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Progress and current challenges for CO_2 capture materials from ambient air

Junya Wang[1], Rong Fu[1], Shikun Wen[1], Ping Ning[1*], Mohamed H. Helal[*2], Mohamed A. Salem[3,4] Ben Bin Xu,[5] Zeinhom M. El-Bahy[4], Mina Huang,[6,8] Zhanhu Guo[8*], Liang Huang[7], Qiang Wang[7]

[1]Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, 650500, Yunnan, China.

[2]Department of Chemistry, Faculty of Arts and Science, Northern Border University, Rafha, KSA.

[3] Department of Chemistry, Faculty of Science & Arts, King Khalid University, Mohail, Assir, KSA

[4] Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City 11884, Cairo, Egypt

[5] Mechanical and Construction Engineering, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne NE1 8ST, UK

[6] College of Materials Science and Engineering, Taiyuan University of Science and Technology, Taiyuan, 030024, China

[7]College of Environmental Science and Engineering, Beijing Forestry University, 35 Qinghua East Road, Haidian District, Beijing 100083, China.

[8] Integrated Composites Laboratory (ICL), Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, TN 37997, USA

*Corresponding author: E-mail: 1456149879@qq.com (P. Ning); zguo10@utk.edu or nanomaterials2000@gmail.com (Z. Guo)

Abstract: As a major component of greenhouse gases, excessive carbon dioxide (CO_2) in the atmosphere can affect human health and ecosystems. Therefore, the capture and transformation of CO_2 has attracted extensive attention in academic circles in recent years. Direct air capture（DAC) of CO_2 is a technology developed in recent years that can capture and collect CO_2 directly from the ambient air, which is a potential negative CO_2 emission technology. Currently, DAC technology is being promoted worldwide. Therefore, given the lack of a timely review of the latest developments in DAC technology, an appropriate and timely summary of this technology and a comprehensive understanding of it is necessary. In this paper, we review the research progress of adsorbent materials for directly capturing CO_2 from ambient air in recent years, including liquid-based absorbent, solid adsorbent, and moisture-swing adsorbent. How their chemical composition, structure, morphology, modification method affects their performance and long-term use is thoroughly discussed. In addition to efficient CO_2 adsorption properties, designing low-cost sustainable materials is critical, especially for practical applications. Therefore, the technical and economic evaluation of CO_2 adsorbents directly capturing from ambient air is reviewed. This review is of great significance for researchers to fully understand the development status and future trends of direct capture of CO_2 from ambient air.

Keywords: Direct air capture of CO_2, CO_2 capture material, capture performance, technical and economic evaluation

1 Introduction

Carbon dioxide (CO_2), mainly emitted by burning fossil fuels and other human social activities, is one of the most important greenhouse gases.[1] As measured by NOAA, the global surface average for CO_2 concentration increased from 280 ppm to 411.75 ppm in December 2019, and close to 417 ppm in February 2021.[2] The average concentration of CO_2 in the global atmosphere in recent years is shown in Figure 1. The current rise in atmospheric CO_2 concentration is unprecedented in recent history and poses serious challenges to the environment, including global warming, ocean acidification, air pollution and rising sea levels, etc.[3] These serious negative consequences require us to take action as soon as possible to decrease CO_2 emissions.

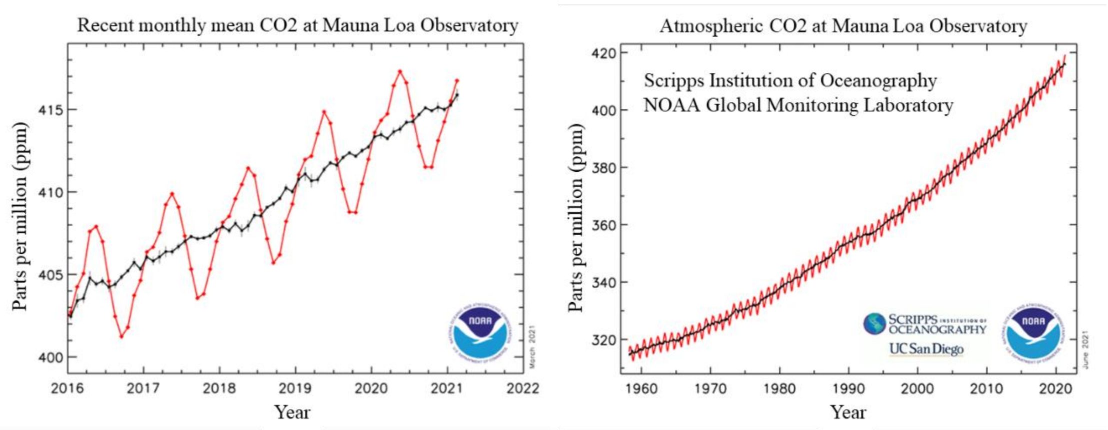

Figure 1. The graph of CO_2 concentration growth in the atmosphere.[2]

At present, a lot of research work has been done on capturing CO_2 from large point sources, including the use of liquid absorbents (e. g. liquid amine, ionic liquid) and solid adsorbents (e. g. lithium silicate, MOFs) to capture CO_2 emitted from large point sources.[4, 5] According to the

IPCC, by 2050, CO_2 emissions must be reduced by 30% to 85% in order to stabilize the volume of CO_2 in the atmosphere at between 350~440 ppm. After 2050, CO_2 emissions must continue to fall to near zero to fully stabilize atmospheric CO_2 concentrations.[3] Thus, even if all CO_2 emissions from point source emissions were captured and collected, developed countries would not be able to achieve an 80% reduction in CO_2 emissions by 2050. It is equally important to reduce CO_2 emissions other than those from concentrated sources, and air capture technology offers an option to address these emissions.[6] Capturing CO_2 from the atmosphere was first reported by Lackner in 1999 as a way to mitigate climate change.[7] Like traditional CCUS technology, DAC also involves long-term storage of CO_2, but unlike traditional CCUS, DAC captures CO_2 directly from the atmosphere, thereby controlling global atmospheric concentration, rather than controlling large-scale fixed points waste gas flow from a pollution source (such as a power plant). DAC could eliminate residual emissions from point source capture and can act as insurance against CO_2 leakage, which could also provide a better option for dealing with emissions from mobile and dispersed sources such as cars and aircraft.[6] The inherent advantages of DAC make it a promising technology to mitigate climate change. Techniques for capturing CO_2 from large point sources have been extensively studied over the past few decades, but there have been relatively few studies on capturing CO_2 directly from ambient air, with only about 200 publications from 2000 to 2020. Given the seriousness of the global climate change, it is believed that this research needs to be scaled up imminently. There is a lot of research to be undertaken in terms of novel materials and economically viable air capture technologies.

DAC technology has been extensively explored in various literature by means of capturing CO_2 from the ambient air.[8, 9] Over the past two decades, there has been a steady increase in publications on DAC. Especially in the past five years, a lot of novel adsorbents have been developed and applied to capture CO_2 directly from ambient air.[10-12] Therefore, we believe that it is important to timely update these adsorbents that directly capture CO_2 from the ambient air, which will benefit both academic and industrial researchers. So far, some researchers have reviewed the application of adsorbent materials in the field of DAC. For instance, in 2016, Sanz-Pérez et al.[9] comprehensively reviewed the history of the DAC field, along with a detailed description of the use of chemical absorbents in this application. In 2019, Shi et al.[13] published a good review on the study of CO_2 directly captured from air by solid adsorbents, which were divided into physical adsorption, chemical adsorption and humidified adsorption according to the adsorption mechanism.

