

## Review Article

# Advances in solid adsorbent materials for direct air capture of CO<sub>2</sub>

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**Abstract:** Direct air capture (DAC) of CO<sub>2</sub> is a carbon-negative technology that is not limited by time and geography and can contribute to the realization of the “dual-carbon” goal. In this paper, the current development of direct air capture of CO<sub>2</sub> is reviewed, focusing on four mainstream solid adsorption DAC technologies, namely, metal-organic frameworks (MOFs), solid amine materials, alkali-metal-based adsorbents, and moisture-altering materials, and their advantages and disadvantages in terms of energy consumption, cyclic stability, and adsorption capacity are analyzed. In addition, the engineering applications of solid adsorbent materials are analyzed and the potential of these technologies in practical applications is demonstrated. Finally, the challenges faced by existing DAC adsorbent materials are summarized and the future development direction is put forward.

**Keywords:** direct air capture of CO<sub>2</sub>; adsorbent; solution absorption; solid adsorption; economic efficiency

## 1. Introduction

The term “greenhouse effect” was first coined by Swedish meteorologists in 1901 in response to the growing problem of climate change caused by global warming<sup>[1]</sup>. According to the Intergovernmental Panel on Climate Change (IPCC), greenhouse gases include carbon dioxide (CO<sub>2</sub>), ozone (O<sub>3</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), and hydrofluorocarbons (HFCs)<sup>[2]</sup>. Its report emphasizes that the rising concentration of greenhouse gases, such as CO<sub>2</sub>, CH<sub>4</sub>, and CO, in the atmosphere is the main cause of the global warming phenomenon<sup>[3]</sup>. As greenhouse gases other than CO<sub>2</sub> are much less concentrated in the atmosphere than CO<sub>2</sub>, which is the most dominant gas contributing to the greenhouse effect<sup>[4]</sup>, the increase in atmospheric CO<sub>2</sub> concentration is considered to be the most closely related to global warming.

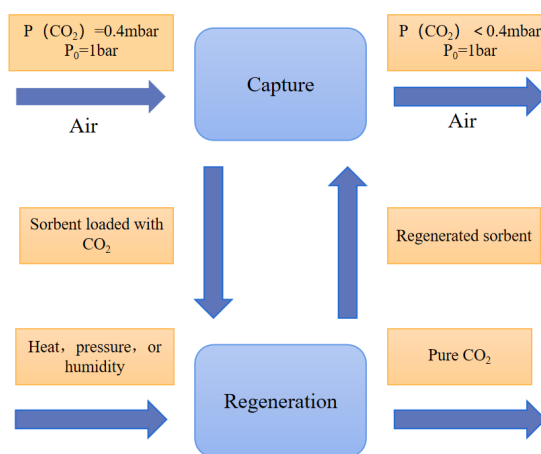
Atmospheric concentrations of CO<sub>2</sub> have increased dramatically, from about 277 ppm at the start of the industrial era in 1750 to about 412 ppm in 2020. In “The State of the Global Climate 2021” published by the World Meteorological Organization (WMO), it is stated that<sup>[5]</sup> sea level rise, ocean warming, and acidification can only be curbed by inventing ways to remove carbon from the atmosphere. Carbon capture, utilization, and storage (CCUS) technology is a key technology for carbon emission reduction, and direct air capture (DAC) as a negative carbon emission technology (technology that removes CO<sub>2</sub> from the atmosphere by increasing natural carbon sinks or utilizing chemical solutions<sup>[6]</sup>) and a backstop technology to realize the “carbon peaking and carbon neutrality goals” has received more and more attention from both academia and industries. DAC technology focuses on capturing and recovering CO<sub>2</sub> emitted from the atmosphere and distributed sources, such as transportation, and can effectively reduce the concentration of CO<sub>2</sub> in the atmosphere by removing CO<sub>2</sub> directly from the air and permanently transforming and sequestering it. Large-scale air capture can produce net negative emissions and reduce CO<sub>2</sub> stored in the atmosphere, oceans, and terrestrial organisms<sup>[7]</sup>. Compared with traditional flue gas capture, air capture of CO<sub>2</sub> has its distinct and unique advantages, which is not only independent of time and geographical constraints but also can be flexibly combined with a number of

low-concentration CO<sub>2</sub> utilizations, such as agricultural and forestry crop yield increases, CO<sub>2</sub> conservation of concrete, etc.<sup>[8]</sup>.

The purpose of this paper is to discuss the current research status of mainstream solid adsorbent material DAC technology based on the introduction of current DAC technology research. The advantages and challenges encountered by each type of technology are analyzed, the development prospects of different routes of DAC technology are clarified, and the future development direction of DAC technology and the important issues that need to be paid attention to are discussed.

## 2. Overview of DAC technology

Creating a carbon-neutral world requires the removal of excess CO<sub>2</sub> from the atmosphere, and Lackner of the University of Arizona introduced the concept of DAC for climate change mitigation in 1999<sup>[9]</sup>, which refers to a technology that traps CO<sub>2</sub> directly from CO<sub>2</sub> gas at a partial pressure of 40 Pa by means of an absorbent. Researchers have questioned whether DAC can mitigate the greenhouse effect due to the low concentration of CO<sub>2</sub> in the air<sup>[10]</sup>. With the development of DAC technology, nowadays it is considered as a viable technology for CO<sub>2</sub> reduction. The technological flow of a DAC system is shown in **Figure 1**<sup>[11]</sup>, where CO<sub>2</sub> in the air is chemically or physically bound by an absorbent, and the CO<sub>2</sub> is returned to the atmosphere at a reduced partial pressure. The absorber is regenerated by heating, pressurization, or changing humidity to release pure CO<sub>2</sub>, which can be recycled again and again. The pure CO<sub>2</sub> output from the DAC system can be stored underground or used to synthesize chemicals, fuels, etc.



**Figure 1.** DAC system process<sup>[11]</sup>.

Lackner<sup>[12]</sup> formally described DAC in 2009 as a technique for separation from 40 Pa of partial pressure using air as the delivery medium for CO<sub>2</sub>. The free energy required to separate 1 mol of CO<sub>2</sub> from a gas mixture is shown in Equation (1):

$$\Delta G = RT \ln\left(\frac{P}{P_0}\right) \quad (1)$$

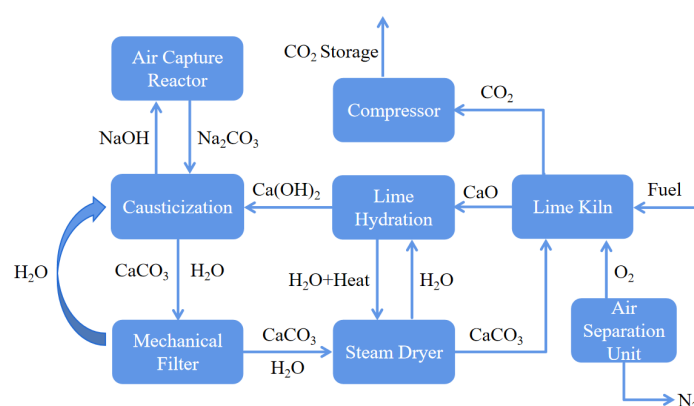
In the above equation,  $R$  is the universal gas constant ( $R = 8.314 \text{ J/mol}\cdot\text{K}$ ),  $T$  is the temperature of the gas (K),  $P$  is the partial pressure of CO<sub>2</sub> at the outlet of the separator (Pa), and  $P_0$  is the atmospheric pressure. At  $T = 300 \text{ K}$ ,  $P_0 = 10^5 \text{ Pa}$ , the free energy of absorbing CO<sub>2</sub> is at least  $|\Delta G| = 20 \text{ kJ/mol}$ , according to the partial pressure of CO<sub>2</sub> in the air of 40 Pa. In the CO<sub>2</sub> capture of flue gas in thermal power plants, the difference in the partial pressures of CO<sub>2</sub> before and after capture is very large, and the adsorbent has to work at low partial pressures ( $<10^4 \text{ Pa}$ ) after the flue gas capture, the minimum being about 1000 Pa, and the binding energy is at

least 13 kJ/mol if  $T = 350$  K. The binding energy of the actual adsorbent is often several times greater than the free energy change ( $>50$  kJ/mol). Therefore, many adsorbents in the flue gas trap are strong enough for airborne  $\text{CO}_2$  capture.

DAC can capture “decentralized” emission sources, such as small fossil fuel combustion units and vehicles, while effectively maintaining and reducing atmospheric  $\text{CO}_2$  concentrations<sup>[13]</sup>. Compared with the traditional carbon capture technology,  $\text{CO}_2$  air capture has its unique advantages: firstly, since the capture source is from the air and the  $\text{CO}_2$  is uniformly distributed in the air, it is not subject to any time and geographical limitations, as it is difficult to capture  $\text{CO}_2$  emitted from any carbon source, and hence DAC plants can be located in any economically viable location (e.g., close to carbon sequestration sites) to minimize the transportation cost. Secondly, transportation is an important and costly part of traditional emission reduction, which can be effectively compensated by air capture with its in-situ carbon capture feature<sup>[12]</sup>. Air capture can also deal with fugitive emissions during the transportation and storage phases of carbon capture, and storage (CCS), which reduces the risk of  $\text{CO}_2$  leakage during geological storage<sup>[14]</sup>.

Current challenges in the development of DAC technology are mainly its high equipment and operating costs<sup>[15]</sup>. It has been shown<sup>[16]</sup> that reducing the amount of carbon electricity and plastic packaging materials used in capture devices can result in some savings in capture costs, predicted to be reduced from \$610/t  $\text{CO}_2$  to \$309/t  $\text{CO}_2$ . The use of captured  $\text{CO}_2$  for plant cultivation, material maintenance, chemical synthesis, etc., has become a hot topic that is currently attracting a lot of attention. Combined with the unique advantages of  $\text{CO}_2$  air capture technology, it is no longer necessary to transport the  $\text{CO}_2$  captured from stationary sources to the designated location through pipelines and hydraulic systems, which enables the DAC technology to be applied to a wider range of areas and is expected to promote the utilization of carbon resources and achieve sustainable development.

