost seriously hinders the practical application of this system. The SSR system is a promising system with a unique regeneration method that makes it suitable for specific environments, but its biggest drawback is that a certain amount of hydroxide needs to be added at the end of each CO<sub>2</sub> capture cycle to replace the anions in the sorbent, and although its regeneration does not require additional energy consumption, the consumption of chemicals can greatly hinder its practical application. However, this does not mean that other regenerative systems other than TSA are not worthy of study, and specific regenerative systems can be used for specific application scenarios, which can help to reduce the application cost of DAC systems.

Among them, MSA system is more suitable for coastal or high humidity areas to reduce the cost of regeneration process. At the same time, the support material used in the MSA system is mainly resin material, which is sensitive to humidity fluctuations and commercially available resin material is cheap and stable. pHSA

system is expensive and not suitable for large-scale industrial DAC. But its high efficiency in capturing CO<sub>2</sub> makes it more suitable for some special small enclosed spaces and efficient in capturing CO<sub>2</sub> to ensure human health. SSR system is suitable for application in island countries and coastal areas due to its unique regeneration method of salt solution, and its lower regeneration cost makes it as potential as TVSA system for large-scale industrialization in DAC field.

### 5. Summary and outlook

In order to mitigate the great threat posed to mankind by the greenhouse effect, it is imperative to reduce atmospheric CO<sub>2</sub> concentration by carbon-negative technologies such as DAC. Amine and polyamine type CO<sub>2</sub> sorbents are widely studied materials in this field. Amine-based sorbents are often used in combination with porous supports for DAC applications, such as porous carbon, MOFs, mesoporous silica, porous organic polymers, and other physical adsorbents. Amine-based sorbents have better adsorption capacity at low CO<sub>2</sub> concentrations compared to these physical



**Fig. 17.** Concept of CO<sub>2</sub> sorption by polyamine-Cu(II) complex. Schematics of (A) the polymeric LAB interaction derived anion exchanger with carbonate binding, and (B) individual steps of the gradual progression of CO<sub>2</sub> sorption (1: CO<sub>2</sub> dissolution, 2: transport of non-ionized H<sub>2</sub>CO<sub>3</sub> inside the ion exchanger, and 3: rapid neutralization with OH<sup>-</sup> followed by selective binding of HCO<sub>3</sub><sup>-</sup>) [114].

**Table 2**  
Different regeneration systems for DAC technology.

Regeneration systems	Operational temperatures (°C)	Operational Energy Efficiency – Full Cycle (kWh/kg CO <sub>2</sub> )	Adsorption Capacity (kg CO <sub>2</sub> /kg sorbent) *100	Time Efficiency (hr/kg CO <sub>2</sub> per kg sorbent)	Refs.
TSA	Capture = 75 Release = 120	0.556	13.8%	18.1	[116–119]
MSA	Capture = 35 Release = 35	0	1.10%	126	[120–122]
pHSA	Capture = 35 Release = 35	0	11.60%	3.88	[49]
SSR	Capture = 25 Release = 25	0	22.44%	–	[114]

adsorbents and lower energy penalty compared to amine-water or alkali metal carbonate systems. Therefore, carbon capture technologies based on amine-based sorbents are being adopted by many carbon capture companies, such as *Global Thermostat* (USA), *Dow* (USA) and *Technic* (Germany). However, although they are some of the advanced industrial CO<sub>2</sub> capture technologies, there are still challenges in the research and development of solid amine sorbents.

While current DAC research is still in its early stages, as research progresses, the cost of DAC will eventually drop to acceptable levels. The most important properties of solid sorbents include adsorption capacity, adsorption kinetics, regeneration energy and cycle stability. These four characteristics basically determine the application performance and cost of the material, and are important for the DAC large-scale applications. Among them, the energy penalty of regeneration is the largest source of cost for DAC, which can be investigated by studying regeneration systems with low energy consumption for regeneration or integrated technologies for CO<sub>2</sub> adsorption and utilization. Besides, O<sub>2</sub> in air is rarely considered in DAC studies for the trapping system, however, amine-based sorbents are extremely sensitive to O<sub>2</sub> and the oxidation resistance

of the material is related to its long-term stability in practical applications. Therefore, the oxidation resistance of sorbents needs to be further investigated. These characterization metrics can be used to provide indicators for comparing different types of CO<sub>2</sub> adsorbents for a given separation process. Therefore, to enable the most accurate cross-study comparisons, the basic adsorption parameters of sorbents must be analyzed over a wide range of variables to provide a comprehensive description of their adsorption behavior and to ensure a balance between improving some metrics at the expense of others. There are a very large number of sorbents used in the DAC field, and the metrics of these sorbents allow rapid screening for suitability for specific applications.

The sorbent is the core of the regeneration system, and a low energy consumption regeneration system is the key to the practical application of DAC. In general, most sorbents are suitable for TVSA systems, which is a universal regeneration method. However, certain sorbents with specific regeneration systems will significantly reduce the cost of DAC. Although these novel regeneration systems are not yet mature, the studies that have been conducted have shown their potential for application. As more researchers explore and investigate more low energy regeneration systems, the



development and application of DAC will be greatly facilitated. In addition, it is more likely that future DAC research will be combined with CO<sub>2</sub> reduction utilization or storage to study the sites of bi-functional materials for CO<sub>2</sub> adsorption and catalytic reduction applied to capture-reduction integration, which not only greatly reduces the overall cost of building the equipment, but also eliminates the energy consumption of sorbents regeneration and reduces the overall cost of the system. At the same time, if the regeneration of the sorbents is not considered, the design of the sorbents can be simpler and more efficient, without considering the high regeneration energy penalty caused by the high affinity of CO<sub>2</sub>. Of course, the design of this DAC bi-functional material requires more consideration of the catalytic reduction performance of the material for CO<sub>2</sub> while maintaining a certain level of CO<sub>2</sub> adsorption performance, which also poses new challenges for researchers.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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