In this paper, it comprehensively reviews the research progress of liquid absorption materials, solid adsorption materials, moisture-swing adsorption materials, and other novel materials in the field of DAC in recent years. In addition, this article also summarizes the latest developments in the combination of some adsorbents and catalysts to capture CO_2 and convert it into other energy substances. At the end of the review, the technical and economic feasibility and future development prospects of CO_2 adsorption materials for direct air capture were also summarized and discussed.

2 Liquid-based CO_2 absorbents

Previous studies have shown that DAC is theoretically possible.[6, 14-16] Capturing CO_2 directly from the ambient air requires large contact surfaces with a high affinity and selectivity for CO_2. Back in the 1930s, some researchers have investigated packed tower processes that use alkaline solution to capture CO_2 from air, although the purpose of that research was not to mitigate climate change.[17-19] Until 1999, the concept of DAC was formally proposed by Lackner.[7] To date, DAC systems generally use a strong alkaline aqueous solution such as NaOH[20-22] or $Ca(OH)_2$[23], KOH[24] that reacts with CO_2 to generate carbonated salts. Although DAC of CO_2 is close to commercial feasibility, sodium or potassium hydroxide absorbing CO_2 to form carbonate often requires high regeneration energy. In order to obtain more efficient and sustainable absorbents, researchers have been working on the development of other new liquid-based absorbents for capturing CO_2. A detailed review is to be focused on the current progress on liquid-based CO_2 capture materials, including aqueous hydroxide absorbents, liquid amine-based absorbents, ionic liquids-based absorbents and phase-changing absorbents.

2.1 Aqueous hydroxide absorbents

2.1.1 Research progress and current challenges of aqueous hydroxide absorbents

DAC is widely regarded as a promising solution to achieve negative emissions, and it has been fully demonstrated that the technology of using alkaline solutions as CO_2 absorbents is feasible.[25] $Ca(OH)_2$ was first used to capture CO_2 directly from air to mitigate climate change. [7] The $Ca(OH)_2$ solution absorbs CO_2 from the air and reacts to produce $CaCO_3$. The $CaCO_3$ is then directly separated and dried, and calcined at a temperature higher than 700 °C to form CaO and release CO_2. $Ca(OH)_2$ is finally regenerated by the hydration of CaO.

Because the $Ca(OH)_2$ solution has a high binding energy with CO_2, a large amount of binding energy causes most of the energy of the process to be input into the regeneration process of the adsorbent.[9] The energy required for calcining $CaCO_3$ is 179.2 kJ mol^{-1}. Although $Ca(OH)_2$ shows excellent performance in capturing CO_2 (CO_2 capture capacity can reach 16.2 mmol g^{-1}), the high energy consumption and other deficiencies in the regeneration process have led to future research improvements focusing on reducing regenerative energy consumption and identifying better absorbents.

Moreover, NaOH as a strong alkaline solution, also has a strong binding of CO_2, like $Ca(OH)_2$ is also suitable for direct capture of low concentrations of CO_2 from the ambient air.[26] The product of the reaction of NaOH with CO_2 is Na_2CO_3, which is highly soluble in water. The reaction of Na_2CO_3 with $Ca(OH)_2$ causes the regeneration of NaOH in the caustic process and the formation of $CaCO_3$. The subsequent calcination of $CaCO_3$ still requires a large amount of energy. It's worth noting that water loss is also a significant energy loss during this process, the $Ca(OH)_2$ needs to be regenerated by hydration in order to complete the cycle and the $CaCO_3$ must be dried before calcination.[9, 27, 28]

The disadvantages of the CO_2 capture system with NaOH and $Ca(OH)_2$ solutions as absorbents mentioned above, i.e., high regenerative energy, low solubility of $Ca(OH)_2$ and water loss during regeneration, are related to the characteristics of the absorbent.[29, 30] Based on these considerations, the development of new-type adsorbents has attracted extensive attention of scholars. However, due to the strong CO_2 binding properties of alkaline hydroxides, some studies have focused on exploring more efficient and lower cost CO_2 capture systems to eliminate these shortcomings.[22, 31] The design of air-liquid contactor will help economic and energy assessment. Large convection towers and packed towers are the most commonly proposed designs.[32] Baciocchi et al.[27] studied the packed tower equipped with Sulzer Mellapak 500Y packing, using 2M NaOH solution to capture CO_2 from the ambient air. However, Zeman et al.[33] chose a chamber filled with filler material, using a 1M NaOH solution to capture CO_2 from the ambient air with CO_2 concentration of 380 ppm and demonstrated the importance of water loss. Moreover, Stolaroff et al.[34] investigated the feasibility of the spray tower and built a prototype contactor to measure the CO_2 captured by the NaOH spray, CO_2 was adsorbed on the wall by NaOH solution. Compared with the inlet, the CO_2 concentration at the exit decreased (as shown in Figure 2). Considering only the spray effect, the absorption rate of CO_2 was 3.7 mmol L^{-1} of solution per pass. Spray provides a large surface area for CO_2 contact with the absorbent.[9] In addition, the use of spray can also avoid the cost of building large packed towers, but the generation of spray can also cause energy loss, especially water loss. However, these shortcomings can be eliminated by increasing the concentration of the solution and reducing the flow rate, and the cost can be significantly reduced if the appropriate fine spray nozzle is used.

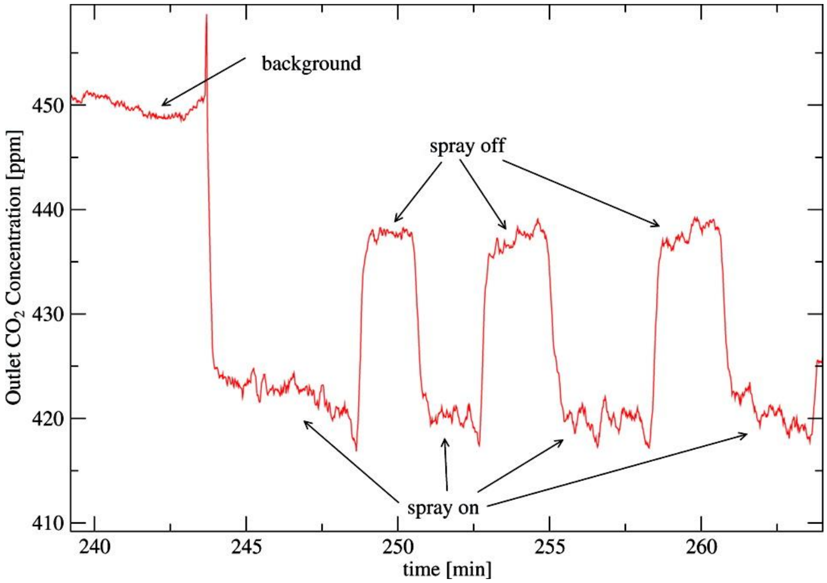

Figure 2. CO_2 concentration at outlet of packed tower.[35]