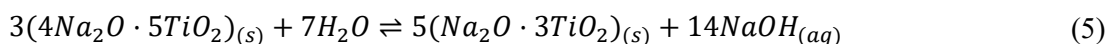
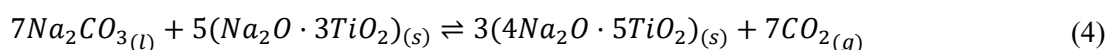
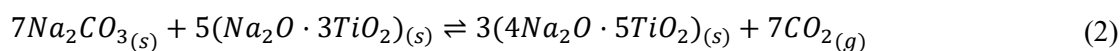
In the solution absorption DAC technique, Keith et al.<sup>[10]</sup> proposed the use of NaOH and CaO to absorb  $\text{CO}_2$ , which was absorbed in a NaOH solution and precipitated as  $\text{CaCO}_3$ . Zeman optimized this technique by proposing a sodium/calcium air capture process, as shown in **Figure 2**<sup>[17]</sup>, where the capture process used a mixture of NaOH and  $\text{Na}_2\text{CO}_3$  for causticizing and partially causticizing with a fixed concentration of NaOH and  $\text{Na}_2\text{CO}_3$ , respectively. The vacuum filtration technique used produced a cake with a water content of less than 30%, which was lower than the water content by Keith et al.<sup>[10]</sup> and Baciocchi et al.<sup>[18]</sup>. The 50% water content of the filter cake and the causticization occurred at ambient temperature, eliminating the heat load required to heat the adsorbent. However, the amount of water lost to evaporation in these experiments averaged 90 g  $\text{H}_2\text{O}$ /g  $\text{CO}_2$ , which is still a large amount of water loss.



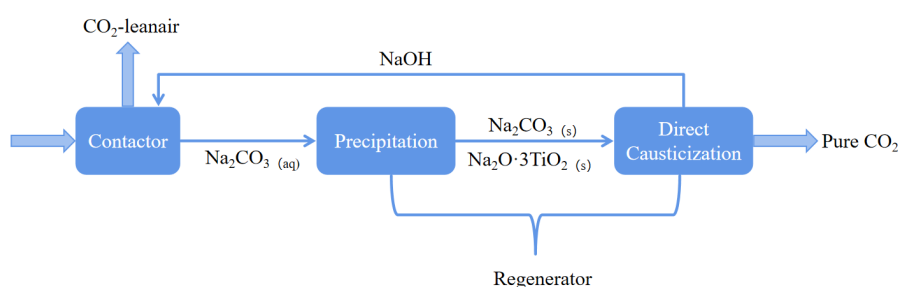
**Figure 2.** Na/Ca air capture process.

Because the evaporation of water requires significant fuel consumption and the resulting precipitate needs to be removed from a solution and dried prior to calcination, Zeman<sup>[19]</sup> continued to design a DAC system to dewater calcite prior to calcination, reducing the overall system energy consumption to 442 kJ/mol CO<sub>2</sub>, which was 237 kJ/mol CO lower than the system proposed by Keith et al.<sup>[10]</sup> The actual energy demand values of the two process scenarios proposed by Baciocchi et al.<sup>[18]</sup>, which were heat released from coal combustion and methane combustion, were about 17 and 12 GJ/t CO<sub>2</sub>, respectively. Even so, excessively high calcination temperatures for CaCO<sub>3</sub> still resulted in significant system energy consumption.

Stolaroff et al.<sup>[20]</sup> used NaOH sprays to capture CO<sub>2</sub> (excluding solution recovery and separation of CO<sub>2</sub>), and the cost of capture was about \$96/t CO<sub>2</sub>, with the lowest cost for sprays of an average drop size of 50 μm. In terms of adsorbent transformation, Mahmoudkhani et al.<sup>[21]</sup> proposed the use of Na<sub>2</sub>O·3TiO<sub>2</sub> instead of NaOH to reduce the temperature required for the desorption stage of CO<sub>2</sub> by more than 50 K. It was found that the main decarbonation reaction in the direct causticization of TiO<sub>2</sub> was the reaction of Na<sub>2</sub>CO<sub>3</sub> with Na<sub>2</sub>O·3TiO<sub>2</sub>, i.e., Equations (2) and (4), and the energy consumption of this method was about half of that of the conventional causticization method, i.e., 90 kJ/mol CO<sub>2</sub>. The formation of 4Na<sub>2</sub>O·5TiO<sub>2</sub> was then hydrolyzed at 100 °C, i.e., Equation (5), and the resulting Na<sub>2</sub>O·3TiO<sub>2</sub> continued to be causticized. The reaction temperature difference between Equations (2)–(4) and (5) was higher than 700 °C, which required high heat transfer efficiency.



**Figure 3** shows a schematic diagram of the NaOH recovery technique from an alkaline aqueous solution of Na<sub>2</sub>CO<sub>3</sub><sup>[22]</sup>. During the causticization process, NaOH is regenerated and CO<sub>2</sub> is released and then compressed. This titanate cycle can substantially reduce the total cost of direct air capture, and the regeneration of concentrated NaOH substantially reduces reactor water loss.



**Figure 3.** Chemical recovery of titanate from air capture.

In the alkali washing process<sup>[23]</sup>, CO<sub>2</sub> is captured in a dedicated air contactor unit and absorbed as K<sub>2</sub>CO<sub>3</sub> in an aqueous solution of KOH. The K<sub>2</sub>CO<sub>3</sub> solution is regenerated by generating calcium carbonate, which is then sent to a calciner to decompose into CaO and CO<sub>2</sub>. Similarly, researchers from Carbon Engineering Ltd.<sup>[24]</sup> constructed a process with KOH and Ca(OH)<sub>2</sub> as the core absorbing solutions and conducted medium-scale trials in Canada. The main flow of the process was the use of a KOH solution to absorb atmospheric CO<sub>2</sub> for conversion into a K<sub>2</sub>CO<sub>3</sub> solution, where Ca(OH)<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> reacted to produce CaCO<sub>3</sub> solids and a KOH solution. The CaCO<sub>3</sub> solids were calcined and decomposed into CO<sub>2</sub> and CaO solids, where the decomposed

CO<sub>2</sub> was compressed and stored, while CaO solids reacted with H<sub>2</sub>O to produce a Ca(OH)<sub>2</sub> solution. The process continued to recycle the reaction, with the loss of K<sup>+</sup> and OH<sup>-</sup> in the absorber in the form of sprays<sup>[25]</sup> and evaporation losses in each process as well. Brethomé et al.<sup>[26]</sup> used an aqueous solution of amino acids (glycine/sarcosine) to produce bicarbonate salts by extracting CO<sub>2</sub> from the air and recovered the amino acids by the crystallization of carbonate anions with bisiminoguanidine solids. The carbonate crystals decomposed at 60 °C to 120 °C to release high-purity CO<sub>2</sub>. Although the temperature required for solvent regeneration is lower compared with the alkaline washing process, both the process proposed by Custelcean et al.<sup>[27]</sup> have higher energy requirements if run continuously. Amino acid solvents have good uptake kinetics but have a low recycling capacity.

Solution-absorption DAC technology has low raw material costs, but the high capacity of the DAC gas treatment makes solution-absorption water loss larger and amine liquid volatilization serious, and because of the high regeneration temperature, the capture cost is high. The energy consumption of DAC technologies based on alkaline solution absorption and solid adsorbent absorption ranges from 2118–2790 kWh and 1400–2777 kWh per ton of CO<sub>2</sub> capture, respectively, and the cost of CO<sub>2</sub> capture ranges from \$200 to \$600 and \$100 to \$400 per ton of CO capture, respectively<sup>[28]</sup>. Overall, solid-adsorbent-based DAC technology performs well in terms of economic efficiency, capture cost, and application potential. There is a need to further reduce the cost of DAC technology to provide important technological support for carbon peaking and carbon neutrality to meet the challenges of climate change.

### 3. Solid adsorption DAC technology

#### 3.1. Molecular sieves and metal-organic frameworks (MOFs)

Molecular sieves are porous crystalline aluminosilicates consisting of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra connected by shared oxygen atoms. Their adsorption properties depend on the size of the cations in the pore structure, the charge density, and the distribution of the cations in the porous structure. Although zeolite is promising for the separation of CO<sub>2</sub> from gas mixtures and has the potential to be used in pressure swing adsorption (PSA), its selectivity for CO<sub>2</sub> is still low compared with gases such as N<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O. Its adsorption capacity decreases rapidly above 30 °C and is almost non-existent after 200 °C<sup>[29]</sup>. The 5A zeolite molecular sieve is structurally stable at very low CO<sub>2</sub> partial pressures, has high cyclic stability and strong adsorption capacity, and can be applied to adsorbent beds to capture low concentrations of CO<sub>2</sub><sup>[30]</sup>. Stuckert and Yang<sup>[31]</sup> compared the new high-microporosity molecular sieves of Li-LSX and K-LSX with NaX molecular sieves with low amine content and found that Li-LSX had an adsorption capacity of 0.82 mmol/g in dry air, which was significantly higher than those of K-LSX and NaX. And there was almost no adsorption of the three in wet air, indicating that the low-silicon X type (LSX) was suitable for use under dry conditions. Wilson and Tezel<sup>[32]</sup> investigated a four-step TVSA cycle (pressurization, adsorption, outgassing, and desorption) and showed that octahedral zeolites with a low silica-to-alumina ratio required dewatering prior to direct CO<sub>2</sub> capture, and energy consumption can be reduced by capturing CO<sub>2</sub> in low-humidity environments and by utilizing the waste heat and heat recovery from the capture process.