Others have also examined the regeneration process of absorbents in order to find a low energy consumption regeneration method. Nikulshina et al.[23, 36] proposed a new type of solar thermochemical cycle that use $Ca(OH)_2$ to capture CO_2 from the ambient air and at the same time use a solar calciner for $CaCO_3$ calcination. The solar-powered calcination process avoids pollutants such as greenhouse gases that are produced during fossil-fuel driven. The reaction process is shown in Figure. 3a. The ambient air, containing 500 ppm CO_2, is drawn from the atmosphere into the carbonator at 25 °C. This is similar in design to the cooling tower, where the CO_2 absorption reaction takes place. The solid product of the reaction is $CaCO_3$, which is transported to a calcining furnace, which is thermally decomposed into CO_2 and CaO. The high temperature of this endothermic reaction is provided by concentrated solar energy. It should be noted that the cost of this process is high, with solar production of CaO costing between \$128 and \$157 per ton, roughly double the current price of conventional lime, but solar production can avoid up to 95% of the greenhouse gas emissions from fossil fuel production.[37] Mahmoudkhani and Kenith proposed a titanate cycle that required half the energy of the traditional caustic process.[32] Using electrochemical system to regenerate the absorbent is also a feasible way. For instance, Sabatino et al.[24] proposed a bipolar membrane electrodialysis method for the solvent regeneration with a thermodynamic energy consumption of 236 kJ·mol^{-1} CO_2, the mechanism is shown in Figure 3b. With the current situation of ion-exchange membrane and energy prices, it may be difficult to become a competitive DAC technology. Moreover, Shu et al.[38] proposed an H_2-recycling electrochemical system that regenerates the alkaline absorbents from DAC and produces a high-purity stream of CO_2 gas. The model simulation results show that the energy consumption of the system can be as low as 164 kJ·mol^{-1} after further optimization.

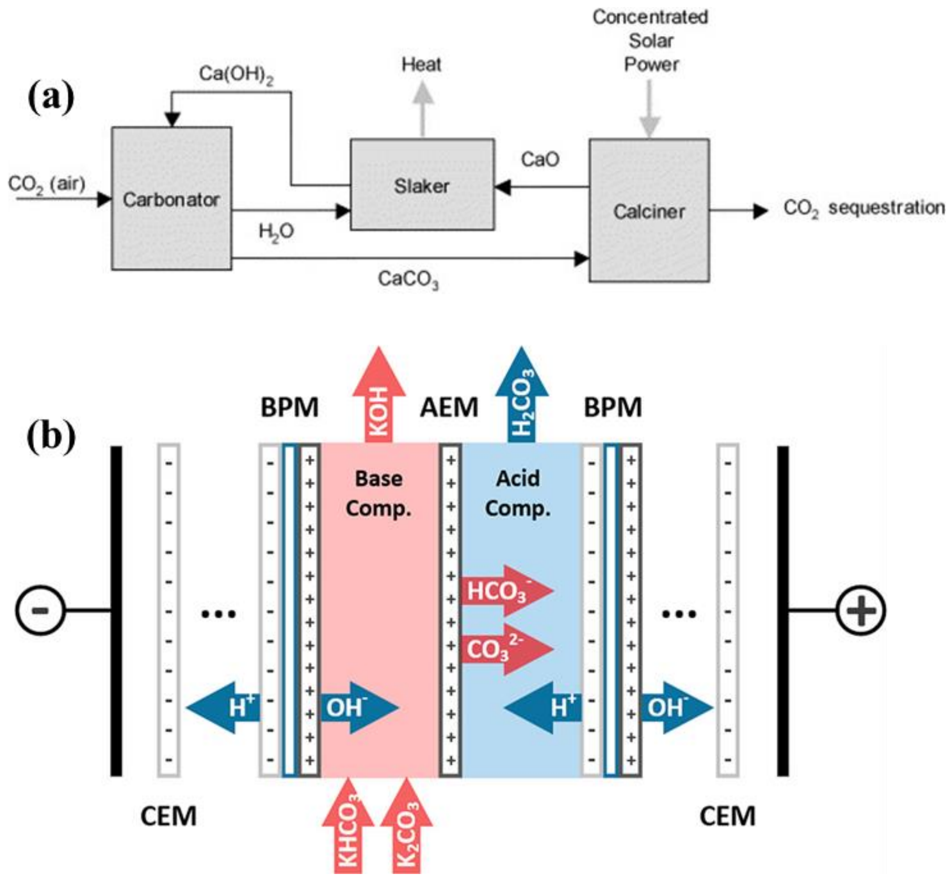

Figure 3. (a) A solar thermochemical cycle by using concentrate solar energy to capture CO_2 from the air.[23] (b) The ionic reactions which describe the CO_2 absorption mechanism.[24]

As an alkaline solution, KOH also has excellent CO_2 absorption performance, and its CO_2 adsorption capacity can get 17.8 mmol g^{-1}. However, KOH is more expensive than NaOH and $Ca(OH)_2$, so there are relatively few studies on using KOH solution to absorb CO_2. Bandi et al.[39] investigated the use of KOH to absorb CO_2 from air in a 2 m packed column, acidified the resulting K_2CO_3 solution with $KHSO_4$ to recover CO_2, and regenerated the absorber solution through an electrodialysis unit. Stucki et al.[40] used a microporous hollow fiber membrane loaded KOH solution to capture CO_2 from the air, and then desorbed CO_2 by electrolysis K_2CO_3. The fiber membrane provides a huge specific surface area for the contact between KOH solution and CO_2. In addition，Keith et al.[41] described the process of capturing CO_2 from the air in an industrial plant. The process captures 10,000 tons of CO_2 per year over a continuous process using a KOH absorbent coupled to a $Ca(OH)_2$ recovery loop.

2.1.2 Summary and outlook of liquid aqueous hydroxide absorbents

In summary, it is very important to have a baseline design for packed towers，using hydroxide solutions to capture CO_2. The cost and complexity of regenerative systems and water loss remain major challenges to the large-scale development of CO_2 capture systems using hydroxide aqueous solutions. Methods of removing CO_2 from the ambient air with hydroxide solutions are still being studied. High energy requirements and high regeneration temperatures are urgent problems to be solved in its practical application. Currently, improved baseline processes and regeneration systems have emerged, but the technology needs to be further improved if it is to be practical. The use of renewable energy and membrane electrodialysis to regenerate the absorbent is a feasible method on a laboratory scale. In the current situation of ion exchange membrane technology and renewable energy, this technology may not have a competitive advantage compared with traditional absorbent regeneration technology. However, with the further development of technology or better process design may change this situation. However, the current research focus is still on the baseline design of the system and the development of low energy consumption and economically viable absorbent regeneration technologies.

2.2 Liquid amine-based absorbents

Aqueous amine is diffusely used as CO_2 absorbent due to its high absorption rate, low viscosity, large CO_2 capacity and high chemical stability, as well as low cost.[42] Amine scrubbing with alkanolamines (typicially MEA, DEA) is considered to be the most mature and economical CO_2 capture technology for industrial processes and has been well proven in larger emission sources.[43-45] Aqueous amine have been used since 1930 to remove CO_2 from flue gas and is still considered a viable technology.[46] Prior to 2010, there were no reports on the use of aqueous amine to remove CO_2 directly from the ambient air. However, due to the high reactivity of chemisorption, amine-based absorbents have great advantages in capturing CO_2 in ultra-diluted CO_2 streams. Since 2011, efforts have been made to explore their applications in DAC.[47] However, this process has a number of problems, such as amine degradation, high regenerative energy, and equipment corrosion, etc.[48] Based on these considerations, the current research on amine-based absorbents for capturing CO_2 directly from ambient air focuses on the development of liquid amine-based absorbents, the impregnation of amines on porous materials, and the use of amine solvents to capture CO_2 directly from the ambient air and convert it into other valuable chemicals like methanol, formic acid.[34, 49, 50] The research progress of liquid amine-based absorbents will be comprehensively reviewed in this session. Studies of amine-impregnated porous materials will be described in detail in Sections 3.