MOFs are characterized by robustness, high thermal and chemical stability, a high internal surface area, a high pore volume, and a high specific surface area. They can bind tightly to hydrophobic polymers to prevent water infiltration and capture CO<sub>2</sub> from the air by physisorption<sup>[33]</sup>. Due to the constant porosity and reasonable stability of some MOFs, the potential application areas of MOFs are similar to those of zeolites<sup>[34]</sup>. The physicochemical properties of MOFs can be rationally designed and systematically modulated, especially through pre-synthesis design and post-synthesis modification<sup>[35]</sup>. Saha et al.<sup>[36]</sup> found that the diffusivity of CO<sub>2</sub> on MOF5 and MOF-177 decreased with increasing pressure, while the diffusivity on 5A zeolite increased with

increasing pressure. This was due to the partial saturation blockage of adsorbent pores at higher adsorption loads and higher pressures, resulting in slower kinetics. As a higher CO<sub>2</sub> adsorption loading on 5A zeolite led to greater surface concentration, molecules slipped on the surface and surface diffusion occurred, and this surface diffusion enhanced the overall intracrystalline diffusivity with increasing pressure.

Oschatz and Antonietti<sup>[37]</sup> investigated the selectivity of CO<sub>2</sub> capture by porous adsorbents and the SIFSIX-2-Cu adsorption in hexafluorosilicate (SIFSIX), which was periodically aligned and highly selective at a temperature of 298 K and a CO<sub>2</sub> partial pressure of 1 bar. The adsorption amount of SIFSIX-2-Cu was 1.84 mmol/g and the adsorption amount of SIFSIX-3-Zn was 2.54 mmol/g. In the presence of CO<sub>2</sub> gas mixtures, the adsorption affinity of water decreased, especially for SIFSIX-3-Zn<sup>[38]</sup>. Shekhah et al.<sup>[39]</sup> prepared H<sub>2</sub>S-resistant MOF—SIFSIX-3-Ni by solvent-free synthesis. The CO<sub>2</sub> adsorption isotherms showed that SIFSIX-3-Ni interactions were stronger than Zn and weaker than Cu, and the heat of adsorption was 7% higher than that of Zn species and 8% lower than that of Cu. At 400 ppm and 298 K, the CO<sub>2</sub> adsorption of SIFSIX-3-Cu was 1.24 mmol/g with a smaller pore size, while the CO<sub>2</sub> adsorption of SIFSIX-3-Zn was 0.13 mmol/g with a larger pore size<sup>[40]</sup>. Ding et al.<sup>[41]</sup> found that the adsorption of flexible MOF materials in a CO<sub>2</sub> isothermal adsorption test at 195 K was significantly higher than the adsorption at 273 K and 298 K. The adsorption amounts of the microporous MOF material in the CO<sub>2</sub> isothermal adsorption test at 195 K and 273 K were substantially higher than that at 298 K. The MOF material showed a greater advantage at low temperatures and was more widely applicable to a wider range of regions. Kumar et al.<sup>[42]</sup> and Madden et al.<sup>[43]</sup> found that MOF physisorbents, such as HKUST-1 and Mg-MOF-74, were able to capture carbon from CO<sub>2</sub>-rich gas mixtures, but competition and reaction with atmospheric moisture significantly reduced the selectivity of the adsorbent for CO<sub>2</sub>, thereby reducing the amount of adsorption in the air-trapped concentration. If physical adsorbents are to compete with chemical adsorbents in the presence of water vapor, it is necessary to further develop adsorbents with high adsorption selectivity for airborne CO<sub>2</sub> and to solve the problem of how to control pore size, pore chemistry, and electrostatic forces to improve adsorption performance and adsorption stability. Prestipino et al.<sup>[44]</sup> studied the role of the copper-based MOF material of HKUST-1 in the dehydration process through XRD, Raman, and other characterization methods. They found that the removal of coordinating water molecules chemically bound to Cu(II) sites did not change the copper oxidation state, and the crystalline nature of the material was preserved.

In order to solve the problems of capacity, selectivity, and stability of porous materials (especially under humid conditions), the use of functional groups or the construction of special pore structures with a uniform distribution of active sites on an adsorbent should be explored to enhance the CO<sub>2</sub> binding energy on the adsorbent. Currently, there are three methods to improve the CO<sub>2</sub> binding energy of MOFs: adjusting the distribution of active sites, adjusting the pore size to design ultra-microporous MOFs, and functionalizing MOFs with amines<sup>[45]</sup>.

McDonald et al.<sup>[46]</sup> used ligand expansion to functionalize unsaturated Mg<sup>2+</sup> ions with N,N'-dimethylethylenediamine (mmen). This compound can adsorb CO<sub>2</sub> at low pressure, with an adsorption capacity of 2.0 mmol/g at 0.39 mbar and 25 °C (approximately air) and 3.14 mmol/g at 0.15 bar and 40 °C (approximately flue gas). After being exposed to flowing simulated air of 390 ppm CO<sub>2</sub> for 1 h at 25 °C, the cyclic adsorption capacity was 1.05 mmol/g. The adsorption capacity did not decrease significantly after 10 temperature cycles, and the service life was long. The Brunauer-Emmett-Teller (BET) specific surface area of amine-modified M<sub>2</sub>(dobdc) drastically decreased from 3270 m<sup>2</sup>/g to 70 m<sup>2</sup>/g, and the average pore size decreased. Zhang et al.<sup>[47]</sup> developed ultramicroporous ZU-16-Co, which showed the highest CO<sub>2</sub> absorption (2.63 mmol/g) at 0.01 bar (10,000 ppm). The synergistic effect of the optimized pore chemical structure and size enabled ZU-16-Co to have good trace carbon capture capabilities. Lee et al.<sup>[48]</sup> used ethylenediamine to

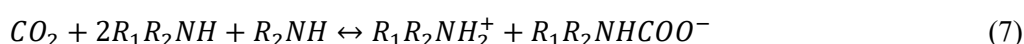
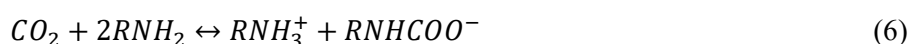
modify  $\text{Mg}_2$  (dobpdc) with amine groups. When the  $\text{CO}_2$  capacity was 0.39 mbar, the adsorption capacity was 2.83 mmol/g. The adsorption capacity dropped slightly after 5 temperature cycles, and the cycle stability was poor. The hydrolytically stable fluorinated metal-organic framework of NbOFFIVE-1-Ni constructed by Bhatt et al.<sup>[49]</sup> had a  $\text{CO}_2$  adsorption capacity of approximately 1.3 mmol/g in an environment of 400 ppm  $\text{CO}_2$  and 298 K. The amount of adsorption was conserved in dry and humid air streams, and water vapor was retained.

Although the use of MOFs for DAC is an effective means to reduce the impact of atmospheric  $\text{CO}_2$  on the global climate, their technical application is still very challenging and requires further research. First, the selectivity and adsorption capacity for  $\text{CO}_2$  must be significant to ensure a significant reduction of atmospheric  $\text{CO}_2$  gas concentration. Second, the materials must be stable for infinite adsorption/desorption cycles without any theoretical loss of properties and with the lowest possible energy to desorb  $\text{CO}_2$  molecules. Overall, the cyclic stability of ligand-extended MOF materials is superior to that of small-molecule grafting. Lastly, since the actual adsorption of  $\text{CO}_2$  occurs under humid conditions, the water stability and  $\text{CO}_2$  affinity of MOFs must be improved. The directions for developing MOF materials are as follows: 1) making the surface of MOFs hydrophobic by surface modification or developing novel MOF materials to improve the stability of adsorbents in the presence of water molecules, as well as improving the affinity for  $\text{CO}_2$  and selectivity, and 2) fabricating materials that can be easily molded and produced by the extension process<sup>[50]</sup>.

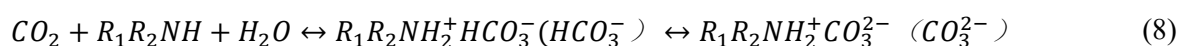
In addition to molecular sieves and metal-organic frameworks, physical adsorption materials include activated carbon and nanomaterials. Activated carbon is a widely used physical adsorbent with low cost and good thermal stability. At low  $\text{CO}_2$  partial pressure, the adsorption capacity and selectivity of activated carbon are lower than those of zeolite<sup>[51]</sup>; at high  $\text{CO}_2$  partial pressure, activated carbon has strong adsorption capacity, is suitable for pressure swing adsorption, is easy to regenerate, and has a reversible adsorption process. Sethia and Sayari<sup>[52]</sup> prepared microporous activated carbon materials with a larger nitrogen content, specific surface area, and pore volume. Under the condition of 25 °C and 1 bar, the  $\text{CO}_2$  absorption amount exceeded 5 mmol/g, indicating that both nitrogen content and ultramicropores had an important impact on  $\text{CO}_2$  adsorption, where ultramicropore adsorption is the main one. Coromina et al.<sup>[53]</sup> prepared a series of activated carbon materials using *Pennisetum giganteum* and camellia as raw materials. The  $\text{CO}_2$  adsorption capacity reached 1.5 mmol/g at 0.15 bar at room temperature, and the  $\text{CO}_2$  adsorption capacity at 1 bar was 5.0 mmol/g. The properties of nanomaterials are generally different from the properties of objects in their overall state and are actively explored by researchers. Sun et al.<sup>[54]</sup> controlled the capture and desorption of  $\text{CO}_2$  by adjusting the charge of boron nitride nanomaterials.  $\text{CO}_2$  molecules formed weak interactions with uncharged boron nitride nanomaterials. When the nanomaterials were negatively charged, the  $\text{CO}_2$  molecules were tightly bound, and the  $\text{CO}_2$  molecules would spontaneously desorb after the electrons were removed. Negatively charged boron nitride nanoadsorbents had high selectivity for  $\text{CO}_2$  in the presence of  $\text{CH}_4$  or  $\text{H}_2$ . Nanomaterials have certain application potential in the field of direct air capture of  $\text{CO}_2$ . Lu et al.<sup>[55]</sup> used 3-aminopropyltriethoxysilane (APTS), modified carbon nanotubes (CNTs), granular activated carbon (GAC), and zeolite under the same conditions. After the modification, the order of the  $\text{CO}_2$  adsorption capacity from high to low was CNTs, zeolite, and GAC. After the modification, the surface properties of these adsorbents changed. The affinity between the  $\text{CO}_2$  molecules and the adsorbent surface increased, and the alkalinity and amine groups increased, allowing these adsorbents to adsorb more  $\text{CO}_2$  gas. Physical adsorption makes it possible for  $\text{CO}_2$  to regenerate at lower temperatures. Generally speaking, in the presence of water vapor and  $\text{CO}_2$  at the same time, physical adsorption is not highly selective for  $\text{CO}_2$ , resulting in weak adsorption capacity and failing to meet the requirements for direct air capture. In the future, adsorption capacity can be improved by controlling the pore size and structure within a crystal, and physical adsorption materials with higher selectivity for  $\text{CO}_2$  adsorption from the air can be further explored.