2.2.1 Screening of amine absorbents suitable for DAC system

Recently, many scholars are developing novel amine-based absorbents to combine the most efficient CO_2 capture with low CO_2 desorption heat[34, 51], which is an important parameter for evaluating renewable energy sources. Compared with monoamine solvent, the reaction kinetics, stability, corrosion problems and regeneration heat of multi-component amine solvent are significantly improved. In recent publications, screening studies of diamine and tri-amine have been conducted. Hanusch et al.[52] investigated the CO_2 absorption performance of pyrrolizidine-based diamines. The reaction mechanism is illustrated in Figure 4a. They found that the uptake of CO_2 by the absorbent varies with the source of the compressed air due to differences in the amount of CO_2 in the air in different regions, which needs to be further investigated in larger-scale experiments. Barzagli et al.[53] conducted a screening study on the CO_2 absorption capacity of a series of aqueous alkanolamine solutions. The result showed that, for DAC process, aqueous unhindered primary amine is the most suitable, while non-aqueous amine absorbent seems not suitable for DAC process. Generally, when reacting with pure CO_2, carbamates and bicarbonates are formed in aqueous solutions, whereas only carbamates are formed in non-aqueous solutions (Figure 4b).[54] However, the alkyl carbonate, which is more unstable than carbamate, can only be produced by reaction with low concentrations of CO_2 (Figure 4c). In addition, the results indicated that aqueous amines are more effective than the same amines in organic diluents. This study may provide an idea for the further screening of CO_2 amine-based absorbents with excellent performance.

2.2.2 Combination of CO_2 capture and conversion

How to deal with the captured CO_2 is also a concern. At present, converting the captured CO_2 into other valuable chemicals has become an attractive and challenging goal. Kothandaraman et al.[49]

demonstrated that CO_2 can be directly captured from the ambient air and converted to CH_3OH by using the homogeneous catalytic system with a conversion rate of 79%. The reaction is shown in Figure 4d. In this system, amines are a promising material for capturing CO_2 and providing feedstock for further reactions. Selecting amines with high boiling point and high nitrogen content is more advantageous to obtaining an appreciable CO_2 absorption and it is also beneficial to the separation of the mixture after hydrogenation reaction. Moreover, Guan et al.[50] reported an economical PN^3P-pincer ruthenium catalytic. In the presence of amine, CO_2 in the air can be effectively converted into formate. The CO_2 conversion technology can not only reduce the carbon emissions, but also is an excellent way to solve the shortage of resources. Due to the low conversion rate of catalysts prepared by traditional methods and the large number of by-products produced, it’s crucial to design novel catalysts with good stability, low cost, and high catalytic performance. In addition, due to the low CO_2 concentration in ambient air, further screening of amine absorbents with high affinity for CO_2 and large capacity is also very critical.

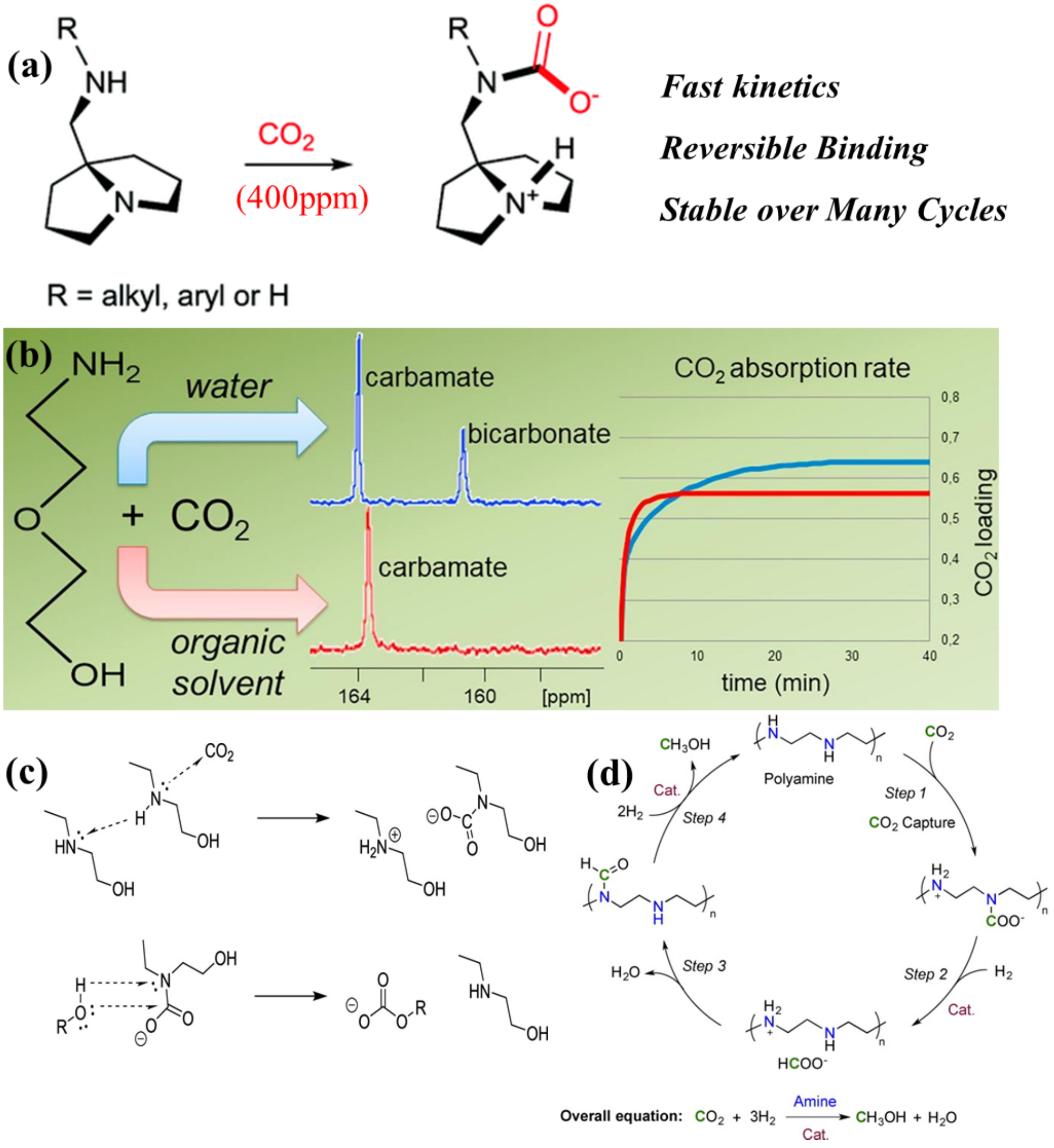

Figure 4. (a) Mechanism diagram of CO_2 capture by pyrrolizidine-based diamines.[52] (b) ^{13}C NMR spectra of aqueous and non-aqueous amine absorbents and the corresponding CO_2 absorption behavior.[54] (c) Two-step reaction mechanism of alkyl carbonate formation in non-aqueous amine solution.[53] (d) Reaction sequence for CO_2 capture and in-situ hydrogenation to methanol using polyamines.[49]