### 3.2. Solid amine materials

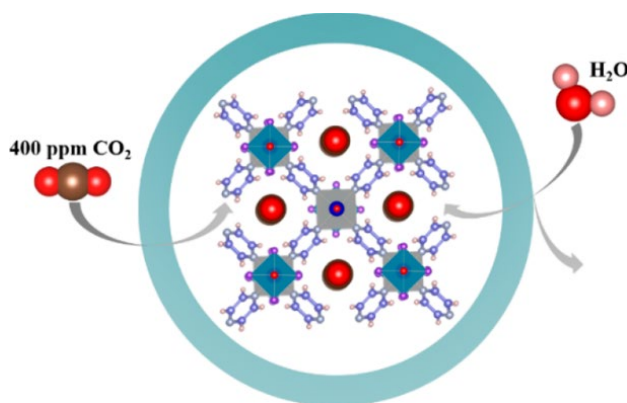
The liquid amine absorption process has many disadvantages, such as corrosion, high energy consumption, and reduced amine concentration in the aqueous phase due to viscosity and foaming problems. When amine solutions are used directly for CO<sub>2</sub> separation, the evaporation of the solution during regeneration of the adsorbent leads to significant heat loss. Solid amines are particularly well suited for the extraction of CO<sub>2</sub> from ultrathin gas mixtures in the air. As unique low-temperature chemisorbents, solid amines can spontaneously absorb CO<sub>2</sub> from ambient air and regenerate it under mild conditions by heat or a combination of heat and vacuum. The principle of CO<sub>2</sub> uptake by solid amines is that the amino group reacts with CO<sub>2</sub> to form carbamate ions. The reaction of CO<sub>2</sub> with amines under anhydrous conditions requires one CO<sub>2</sub> molecule and two primary (Equation (6)) or secondary (Equation (7)) amine groups to give ammonium carbamate<sup>[13]</sup>.



When moisture is present, CO<sub>2</sub> reacts with amines to produce ammonium carbonate or bicarbonate (depending on pH), i.e., Equation (8), and the maximum CO<sub>2</sub>/N ratio that can be obtained by the chemical reaction under moist conditions is 1:1, which is twice as much as that obtained under the corresponding anhydrous conditions<sup>[13,56]</sup>.



Didas et al.<sup>[57]</sup> prepared aza-amines through in-situ polymerization on mesoporous silica supports and synthesized hyperbranched aminosilica (HAS). And a series of mesoporous silica materials grafted only with primary (3-aminopropylsilyl), secondary (N-methyl-3-aminopropylsilyl), and tertiary (N,N-dimethyl-3-aminopropylsilyl) amines were prepared and characterized, and tertiary amine (N,N-dimethyl-3-aminopropylsilyl)-grafted mesoporous silica materials were prepared and characterized. Under dry conditions, the primary amine CO<sub>2</sub> had the highest capture potential, the secondary amine had a much lower adsorption capacity, and the tertiary amine was virtually inactive. The isothermal heats of adsorption for the materials containing primary and secondary amines were 112 and 84 kJ/mol, respectively. The enthalpies of the reaction of the primary amines with CO<sub>2</sub> were higher than those of the secondary amines, and the oxidation was stable. In the absence of water, 2 mol of amine was required to capture 1 mol of CO<sub>2</sub>, whereas only 1 mol of amine was required to capture 1 mol of CO<sub>2</sub> in the presence of water. Thus, water improved the amine efficiency of carbon capture<sup>[58]</sup>. **Figure 4** shows a schematic diagram of air capture by a solid amine adsorbent.

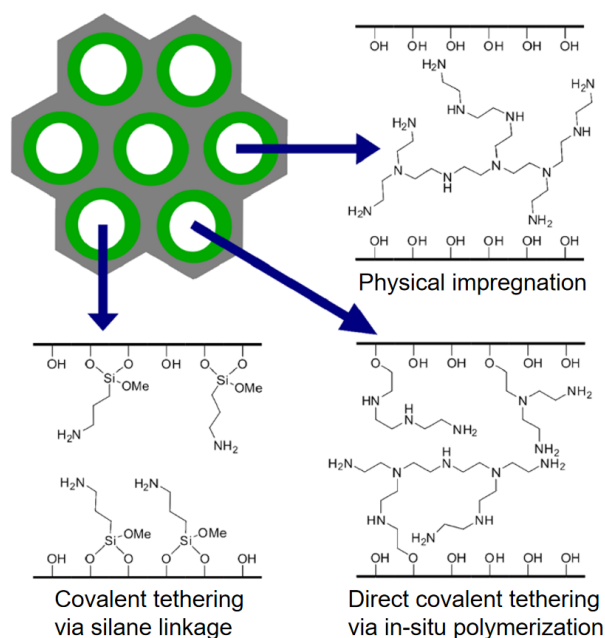


**Figure 4.** Schematic diagram of solid amine adsorbent air capture<sup>[59]</sup>.

As shown in **Figure 5**, solid amine adsorbents are classified into three categories according to the binding mode of organic amines and carriers; Category 1 is solid amine adsorbents prepared by physically



impregnating the amine into the pores of the carrier; in Category 2, the amine is grafted onto the carrier through covalent bonding, such as organosilanes, which can form a covalent bond to silica carriers; and in Category 3, the amine monomers are bound covalently with the carriers by means of in-situ polymerization<sup>[13,57,58]</sup>.



**Figure 5.** Schematic diagram of three types of solid amine adsorbents<sup>[13]</sup>.

Xu et al.<sup>[60]</sup> used the first type of solid amine preparation method to fix branched polyethyleneimine (PEI) in the channels of a mesoporous molecular sieve and prepared a PEI-modified MCM-41 mesoporous molecular sieve. (MCM-41-PEI). The modification significantly improved the adsorption capacity of MCM-41. The desorption rate of MCM-41-PEI for CO<sub>2</sub> was faster than that of pure PEI, and the cycle was stable at relatively high temperatures. Guo et al.<sup>[59]</sup> prepared a novel composite of metal-organic frameworks (MOF) and polyacrylate (PA): NbOFFIVE-1-Ni@PA. At 400 ppm and 298 K, the CO<sub>2</sub> uptake of the NbOFFIVE-1Ni@PA composite (1.44 mmol/g) was higher than that of pristine NbOFFIVE-1-Ni (1.30 mmol/g), and the time cost for a complete adsorption/desorption cycle in a fluidized bed was shortened to 25 min, with good thermal stability and water resistance. With a macroporous methacrylate adsorption resin as the carrier and PEI as the organic amine, Zhao et al.<sup>[61]</sup> used the liquid phase impregnation method to prepare a solid amine adsorbent and studied its adsorption behavior for low-concentration CO<sub>2</sub> at room temperature. The results showed that the macroporous resin has the best adsorption performance when loading 50% PEI (mass fraction), and the maximum adsorption capacity of pure CO<sub>2</sub> was 175 mg/g (3.97 mmol/g). The adsorption behavior of CO<sub>2</sub> was determined by diffusion kinetics and adsorption thermodynamics. A low temperature was conducive to increasing the adsorption capacity. The adsorbent had excellent dynamic adsorption performance for CO<sub>2</sub> with a concentration of 400 ppm–15%. Chaikittisilp et al.<sup>[62]</sup> prepared a mesoporous  $\gamma$ -alumina-supported polyethyleneimine composite and found that its saturated adsorption capacity for 400 ppm CO<sub>2</sub> was 1.33 mmol/g at 25 °C, and the adsorbent was treated with steam at 105 °C. After desorption, the CO<sub>2</sub> absorption capacity of the adsorbent supported on mesoporous  $\gamma$ -alumina dropped by 25% compared with the initial value, indicating that the adsorption capacity and cycle stability of this supported amine adsorbent were high. Type I solid amine adsorbents are sensitive to changes in temperature and humidity. Although the physical adsorption capacity is high, when the PEI loading capacity is high, there is competitive adsorption of CO<sub>2</sub> and H<sub>2</sub>O, and the stability needs to be improved. The adsorption capacity decreases significantly after several adsorption-

desorption cycles. The increase in the PEI pore load will increase the mobility of PEI. Excessive PEI increases diffusivity and is easy to aggregate. Dispersion in carriers such as Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> is the focus of research<sup>[63]</sup>.