2.2.3 Summary and outlook of liquid amine-based absorbents

At present, the application of amine to industrial CO_2 capture has been relatively mature. However, poorly research has been done on the use of amines for the low concentration CO_2 capture. In the current studies, the vast majority of researchers only studied the effect of single amines directly capturing CO_2 from the air, and few studies were conducted on blended amines and biphasic solvents with good overall performance. Blended amine solvents are expected to be widely used in industrial applications in the future due to their excellent CO_2 absorption properties, including low regenerative heat and fast absorption kinetics.[5] Given these advantages of blended amines solvents, we may be able to explore the performance of a range of blended amine solvents in DAC systems. In the current screening work, the performance of amine solvents in capturing CO_2 from dilute CO_2 streams is relatively excellent. In particular, PEHA shows the unparalleled CO_2 capture performance compared with other amine solvents. [49] Therefore, future research will focus on the screening of amine-based solvents with excellent CO_2 capture performance or try to use mixed amines and bidirectional solvents with good comprehensive performance to capture CO_2 from ambient air. The CO_2 capture performance of amine-based absorbents and are shown in Table 1.

Table 1. Summary of CO_2 capture performance of amine-based adsorbent.

amine	diluent	CO_2 uptake	adsorption condition	Ref
PEHA	H_2O	6.85 mmol g^{-1}	400 ppm, 25 °C	[49]

MEA	H_2O	1.92 mmol g^{-1}	440 ppm, 25 °C	[53]
	EG/PrOH	1.85 mmol g^{-1}	440 ppm, 25 °C	[53]
	DEGMEE	1.46 mmol g^{-1}	440 ppm, 25 °C	[53]
AMP	H_2O	1.09 mmol g^{-1}	440 ppm, 25 °C	[53]
	EG/PrOH	0.45 mmol g^{-1}	440 ppm, 25 °C	[53]
	DEGMEE	0.15 mmol g^{-1}	440 ppm, 25 °C	[53]
DGA	H_2O	1.09 mmol g^{-1}	440 ppm, 25 °C	[53]
	EG/PrOH	1.06 mmol g^{-1}	440 ppm, 25 °C	[53]
	DEGMEE	0.73 mmol g^{-1}	440 ppm, 25 °C	[53]
MDEA	H_2O	0.30 mmol g^{-1}	440 ppm, 25 °C	[53]
EMEA	H_2O	1.29 mmol g^{-1}	440 ppm, 25 °C	[53]
	EG/PrOH	0.87 mmol g^{-1}	440 ppm, 25 °C	[53]
	DEGMEE	0.43 mmol g^{-1}	440 ppm, 25 °C	[53]
BUMEA	H_2O	0.97 mmol g^{-1}	440 ppm, 25 °C	[53]
	EG/PrOH	0.59 mmol g^{-1}	440 ppm, 25 °C	[53]
	DEGMEE	0.31 mmol g^{-1}	440 ppm, 25 °C	[53]
DMMEA	H_2O	0.61 mmol g^{-1}	440 ppm, 25 °C	[53]
DIPA	H_2O	0.58 mmol g^{-1}	440 ppm, 25 °C	[53]
DEA	H_2O	0.95 mmol g^{-1}	440 ppm, 25 °C	[53]

TBMEA	H_2O	0.64 mmol g^{-1}	440 ppm, 25 °C	[53]

2.3 Ionic liquid (ILs) absorbents

2.3.1 Progress on Ionic liquid (ILs) absorbents

ILs are regarded as one of the most promising classes of materials for capturing CO_2, due to their low volatility, low corrosivity, excellent chemical/thermal stability, non-flammability and low vapor pressure.[55, 56] ILs are organic salts with low melting points (<100 °C). Most ILs exist as solid at ambient temperatures. Moreover, ILs can be yielded by combining cations and anions, and this flexibility can be used to adjust the chemical and physical properties of the absorbent.[57] By selecting the types of anions and cations, IL can be designed for practical applications.[58] ILs are usually divided into physical ILs and functional ILs.[5] While the interaction between physical ILs and CO_2 (van der Waals forces) is usually very weak, resulting in low regenerative energy, limiting its absorption rate, capacity and selectivity to CO_2.[5] These disadvantages of physical ILs hinder their large-scale development. Thus, functionalized ILs with chemisorption sites possessed good CO_2 absorption properties and become potential absorption materials for the DAC process. At present, ILs have been widely investigated for capturing CO_2 from flue gas, but there are relatively few reports were reported in DAC process. So far, no more than five publications have reported ILs that capture CO_2 directly from the ambient air. Therefore, the development of ILs suitable for DAC system is still the focus of current research.

To date, a part of ILs have been shown to be effective in capturing CO_2 under ambient conditions, which provides the possibility for ILs to capture CO_2 directly from the ambient air.[59-61] Chen et al.[62] developed a metal-free and highly efficient catalytic system composed of task-specific ILs and pyrene-based conjugated polymers to directly remove CO_2 from the ambient air and further reduce it to CO (Figure 5a). ILs can quickly and effectively absorb CO_2 and H_2O from the air. After 12 h, the capture capacity of the IL can reach 350 mg/g_{IL}, and the capture amount of CO_2 is only ~33 mg/g_{IL} (0.75 mmol g^{-1}). This value is much lower than the CO_2 capture capacity of IL in anhydrous and pure CO_2 atmosphere, Figure 5b shows the mass ratio of CO_2 and H_2O absorbed within 48 hours, indicating that there is competitive absorption between H_2O and CO_2 in the ambient air. The presence of H_2O molecules in air is an important factor affecting the capture of CO_2 by ILs. Moreover, Lombardo et al.[63] demonstrated that, under ambient conditions, the metal-free and solvent-free absorption and reduction of a good deal of CO_2 to formates can be realized by combining a pyrrolidinium-based IL with a borohydride anion. In addition, the CO_2 capture capacity of the IL in the adsorption test was about 1 mol_{CO2}/mol_{IL} (7.76 mmol g^{-1}), which is unparalleled in absorption performance compared with other ILs (the range of 0.2~0.9 mol_{CO2}/mol_{IL}).[57, 64] More recently, they have studied a tetraalkylammonium IL, which combines with borohydride to capture and reduce the low concentration of CO_2 in the atmosphere, and can reduce CO_2 to formate under environmental conditions.[65] Among the three alkylammonium IL (TEAB, TPAB and TBAB) studied, compared with TEAB and TPAB, TBAB can avoid partial hydrolysis and react faster (Figure 5(c,d)). TBAB is considered as the best choice for direct air capture, because its hydrophobicity limits the side reaction of hydrolysis and the capture capacity can reach 3.83 mmol/g_{TBAB} (including CO_2 absorption and partially to hydrolysis of BH_4^-). Therefore, the longer alkyl chain can partially prevent the hydrolysis reaction due to its hydrophobicity. Looking for nitrogen-based cations with the best CO_2 affinity, such as polymeric ILs, is a possible way to improve its CO_2 absorption capacity.