Type 2 solid amine adsorbents have amine functional groups chemically grafted on the carrier surface and are more stable during regeneration than Type 1 adsorbents. It can be prepared by a variety of methods:

- 1) Silane chemical reaction: The siloxane groups of amine-containing silanes are first hydrolyzed (or alcoholized) and then combined with active hydroxyl groups, which condense on the surface of the porous material to produce a single layer of amine groups.
- 2) Combination with coupling agent: A coupling agent is a chemical substance that can be combined with both porous materials and amine-containing compounds. First, the coupling agent is grafted onto the surface of the porous material, and then the amine-containing compound is combined with it<sup>[51]</sup>.

Belmabkhout et al.<sup>[64]</sup> used the gravimetric method to study the adsorption of CO<sub>2</sub>, N<sub>2</sub>, and other gases by triamine-grafted porous expanded mesoporous silica (TRIFE-MCM-41). The material exhibited a high affinity for CO<sub>2</sub> over the entire pressure range. Column penetration dynamic measurements showed that when the CO<sub>2</sub> concentration was in the range of 5%–50%, the selectivity of the adsorbent to CO<sub>2</sub> was higher than that of N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O. TRIFE-MCM-41 had high stability over hundreds of cycles of temperature swing adsorption-desorption and pressure swing adsorption-desorption. Brillman and Veneman<sup>[65]</sup> loaded tetraethylene pentamine onto a silica gel to prepare a solid amine adsorbent and examined its adsorption performance and desorption energy consumption at low CO<sub>2</sub> partial pressures (200–1600 ppm).

Type 3 amine adsorbents have relatively high loading capacity and stability, and in-situ polymerization of amine monomers and carriers makes them excellent for regeneration. Drese et al.<sup>[66]</sup> prepared a hyperbranched aminosilica (HAS) adsorbent through aziridine ring-opening polymerization in the presence of a mesoporous silica SBA-15 carrier. The synthesis of HAS occurred through the interaction with surface OH groups. The ring-opening polymerization of the group formed Si-O-C bonds, which combined organic functions on the SiO<sub>2</sub> surface. Choi et al.<sup>[67]</sup> prepared a solid amine adsorbent through in-situ ring-opening polymerization of aziridine. When the amine content was high (10 mmol/g, calculated as N), its adsorption capacity for 400 ppm CO<sub>2</sub> was 1.72 mmol/g; some amine adsorbents and their adsorption capacities are shown in **Table 1**.

**Table 1.** CO<sub>2</sub> adsorption capacity of some amine adsorbents at 298 K.

Adsorbent	CO <sub>2</sub> concentration (ppm)	Maximum adsorption capacity (mmol/g)	Ref.
NbOFFIVE-1-Ni@PA	400	1.44	[59]
NbOFFIVE-1-Ni	400	1.3	[59]
SIFSIX-3-Zn	400	0.13	[40]
SIFSIX-Cu	400	1.24	[40]
SIFSIX-3-Ni	400	0.18	[51]
SynA40	400	1.33	[62]
HAS6	400	1.72	[67]
FS-PEI	420	1.71	[68]

Goepfert et al.<sup>[69]</sup> summarized the technology of capturing CO<sub>2</sub> from the air and pointed out that solid amine adsorbents have the advantages of high CO<sub>2</sub> adsorption capacity, low regeneration energy consumption, and good water resistance. Solid amine adsorbents have a higher selectivity for CO<sub>2</sub> than other gases in the air,

such as O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O, and have good cycle stability. However, research on the use of solid amine adsorbents for CO<sub>2</sub> capture from the air is still in its infancy. For the capture of low-concentration CO<sub>2</sub>, the adsorption performance and amine utilization are still low due to the limitation of CO<sub>2</sub> kinetic diffusion. Moreover, the carrier preparation process is complex, resulting in the high cost of the capture process and difficulty in large-scale applications.

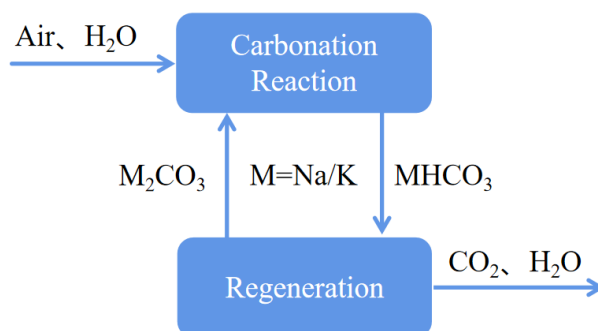
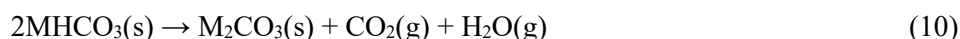
### 3.3. Alkali-metal-based adsorbents

Dry decarbonization technology using alkali-metal-based adsorbents first emerged in the 1990s. It is prepared by attaching alkali metal carbonate to a carrier material and has many advantages, such as high specific surface area, high porosity, and good adsorption performance. The carbonation reaction temperature of the adsorbent is between 60 °C–80 °C, and the regeneration reaction temperature is between 100 °C–200 °C. The adsorbent is not easily deactivated and can maintain a high conversion rate after multiple cycles. The technology has the advantages of both chemical absorption and physical adsorption processes. Not only can the adsorbent react with CO<sub>2</sub> quickly and efficiently, but it also avoids equipment corrosion and regeneration energy consumption problems caused by wet operations. The chemical reaction formulas are shown in Equations (9) and (10), and **Figure 6** shows the principle of the air capture by alkali-metal-based adsorbents.

Carbonation reaction:



Regeneration reaction (M is Na or K):



**Figure 6.** Schematic diagram of alkali-metal-based adsorbent air capture.

Zeman<sup>[70]</sup> proposed using alkaline earth metals to dissolve CO<sub>2</sub> into a solution to precipitate carbonates. CO<sub>2</sub> is regenerated through thermal decomposition or calcination of carbonate and compressed for storage. This process can combine and modify existing industrial processes to improve energy efficiency. Ca(OH)<sub>2</sub> and CaO in steel slag or concrete waste are soluble in water and react with CO<sub>2</sub> in ambient air to safely and permanently capture and store carbon in the form of stable carbonate minerals (CaCO<sub>3</sub>). Stolaroff, Lowry, and Keith<sup>[71]</sup> found that most available Ca metals dissolve within 10 h, which is fast enough for industrial processes. Przepiórski et al.<sup>[72]</sup> prepared MgO/CaO-supported carbon materials by pyrolysis of a mixture of ethylene glycol phthalate and natural dolomite. MgO and CaO are both alkaline oxides and were easily washed out of the hybrid material, thereby obtaining a new type of highly porous carbon rich in micropores and mesopores. The increased reaction contact area increased the carbonation rate. Hu et al.<sup>[73]</sup> synthesized Ni-supported CaO microspheres as bifunctional materials and used porous CeO<sub>2</sub> as an active accelerator. Uniformly mixed CeO<sub>2</sub>

acted as an active accelerator, enhancing the CO<sub>2</sub> affinity of CaO, the low-temperature activity of Ni, the CO<sub>2</sub> capture and conversion capabilities at 650 °C, the sintering resistance of CaO, and the dispersion of Ni.

Nikulshina et al.<sup>[74]</sup> experimentally studied the process of CaO/Ca(OH)<sub>2</sub> capturing CO<sub>2</sub> from the air through two carbonization reactions through thermogravimetry. The rates of both carbonization reactions increased with increasing temperature. The Ca(OH)<sub>2</sub> carbonation reaction was less hindered by diffusion under the catalysis of water. The team then tried to capture CO<sub>2</sub> at room temperature and studied the air capture of three Na-based thermochemical cycles<sup>[75]</sup>. Using 500 ppm CO<sub>2</sub> in air at 25 °C, the carbonization degree of NaOH reached 9% after 4 h, while the carbonization degree of Na<sub>2</sub>CO<sub>3</sub> using water-saturated air reached 3.5% after 2 h. The thermal decomposition of NaHCO<sub>3</sub> in the three cycles was in the range of 90 °C–200 °C. The reaction speed of the carbonation step is very slow, so a relatively large mass flow rate is required. If the reactor process is scaled up, it will become very complicated, hindering the application of sodium-based adsorbents to capture CO<sub>2</sub> in the air. Later, in order to further reduce energy consumption, this team proposed a capture method that used concentrated solar energy as a heat source for high-temperature processes<sup>[76]</sup>. Through continuous CaO carbonization and CaCO<sub>3</sub> calcination steps, CO<sub>2</sub> in the ambient air was continuously removed. Water vapor was introduced into the process to enhance its dynamics. The presence of water vapor significantly enhanced the surface kinetics of CO<sub>2</sub> adsorption by OH groups on solid surfaces, but the changes in water concentration in the range of 3%–17% had little effect on CO<sub>2</sub> absorption<sup>[77]</sup>.

Researchers have tried to increase the reaction contact area and use porous carriers to load alkali metal carbonates to improve the adsorption performance of adsorbents at ultra-low CO<sub>2</sub> partial pressure. Shigemoto et al.<sup>[78]</sup> used activated carbon as a carrier and loaded Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Rb<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, and other substances on the activated carbon to make different alkali-metal-based adsorbents in the presence of water vapor. Under the conditions, CO<sub>2</sub> was absorbed sequentially in the reaction temperature range of 40 °C–120 °C. It was found that all the adsorbents except the loaded Na<sub>2</sub>CO<sub>3</sub> had good CO<sub>2</sub> adsorption performance, and the prepared adsorbents were easy to regenerate and cycle. Lee et al.<sup>[79]</sup> made different potassium-based adsorbents by loading K<sub>2</sub>CO<sub>3</sub> on SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, AC, MgO, Al<sub>2</sub>O<sub>3</sub>, CaO, and other carriers. The results showed that when K<sub>2</sub>CO<sub>3</sub> was loaded on AC, TiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>, the carbonation reaction efficiency of the adsorbent was high. Among them, the carbonation reaction product of KHCO<sub>3</sub> of the adsorbents under the load of AC, ZrO<sub>2</sub>, and TiO<sub>2</sub>, was completely regenerated at around 150 °C with high cycle stability. In addition, the authors also studied the effects of water vapor, temperature, and loading on the carbonation reaction of potassium-based adsorbents<sup>[80]</sup>.