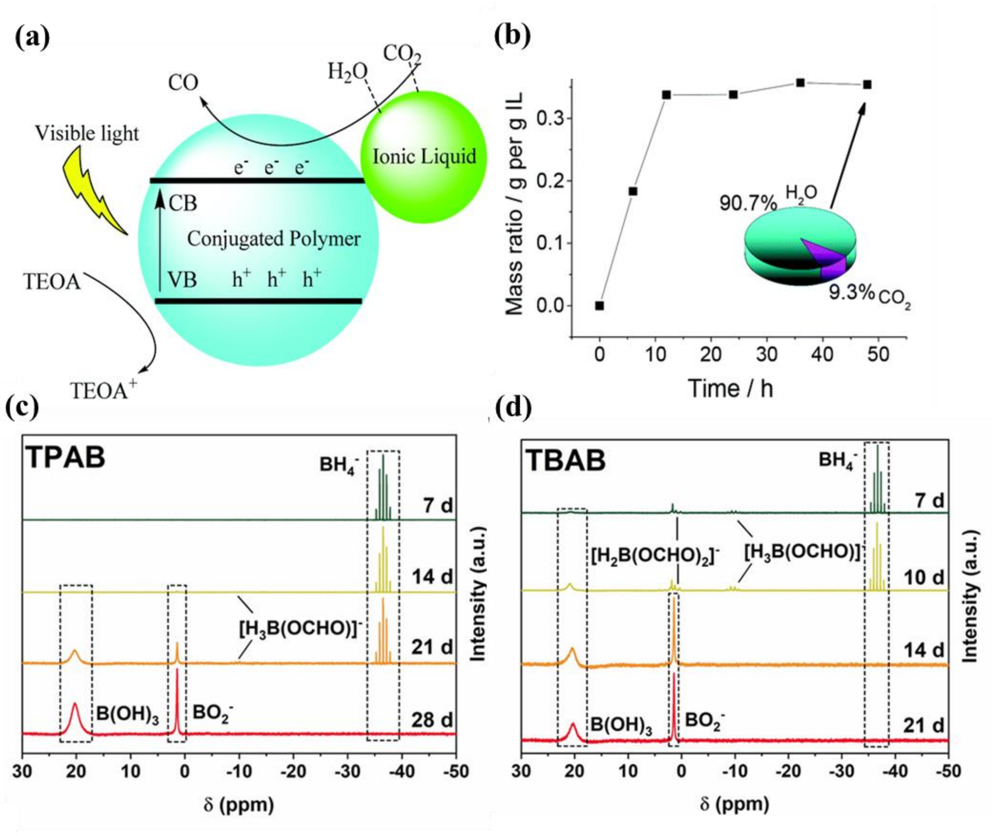

Figure 5. (a) Mechanism diagram of (P_{4444})(p-2-O) capturing CO_2 directly from air.[62] (b) The inset shows the mass ratio of absorbed CO_2 and H_2O for 48 h.[62] (c) Evolution of the ^{11}B NMR peaks as a function of time for TPAB, and (d) TBAB， when exposed to air.[65]

2.3.2 Summary and outlook of ILs absorbents

ILs are regarded as promising absorption solvents for capturing CO_2 because of their low regenerative heat, low volatility, low degradability, and good stability.[66-68] However, ILs have some obstacles, such as the expensive cost compared with amines and better ability to bind to H_2O than CO_2 in ambient air, which limit the further application of ILs in DAC field.[62, 64] The behavior of H_2O molecules has always been an important topic in the study of gas separation.[69, 70] Thus, when exploring the application of ILs in the field of DAC, the influence of water molecules on the absorption performance should be further considered. Developing hydrophobic ILs or finding ILs with optimal CO_2 affinity (such as polymeric ILs) are possible ways to improve the application of ILs in DAC field. At present, the application of ILs in DAC field is still in the laboratory research stage. Future efforts should focus on the development of novel ILs suitable for DAC systems. In addition, the feasibility and economics of the system need to be evaluated before large-scale application of ILs. ILs and their CO_2 capture performance are shown in Table 2.

2.4 Phase-change absorbents

2.4.1 Progress on phase-change absorbents

Recently, a type of novel phase-change absorbent has been reported in the DAC process because they possess the potential to significantly decrease the energy consumption of CO_2 capture. When CO_2 is absorbed, the homogeneous solvent can be divided into CO_2-rich phase and CO_2-poor phase which are easily separated.[71] Wang et al.[72] have previously outlined the research progress of phase-change solvents for capturing CO_2 from the flue gases in 2015. While in the past five years, researches have been made to explore their application in the DAC process. At present, phase change bis(iminonoguanidine) absorbent and aqueous amino acid absorbent have been investigated for the DAC of CO_2. Custelcean and his team have been studying guanidine solvents for capturing CO_2 from the air since 2017. [73] In 2017, they reported a simple aqueous guanidine absorbent (PyBIG) that can capture CO_2 from the ambient air and bind it to crystalline carbonate via guanidinium hydrogen bonding, finding that it can heat the crystals under relatively mild conditions (80~120 °C) quantitatively regenerate the guanidine absorbent and release CO_2. The CO_2 capture process is shown in Figure 6a. This method captures CO_2 from the air with minimal energy and chemical input and offers the prospect of low-cost DAC technology. Moreover, Cai et al.[74] designed and synthesized a trichelating iminoguanidine ligand (BTIG) for capturing CO_2 from the ambient air. The CO_2 capture process of BTIG is similar to PyBIG. The adsorption curve is shown in Figure 6b. The results indicated that the CO_2 absorption capacity of BTIG (4.24 mmol g^{-1}) is much higher than that of PyBIG (3.08 mmol g^{-1}) in DAC.[73] To understand the structural factors that determine the DAC chemistry of BIGs, Custelcean et al.[75] conducted a systematic study on the structure-properties relationship of the type of absorbent. The crystal structures were analyzed by X-ray and neutron diffraction. The results showed that minor structural modifications in the molecular structure of BIGs (i.e. the substitution of one or two hydrogen atoms with methyl groups) result in significant changes in crystal structure and solubility within the series, thus improving the performance of the DAC. Therefore, the adsorption properties of guanidine compounds can be improved by introducing different functional groups or by mixing them with other solvents, such as amino acids and amines.

Amino acids are regarded as promising solvents for capturing CO_2 because that they are readily available, environmentally friendly and have low volatility compared to amines.[71] The use of amino acid solvents to capture CO_2 directly from the air was first explored by Custelcean et al. in 2018.[76] After 24 h of absorption experiment, the final CO_2 loading capacity of glycine and sarcosine were about 6.73 mmol g^{-1} and 5.43 mmol g^{-1}, respectively. Furthermore, the absorbent can be easily regenerated by adding simple guanidine compounds, and the concentrated solar energy is used to heat the carbonate crystals relatively gently to achieve the desorption of CO_2 and the quantitative regeneration of guanidine compounds, thus greatly reducing the energy consumption during the regeneration process. [76] Although the amino acid absorbents can be regenerated by adding PyBIG, its cycle capacity is about 2.36 mmol g^{-1}, but by replacing the PyBIG compound with a more soluble and basic analogue, the process will be significantly improved.[76] Recently, they demonstrated a way to capture CO_2 by combining a peptide with a guanidine compound, which is a promising method for capturing CO_2 to maximize the cyclic CO_2 capacity.[77] The results indicated that the CO_2 loading capacity of GlyGly (about 3.79 mmol g^{-1} after 48 h) was lower than that of aqueous amino acids, but the average cyclic capacity of Glygly/GBIG was twice that of Gly/GBIG. In addition, other studies have shown that the regeneration of amino acid solvents can also be solved by heating.[78, 79] Compared with guanidine compounds for amino acid regeneration, the traditional heat-induced amino acid regeneration had excellent working ability, and the cyclic capacity of amino acid regenerated by reflux boiling was up 4.85 mmol g^{-1}, which was 2~3 times that of amino acids/guanidine compounds.[78] By comparing the minimum regeneration energy of PyBIG, m-BBIG, $CaCO_3$ and aqueous sodium glycinate (Figure 6c), although the regeneration energy of $CaCO_3$ is lower than that of PyBIG and m-BBIG, it requires an extremely high temperature of about 900 ºC. By contrast, m-BBIG and PyBIG can be regenerated at low temperatures of 60~120 ºC.[78]