In order to obtain the adsorption mechanism of CO<sub>2</sub> by potassium-based adsorbents with different carriers, Wang et al.<sup>[81]</sup> loaded K<sub>2</sub>CO<sub>3</sub> on three carriers (circulating fluidized bed boiler fly ash, activated carbon, and alumina), which were reacted at a reaction temperature of 70 °C. The results showed that the K<sub>2</sub>CO<sub>3</sub>/AC adsorbent had the best CO<sub>2</sub> adsorption performance, while the K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> adsorbent had the worst adsorption performance. The specific surface area of an adsorbent plays an important role in the carbonation reaction. As the reaction temperature increases, the internal diffusion resistance increases significantly. Lee et al.<sup>[82]</sup> studied the CO<sub>2</sub> adsorption performance of a potassium-based TiO<sub>2</sub> adsorbent in a fixed-bed reactor at 60 °C. The structure of the adsorbent was affected by the calcination atmosphere and calcination temperature. The rutile structure of TiO<sub>2</sub> prevented the formation of new structures, such as K<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>. In order to obtain high CO<sub>2</sub> capture capacity, it is necessary to control the formation of new structures during the preparation process of adsorbents to ensure the role of active components.

Zhao et al.<sup>[83]</sup> selected activated carbon (AC), Al<sub>2</sub>O<sub>3</sub>, 5A zeolite, 13X zeolite, and silica aerogels (SG) as carriers and K<sub>2</sub>CO<sub>3</sub> as the active component. The CO<sub>2</sub> adsorption performance of the adsorbents was experimentally verified at ambient temperature and CO<sub>2</sub> concentration of 5000 ppm. It was found that

$\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  has the highest  $\text{CO}_2$  adsorption capacity, while  $\text{K}_2\text{CO}_3/\text{AC}$  has the highest carbonation conversion rate. The increase in  $\text{H}_2\text{O}$  content helped increase the  $\text{CO}_2$  adsorption capacity. At ambient temperature, the  $\text{K}_2\text{CO}_3/\text{AC}$  adsorbent was more effective in removing  $\text{CO}_2$  in confined spaces. The same team<sup>[84]</sup> studied the carbonization behavior of  $\text{K}_2\text{CO}_3/\text{AC}$  using a thermogravimetric analyzer at a low reaction temperature of 20 °C–60 °C and a low  $\text{CO}_2$  concentration of 0%–4%. It was found that the reaction path of  $\text{K}_2\text{CO}_3/\text{AC}$  consisted of two steps: a hydration reaction occurred first to form  $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$  and  $\text{K}_4\text{H}_2(\text{CO}_3)_3 \cdot 1.5 \text{H}_2\text{O}$ , and then  $\text{KHCO}_3$  was rapidly generated. The effect of  $\text{CO}_2$  concentration on the carbonation reaction path of  $\text{K}_2\text{CO}_3/\text{AC}$  was not significant; instead, relative humidity played an important role in this process. And when the temperature was kept constant and the heat transfer of the system was ignored, a kinetic model of  $\text{CO}_2$  adsorption by  $\text{K}_2\text{CO}_3$  particles was established based on the shrinking core model<sup>[85]</sup>. It was found that the process of  $\text{CO}_2$  adsorption by  $\text{K}_2\text{CO}_3$  was mainly composed of surface chemical and diffusion reactions. The activation energies were 33.4 kJ/mol and 99.1 kJ/mol, respectively.

Dong<sup>[86]</sup> studied the adsorption and desorption characteristics of  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  doped with  $\text{TiO}_2$  and found that loading a 1%–3% mass fraction of  $\text{TiO}_2$  in  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  improved the  $\text{CO}_2$  adsorption rate of the adsorbent, but excessive doping of more than 5% impurities blocked the micropores of the carrier and reduced the adsorption capacity and rate. Masoud et al.<sup>[87]</sup> prepared carbon-loaded  $\text{K}_2\text{CO}_3$  particles of different sizes by adjusting the  $\text{K}_2\text{CO}_3$  loading. The study found that  $\text{K}_2\text{CO}_3$  with the smallest particle size adsorbed the fastest and required the lowest temperature for  $\text{CO}_2$  desorption. Therefore, particle size directly affects the kinetics of the process and the energy input required. An ideal adsorbent based on the loading of  $\text{K}_2\text{CO}_3$  must have a higher  $\text{K}_2\text{CO}_3$  loading and a smaller particle size.

Derevschikov et al.<sup>[88]</sup> used a  $\text{K}_2\text{CO}_3/\text{Y}_2\text{O}_3$  composite adsorbent for the air capture of  $\text{CO}_2$ . When the regeneration temperature increased from 150 °C–250 °C to 300 °C–350 °C, the  $\text{CO}_2$  absorption amount dropped from 0.64 mmol/g to 0.23 mmol/g. The permeability of the adsorbent layer also deteriorated. Potassium-containing substances interacted with the high-temperature surface of yttrium oxide to generate a certain crystalline phase. Veselovskaya et al.<sup>[89]</sup> synthesized a  $\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  composite adsorbent to overcome the problem of the low carbonation rate by placing the active components in a porous carrier. Experiments on  $\text{CO}_2$  absorption and desorption from the air were conducted. When the regeneration temperature was 250 °C–300 °C, stable  $\text{CO}_2$  absorption of 0.64 mmol/g–0.7 mmol/g was obtained through recycling. In 2021, researchers synthesized a  $\text{K}_2\text{CO}_3/\text{ZrO}_2$  composite material based on mesoporous zirconia aerogels<sup>[90]</sup> and using  $\text{K}_2\text{CO}_3$  impregnation solutions with different molar concentrations. The adsorption reaction was carried out at a temperature of 25 °C and a relative humidity of 25%, and the thermal regeneration reaction was carried out at 200 °C. After 14 adsorption-desorption cycles, the decrease in  $\text{CO}_2$  adsorption amount was very low. The adsorbent had good cycle stability, and reducing the regeneration temperature was beneficial for reducing reaction energy consumption. A portion of  $\text{K}_2\text{CO}_3$  loaded into zirconia mesopores formed surface species that did not actively participate in the  $\text{CO}_2$  absorption and desorption processes. The  $\text{CO}_2$  absorption capacity of the  $\text{K}_2\text{CO}_3/\text{ZrO}_2$  composite when the  $\text{K}_2\text{CO}_3$  loading was 23% was higher than that of the  $\text{K}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  composite studied under the same conditions. Compared with amine adsorbents, potassium alumina adsorbents have great prospects in air capture if there is sufficient heat to cope with the temperature fluctuations required during the adsorbent circulation process<sup>[91]</sup>. The adsorption capacity of some alkali metal adsorbents for  $\text{CO}_2$  is shown in **Table 2**.

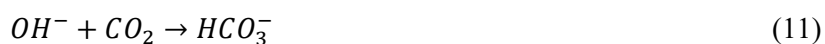
**Table 2.** Adsorption capacity of some alkali metal adsorbents for CO<sub>2</sub>.

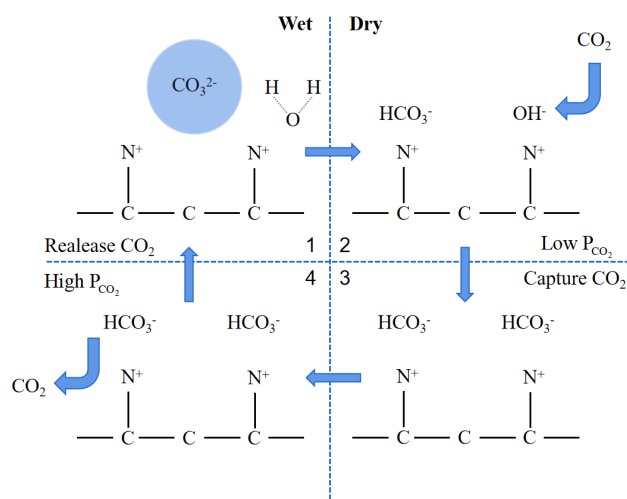
Adsorbent	Adsorption and regeneration temperature (K)	Relative humidity (%)	Maximum adsorption capacity (mmol/g)	Ref.
K <sub>2</sub> CO <sub>3</sub> /ZrO <sub>2</sub>	298/523–573	25	0.74	[90]
Ru+Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	298/573	90	1.3	[92]
CaO/CaCO <sub>3</sub>	673/1043	100	0.06	[76]
AlK10	298/523	0	0.7	[91]
K <sub>2</sub> CO <sub>3</sub> /Y <sub>2</sub> O <sub>3</sub>	298/423–523	-	0.64	[88]
K <sub>2</sub> CO <sub>3</sub> /Y <sub>2</sub> O <sub>3</sub>	298/573–623	-	0.23	[88]
K <sub>2</sub> CO <sub>3</sub> /AC	293/673	63	0.037	[83]
K <sub>2</sub> CO <sub>3</sub> /5A	293/673	63	0.09	[83]

Excessive regeneration temperature is the main reason for the high energy consumption of alkali-metal-based solid adsorbents in practical applications. Compared with physical adsorption, H<sub>2</sub>O is usually a required component for adsorption reaction, so the presence of H<sub>2</sub>O generally does not affect the adsorbents' selectivity to CO<sub>2</sub>. Among alkali-metal-based solid adsorbents, potassium-based adsorbents have a higher carbonation reaction activity than those of sodium-based adsorbents. In-depth development of potassium-based adsorbents is more conducive to the industrial use of alkali metal decarburization technology. The reaction activity of soda ash metal carbonate is relatively low, and the reaction takes a long time. Therefore, in order to improve the activity of the adsorbent, it is necessary to find suitable carrier materials and develop high-loading adsorbents.

### 3.4. Wetting materials

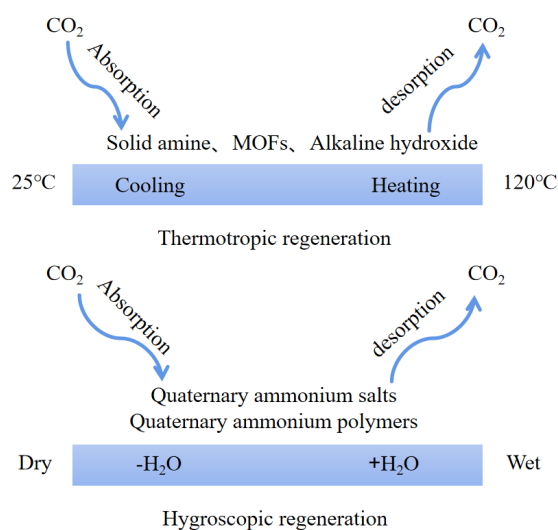
To explore how to further reduce energy consumption, Lackner et al.<sup>[14]</sup> saturated a resin with CO<sub>2</sub> and added 1 mol of CO<sub>2</sub> to each mole of positive charge on the resin surface. The compound produced by absorption had the same CO<sub>2</sub> charge ratio as that of NaHCO<sub>3</sub>, with one CO<sub>2</sub> for every two charges. The basic reaction was the direct formation of bicarbonate on the resin, as shown in Equations (11)–(13). Absorption continued until the material was completely converted to the bicarbonate state, with an absorption rate comparable to the absorption rate of 1 mol NaOH solution into a NaHCO<sub>3</sub> solution, that is, between 10–80 μmol/m<sup>2</sup>·s. The principle of humidity swing adsorption is shown in **Figure 7**. There are three main steps in humidity swing adsorption: first, in a dry environment, the alkaline groups on the surface of the adsorbent adsorb CO<sub>2</sub> in the air; second, CO<sub>2</sub> is desorbed from the adsorbent when the humidity is high; and third, the desorbed CO<sub>2</sub> is stored or recycled.





**Figure 7.** Schematic diagram of principle of humidity swing adsorption.

A quaternary ammonium (QA) adsorbent is attached to its carrier through functional groups. Wang et al.<sup>[93]</sup> used an amine-based anion exchange resin prepared in an alkaline form to capture CO<sub>2</sub> from the air. The resin absorbed CO<sub>2</sub> when the air was dry and released CO<sub>2</sub> when the air was wet. This humidity swing adsorption process can achieve direct air capture of circulating CO<sub>2</sub>. Humid resin in the air will automatically dry out and then absorb CO<sub>2</sub>, forming a cycle caused by moisture. At a given load condition, the CO<sub>2</sub> equilibrium partial pressure on the resin can be increased by two orders of magnitude by wetting the resin regeneration. Wang et al.<sup>[94]</sup> developed a DAC adsorbent with moisture swing adsorption (MSA) capability and ultra-high kinetics by grafting QA functional groups onto mesoporous polymers with high specific surface areas. The half-adsorption time of this adsorbent in an atmospheric environment was 2.9 min, reaching an ultra-high kinetic value, and the MSA cycle adsorption capacity was 0.26 mmol/g. Adsorption thermodynamic studies show that adsorbents with a uniform cylindrical pore structure have higher functional group efficiency and CO<sub>2</sub> adsorption capacity. The pore structure can also modulate the MSA capacity of the adsorbent through capillary condensation of water within the mesopores. Wang et al.<sup>[95]</sup> used QA salt cations and carbonate anion model compounds as research objects and revealed the mechanism of humidified CO<sub>2</sub> adsorption through theoretical calculations. The results showed that negative ions were chemically more conducive to CO<sub>2</sub> adsorption than positive ions; water promoted CO<sub>2</sub> adsorption by lowering the proton transfer energy barrier. The adsorption/desorption equilibrium shifted to desorption with the addition of water. The adsorption of CO<sub>2</sub> weakened the hydrophilicity of the adsorbent, resulting in the release of water. Within a certain humidity range, the absorption of CO<sub>2</sub> was an endothermic process, in which the adsorbent was simultaneously dehydrated. During the CO<sub>2</sub> absorption process, when the mobile anion changed from CO<sub>3</sub><sup>2-</sup> to HCO<sub>3</sub><sup>-</sup>, the hydrophilicity of the polymer ionic liquid (PIL) decreased. The detachment of water from the PIL took away heat, which was completely different from the competitive adsorption of CO<sub>2</sub> and H<sub>2</sub>O. Wang et al.<sup>[96]</sup> used molecular simulation to clarify its mechanism. **Figure 8** shows the comparison between temperature swing adsorption and humidity swing adsorption.



**Figure 8.** Temperature swing adsorption and humidity swing adsorption.

Regarding the characteristics of QA materials, Xu et al.<sup>[97]</sup> found that as the ambient temperature increased, the overall temperature rise of the bed decreased at different temperatures. The maximum temperature rise was only 7–8 °C. The temperature rise hardly affected the total adsorption capacity and reduced porosity. The particle size of the particles can reduce the maximum temperature rise of the bed, and at both 20% and 40% relative humidity values, it can be observed that the solid phase temperature in the late adsorption period was slightly lower than the initial temperature for a long time, confirming that quaternary ammonium material has self-cooling adsorption characteristics.

Different carrier scaffolds have a significant impact on CO<sub>2</sub> adsorption. He et al.<sup>[98]</sup> used carbon black-grafted polymers, ordered colloidal crystal templates, and high internal phase emulsions to synthesize three polymer materials for humidity swing adsorption for reversible CO<sub>2</sub> capture. The high internal phase emulsions had the highest desorption rate, which was 0.033 mmol/g/min. Compared with commercial materials with similar functional groups, the porous polymer showed an order of magnitude of improvement in adsorption and desorption kinetics, with a certain reduction in physical size. In order to obtain better CO<sub>2</sub> capture performance, a balance should be sought between surface area, pore size, and structure, and the quality of the porous structure should be paid attention to. Armstrong et al.<sup>[99]</sup> found that 90% of the particles in porous fiber scaffolds can be used for CO<sub>2</sub> adsorption, while only 50% of the particles in dense fiber scaffolds can be used for CO<sub>2</sub> adsorption. The ion exchange resin embedded in porous electrospun fibers had the largest circulation capacity and an adsorption rate of 1.4 mol CO<sub>2</sub>/g·h. The effective surface area of the resin particles in the fiber form was larger than that of the film form. It contacted the particles from all directions, thereby reducing the need for fluids to diffuse through the particles. Song et al.<sup>[100]</sup> used low-cost quaternary ammonium chitosan/polyvinyl alcohol (PVA) hybrid aerogels and hydroxide ions to capture CO<sub>2</sub> in ambient air through humidity changes. The CO<sub>2</sub> cycle capture capacity of the aerogels was approximately 0.18 mmol/g. The increase in temperature increased the peak adsorption rate and shortened the time to reach the peak adsorption rate.

MSA materials can also be used in industrial processes. Sun et al.<sup>[101]</sup> used a humidification process to capture CO<sub>2</sub> in industrial processes and demonstrated the removal of CO<sub>2</sub> from natural gas. Compared with CO<sub>2</sub> capture from air, since the CO<sub>2</sub> concentration in the gas mixture was much higher (1%–20%), the adsorption capacity significantly improved, achieving a stable circulation capacity of approximately 1.0 mmol/g. CO<sub>2</sub> was removed from natural gas through ion exchange membrane adsorbents loaded with CO<sub>3</sub><sup>2-</sup>



ions. The CO<sub>2</sub> adsorption/desorption cycle was driven by the reversible transformation of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> at room temperature and pressure. In addition, a process flow for natural gas decarbonization based on the variable wetting method was developed and analyzed for energy consumption of the variable wetting decarbonization method with the industrially used amine scrubbing technique, i.e., the MDEA method. It was found that the energy consumption of the wetted decarbonization process was less than half of that of MDEA (187.38 kJ/Sm<sup>3</sup> and 954–1304 kJ/Sm<sup>3</sup>, respectively).

Variable humidity adsorption can realize the CO<sub>2</sub> adsorption-desorption cycle by changing the partial pressure of water vapor in the environment, and the whole process is carried out at room temperature, using the free energy of water evaporation to supply energy for CO<sub>2</sub> regeneration, which reduces the energy consumption of DAC and has high binding energy for CO<sub>2</sub>. However, the ultra-low partial pressure of CO<sub>2</sub> in air and the large water demand during regeneration make the enhancement of adsorption capacity and regeneration rate highly challenging.