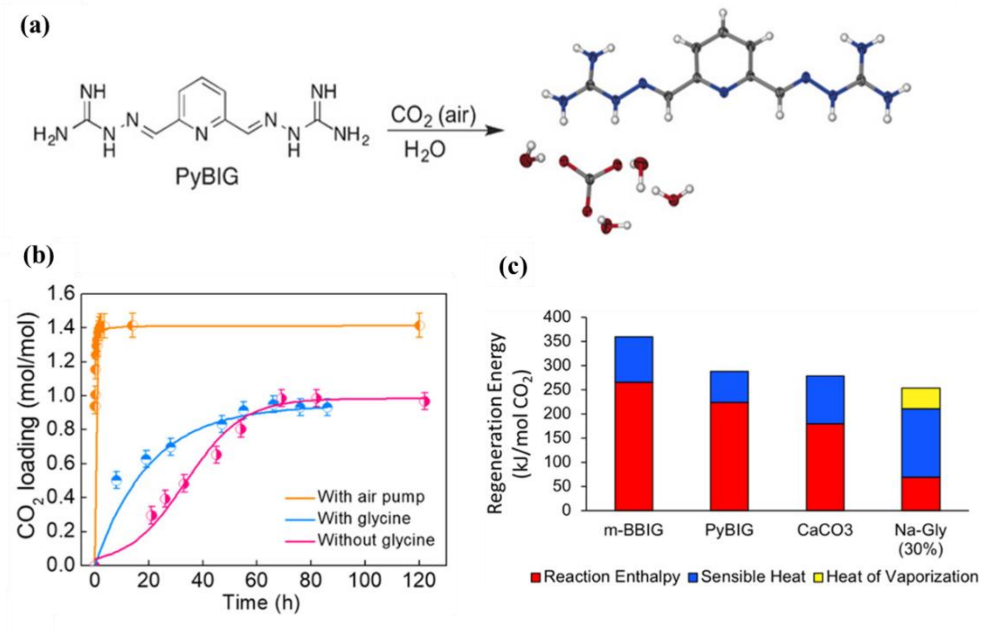

Figure 6. (a) The mechanism of CO_2 capture from the air into BTIG.[73] (b) The kinetics of BTIG solution capturing CO_2 from the air.[74] (c) Comparison of regeneration energy for m-BBIG, PyBIG, $CaCO_3$ and aqueous sodium glycinate.[78]

2.4.2 Summary and outlook of phase-change absorbents

In general, the application of phase-change absorbents for capturing CO_2 directly from the air is still in its early stages, and much work remains to be done to enhance the CO_2 capture capacity, cycling performance and decrease costs of absorbents. Currently, the phase-change absorbents studied in DAC are mainly guanidine compounds and amino acid solvents. However, guanidine compounds are expensive, so their utility of CO_2 capture is still questionable. At present stage, guanidine compounds are difficult to compete with traditional alkaline solvents. Amino acids, which are environmentally friendly, low volatile and non-toxic, are considered as potential CO_2 absorbents.[80, 81] However, poor cycle performance and slow reaction kinetics are the technical challenges that need to be solved in its application.[76] At present, the main challenge in the application of phase-change solvents in DAC field is still to develop new solvents with high CO_2 cycle capacity, fast absorption, high stability, and low volatility, and to develop DAC processes that can further reduce energy consumption and cost. The CO_2 capture performance of phase-change absorbents are summarized in Table 2.

Table 2. Summary of CO_2 capture performance of phase-change and ILs absorbents.

Sorbents	CO_2 uptake	Absorption condition	Ref
IL (P_{4444})(p-2-O)	0.75 mmol g^{-1}	ambient air	[62]
(EMPY)(BH_4)	7.76 mmol g^{-1}	dry compressed air	[63]
TBAB	3.83 mmol g^{-1}	ambient air	[65]
BTIG	3.0 mmol g^{-1}	ambient air	[74]
	4.24 mmol g^{-1}	air bubbling	[74]
Gly	6.73 mmol g^{-1}	ambient air	[76]
Sar	5.43 mmol g^{-1}	ambient air	[76]
GlyGly	3.8 mmol g^{-1}	ambient air	[77]

3 Solid-based CO_2 adsorbents

3.1 Solid amine-based adsorbents

Amine scrubbing is currently a commercial and extensively used method to separate CO_2 from flue gas.[82] In recent years, many researchers have explored liquid amines that capture CO_2 directly from the air.[49, 52, 53] In 2.2, the application of liquid amine in DAC field was also reviewed in detail. Although liquid amine have high reactivity and selectivity to CO_2,[83] they also present shortcomings like corrosion equipment, high energy consumption for regeneration, relatively high volatility and oxidative degradation.[84] Therefore, the development of novel CO_2 capture materials with low heat capacity and high stability is one of the most crucial challenges for capturing CO_2. In order to replace liquid amine, a variety of solid porous physical adsorbents have been proposed as supported for liquid amine, such as silica[85-87], zeolite[4, 88, 89], MOF[90, 91], porous polymers[92, 93], cellulose[94, 95] and metal oxides[96-98]. Although the adsorption capacity of physical adsorbents can be changed by adjusting their structural parameters, no competitive adsorption values can be obtained under the required conditions.[99] Based on the high reactivity and selectivity of amines with CO_2 and their low volatility and corrosiveness when loaded into porous materials, solid amine as a promising adsorbent has been widely investigated to capture CO_2 from the ambient air. [100] Sayari et al.[101] first used amine-functionalized silica to remove CO_2 from the ambient air. The CO_2 adsorption capacity of the TRI-PE-MCM-41 was 0.9 mmol g^{-1} at 400 ppm, 25 °C. Since then, researchers have been working on the synthesis of amine-based solid adsorbents with better performance, including screening the appropriate amine, modifying the amine and optimizing the supports.[102-104] Previously, we also summarized the performance and future development trends of solid amine-based adsorbents for capturing CO_2 from high-concentration CO_2 streams.[105] However, due to the diversity of support types in solid amine-based adsorbents, in this paper, solid amine-based are classified adsorbents according to the different supports, and will be reviewed in detail in Section 3.2-3.5.

3.2 MOF-based adsorbents

MOFs composed of metal ligands linked with organic molecules are a new-type class of nanoporous crystalline materials[5]. It is a hot research topic of CO_2 adsorption materials in recent years. In recent years, the application of MOFs in post-combustion and pre-combustion capture, the removal of intermediate and high CO_2 concentrations has been extensively studied.[106-108] The high pore volume and specific surface area of MOFs provide abundant void space and a large number of adsorption sites for CO_2 adsorption. Because of these excellent structural characteristics, MOFs has become the focus of research in DAC field in recent years. Since 2012, researchers have begun to explore the application of MOFs materials in DAC field[109], and a great deal of efforts have been made to synthesize adsorbents with better performance and to further understand the influence of external impurities on MOFs adsorption of CO_2.[9] Currently, research mainly focuses on the synthesis of novel MOFs materials suitable for capturing CO_2 from dilute gases, functionalized MOFs materials, and the effect of water on the structure and stability of MOFs.