#### 4. Engineering application analysis of DAC solid adsorption materials

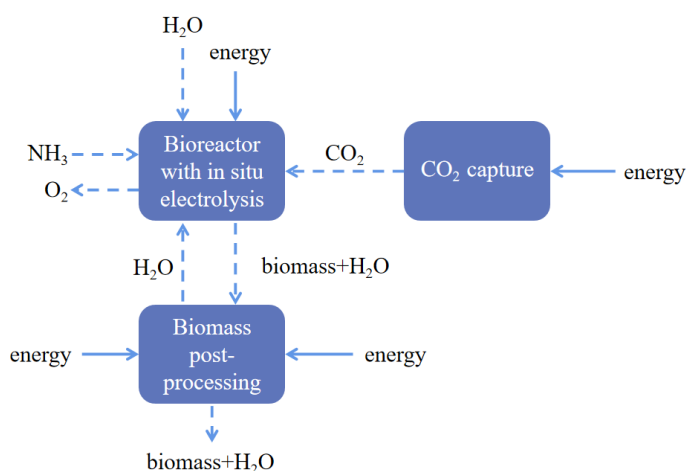
CO<sub>2</sub> removal costs will decline significantly over time but remain relatively expensive (about \$200/t CO<sub>2</sub> by 2050). Researchers have a low consensus on which DAC technology will be more popular, with energy use and policy support being the most critical factors driving the future growth of these technologies<sup>[102]</sup>. Coupling other advanced technologies with DAC technology and conducting full life cycle assessments is a promising development direction. Xing et al.<sup>[103]</sup> introduced the cost-reduction method of DAC adsorbents and the method of coupling chemical systems to DAC systems. With the gradual formation of the carbon trading market and carbon tariff, DAC technology will develop more rapidly. The feasibility of DAC technology has always been questioned due to its high energy consumption and its associated environmental impact. Wang et al.<sup>[104]</sup> analyzed and commented on the current status of DAC life cycle assessment research, showing that both solution absorption and solid adsorption technologies can achieve air capture, but the carbon removal efficiency of DAC systems ranged from 10% to 95%, mostly depending on the energy consumption and energy source of the system. Bao et al.<sup>[105]</sup> coupled DAC technology with a comprehensive joint optimization of energy system configuration and operation and used the CO<sub>2</sub> captured by the DAC equipment and the hydrogen produced by electrolyzed water for methanol synthesis. The DAC system was driven by renewable energy to realize stable and pollution-free operation and it produced certain environmental and economic benefits. Gutknecht et al.<sup>[106]</sup> created a comprehensive and safe solution to permanently remove CO<sub>2</sub>. The DAC technology injects CO<sub>2</sub> into basalts and permanently stores the injected carbon by mineralizing it. It can be deployed on a scale of 1 billion tons as early as 2030. For CO<sub>2</sub> removal efforts, it is important to scale up and optimize operations.

Utilizing this rapid mineralization technology, the world's largest container-like DAC unit began operations on 8 September 2021<sup>[107]</sup>. The unit can capture 4000 t CO<sub>2</sub> per year from air at full capacity, which is equivalent to the emissions of 870 cars. The capture device, an example of which is shown in **Figure 9**, uses a fan to draw air into a collector filled with the filter material, which closes when the filter material is filled with CO<sub>2</sub>. The filter material is then warmed to release a high concentration of CO<sub>2</sub>, which is then collected and injected into basalt rocks with a mixture of CO<sub>2</sub> and water. Optimists believe this technology could be a major tool in the fight against climate change, but others believe it is still too expensive and could take decades to operate at scale.



**Figure 9.** Large-scale installation of DAC in Switzerland.

Sillman et al.<sup>[108]</sup> generated bacterial proteins for food and feed through renewable energy and direct air capture of CO<sub>2</sub>, producing protein-rich biomass in a closed, climate-independent system utilizing bacteria that oxidize H<sub>2</sub>O and renewable electricity with direct air capture of CO<sub>2</sub>. This technology can increase protein yields several times per plot and uses about one-tenth the water of soybean production. The material and energy flows required to produce 1 kg of bacterial biomass are shown in **Figure 10**.



**Figure 10.** Main material and energy flows required to produce bacterial biomass.

Sadiq et al.<sup>[109]</sup> designed a mobile air capture unit using MOF materials, as shown in **Figure 11**, with a single module consisting of a blower, adsorption chamber, and vacuum pump. Atmospheric pressure adsorption greatly reduces the energy and cost of feedstock compression. The energy-efficient blower produced flow rates up to 50 m<sup>3</sup>/h with a back pressure of less than 100 Pa without degrading performance. The MOF-polymer nanocomposites were wrapped in thin layers on long resistive heating sheets, wound in a spiral shape, and mounted in each adsorption chamber. The regeneration stage utilized an efficient resistive heating technique with low energy consumption. A vacuum pump removed excess air from the module after the adsorption step; after the target regeneration temperature was reached in the desorption phase, CO<sub>2</sub> was discharged from the adsorption chamber.

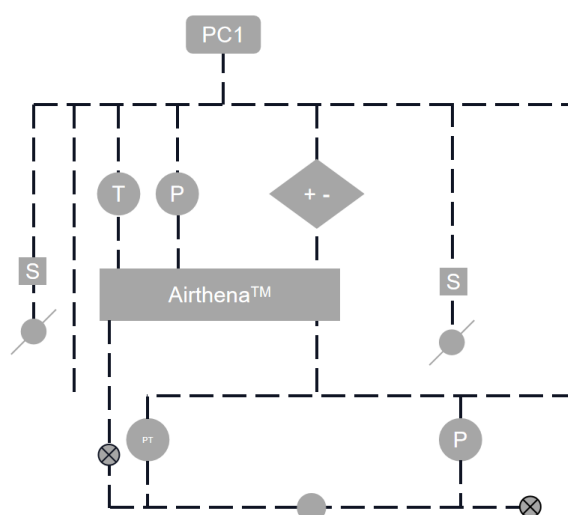


Figure 11. Single DAC module.

To sum up, DAC technology still has a lot of room for development. Before combining DAC technology with other technologies and commercialization, it is necessary to make a detailed techno-economic and environmental assessment of the cycle stability of adsorbent materials, as well as a full life cycle evaluation of the process to ensure the safety of people, ecology, and food and to take reasonable precautions to prevent new problems that may be caused by small-scale and large-scale pilot plants. Although the development of DAC technology is relatively fast, we still need to face the problem of climate change, and we cannot reduce the investment in building low-carbon energy systems just because of DAC technology. DAC technology not only needs to capture CO<sub>2</sub> from the air but also includes storing and utilizing the captured CO<sub>2</sub>, and it needs to improve the purity of regenerated CO<sub>2</sub>, and so it is also crucial to control the cost of the whole capturing process<sup>[110]</sup>.

## 5. Conclusion

Given the magnitude of the global climate challenge and the urgency of successful implementation of the carbon peaking and carbon neutrality goals, direct air capture of CO<sub>2</sub> technology has distinct advantages, as it is not constrained by time and geography and has the flexibility to be combined with a number of utilization options of low-concentration CO<sub>2</sub>. Air capture technology is not highly coupled to existing industrial infrastructure, and the costs of adapting large-scale facilities for production are small. There is still a significant amount of research and development work to be done on the various materials, components, and processes of direct air capture technology, and future development of DAC technology approaches will need to focus on the following areas:

- 1) Solution absorption DAC technology needs low regeneration temperature, low equipment corrosion, and structurally stable absorption materials to reduce the cost of DAC. Alkali-metal-based solid adsorbents must find a suitable carrier material and reasonable modification to reduce the reaction energy barrier in order to achieve low-temperature capture and low regeneration energy. High-loading adsorbents should be developed and, if necessary, can be used in a combination of various carriers and active components. Solid amine adsorbents for low concentrations of CO<sub>2</sub> are limited by CO<sub>2</sub> kinetic diffusion, while the adsorption performance and amine utilization are still low and the carrier preparation process is complicated. There is a need to improve the stability of the cycle on the basis of exploring advanced regeneration methods with a view to large-scale applications. MOF adsorbent materials have not yet been

researched in-depth, and there is a need to improve their selectivity for CO<sub>2</sub> and water stability through surface modification. There is a need to improve the selectivity and water stability of CO<sub>2</sub>, to make the surface of MOFs hydrophobic through surface modification, or to develop novel products to create materials that are easy to mold and produce. Metamorphic adsorbent materials are challenging to enhance adsorption capacity in the presence of ultra-low partial pressures of air CO<sub>2</sub> and large water demand, and there is a need to explore the effects of functional group grafting and the morphology of the pores on the reaction.

- 2) Before a set of mature DAC technology is put into production, it is necessary to make a detailed techno-economic and environmental assessment of the cycle stability of adsorbent materials, analyze the process in combination with a full life cycle assessment to ensure the safety of personnel and ecology, and take reasonable precautions to prevent new problems that may arise after small-scale pilot plants are put into a large scale to obtain a higher production efficiency. Reducing costs and improving the economics of coupling DAC technology with other technologies in the energy industry through methods such as the use of renewable energy drives can be realized through the use of renewable electricity to power DAC facilities or integration with other energy systems.
- 3) In addition to capture, CCUS technology also includes the storing and utilizing of CO<sub>2</sub>. Before the commercialization and scaling up of DAC technology, it is necessary to comprehensively consider the cost needed for the whole air carbon capture process, make a standardized techno-economic assessment of the complete process, and not relax the vigilance on climate change and pay attention to the research and development of clean energy. Governments and international organizations should formulate incentive policies to support the development and application of DAC technology, such as carbon pricing mechanisms, tax reduction incentives, adequate research and development funding, enhanced international cooperation and technology sharing, etc. They should also enhance public education and technology popularization so as to enable the public to understand the potential of DAC technology and encourage them to support and adopt this technology.

## Author contributions

Methodology, XC and JM; investigation, JZ; resources, JZ; data curation, JZ; writing—original draft preparation, JZ; writing—review and editing, XC and JM; funding acquisition, XC and JM. All authors have read and agreed to the published version of the manuscript.

## Funding

This research was funded by Jiangsu Province Carbon Peaking and Carbon Neutrality-Frontier Basic Project of “Basic Research on Multi-Source CO<sub>2</sub> Low-Energy-Consumption Capture and Efficient Conversion and Utilization Based on Solid Absorbent/Catalyst” (project number: BK20220001).

## Acknowledgments

We would like to thank the Jiangsu Province Carbon Peaking and Carbon Neutrality Special Project (BK20220001) for financial support.

## Conflict of interest

The authors declare no conflict of interest.

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