3.2.1 Tuning the structural properties of MOFs

Although MOFs has excellent CO_2 capture performance in high-purity CO_2 streams due to its excellent structural characteristics, its adsorption capacity is poor when dealing with mixed gases.[13] The pore size has a great influence on the adsorption capacity of the adsorbent. By accurately constructing microporous structures with pore size close to that of CO_2 molecules, the porous structure of the adsorbent keeps larger molecules out, thus enhancing the adsorption capacity of MOFs materials to CO_2. Shekhah and co-workers first reported the removal of trace and low concentration CO_2 by adjusting the pore sizes of physical adsorption-based MOFs (Figure 7).[110] Their work showed that the metals used in the synthesis process cause slight changes in the unit cell and crystal aperture, and the substitution of Cu(II) for Zn(II) to form SiFSIX-3-Cu will potentially induce additional pore shrinkage due to the Jahn-Teller distortions of the octahedral ligand geometry of Cu(II). At 400 ppm and 298 K, the adsorption capacity of SIFSIX-3-Zn was only 0.13 mmol g^{-1}, while the adsorption capacity of SIFSIX-3-Cu (1.24 mmol g^{-1}) was much higher than that of SIFSIX-3-Zn due to pore size shrinkage. In addition, SIFSIX-3-Zn and SIFSIX-3-Cu have also been demonstrated to be recyclable and water-stable MOFs, and can perform complete desorption under mild conditions. Kumar et al. found that the combination of precise control of narrow aperture and electrostatic interaction can achieve high-capacity capture of CO_2.[111] Recently, Cui et al.[112] reported an anion-functionalized ultramicroporous Zu-16-Co, which exhibits a one-dimensional pore channel adorned with abundant F atoms and has a high CO_2 capture capability (1.05 mmol g^{-1}) under environmental conditions. This Zu-16-Co has high CO_2 capture ability, which is mainly due to fine pore size with strong F···C=O interaction and large pore volume caused by its longer coordinated Ti-F-Co distance in c direction. In view of this study, further improvement of CO_2 capacity by adjusting the pore structure of MOFs can be further explored in future studies.

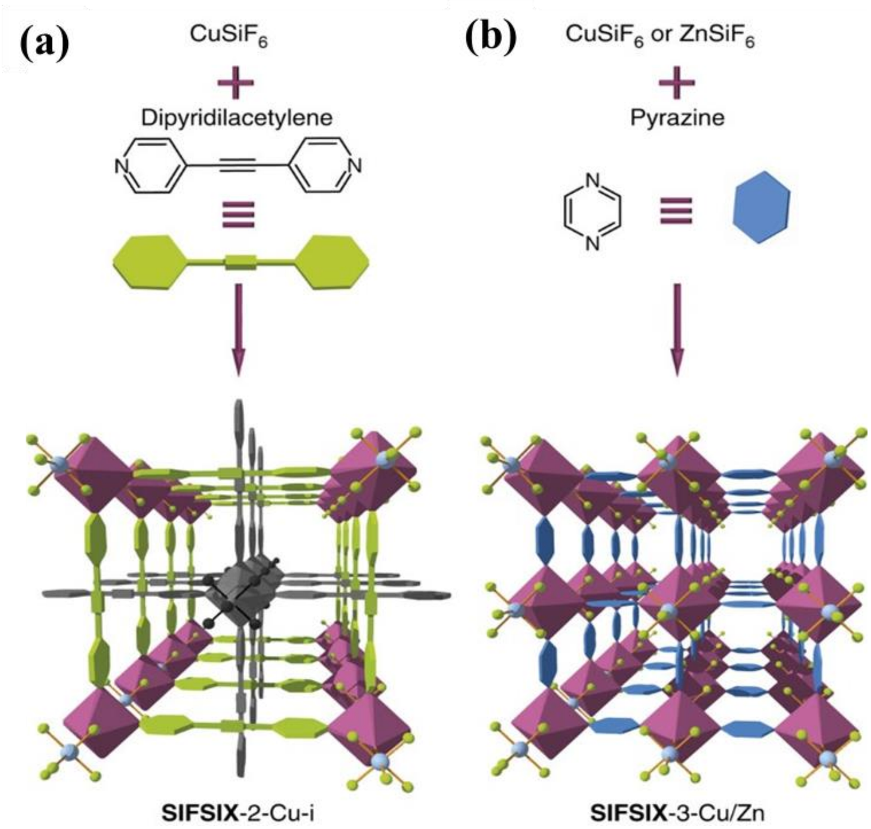

Figure 7. Schematic diagram of the channel structure adjustment for SIFSIX-3-X.[110]

3.2.2 Amine functionalized MOF

Since most of the MOF materials adsorb CO_2 through weak physisorption, most of the MOF materials exhibit poor adsorption capacity and medium N_2/CO_2 selectivity at low CO_2 partial pressure.[113] The maximum adsorption capacity of the MOF material studied so far is only 1.3 mmol g^{-1} under ambient air conditions.[114] In addition, water vapor in the air will also affect the adsorption performance of MOF, because some MOF materials are hydrophilic, so partial or complete drying of the gas stream may be required when MOF adsorbs CO_2. Amines are known to be highly effective at absorbing CO_2 and suitable for use in dry and wet conditions.[115] At present, one method to improve the performance of MOF material is to use the active metal site chelating amines in MOF materials to load amines in the pores, so as to improve the adsorption performance.[116, 117]

Choi et al.[109] first reported the use of amine-modified MOF adsorbents for capturing CO_2 from the simulated air. In their work, they used ED functionalized Mg/DOBDC as the adsorbent. The CO_2 adsorption capacity and regeneration of Mg/DOBDC and ED-Mg/DOBDC MOF were monitored using TGA. The stability test results of multiple cycles are shown in Figure 8a. The CO_2 adsorption results were compared with the conventional amine modified materials. It was found that the initial capacity of PEI impregnated silica was the highest among the four materials, but the CO_2 adsorption capacity was reduced by 30% after four cycles due to the degradation or leaching of amine.[118] The adsorption capacity of the Mg/DOBDC was significantly lower than that of ED-Mg/DOBDC, and the adsorption capacity dropped sharply from the second cycle due to the stability of the material. In contrast, the Mg/DOBDC functionalized by ED showed higher adsorption capacity and stability. This indicated that the addition of ED at low CO_2 partial pressure can improve the CO_2 adsorption capacity of Mg/DOBDC and increase its stability and regeneration performance.

Long et al.[119] suggested that the introduction of basic alkylammonium into the MOF pores would be a potential strategy to enhance the CO_2 adsorption capacity of MOF from the ultra-diluted flow. They found that narrow one-dimensional channels may prevent the amine from diffusing efficiently into the framework, while larger pores make it easier to functionalize and enhance gas diffusion. In 2012, Long et al.[119] reported an extended analogue of the M_2(dobpdc) structural type, which has a wide channels with open metal coordination arranged in the channels and shows excellent CO_2 adsorption performance when functionalized with N,N′-dimethylethylenediamine (mmen). At extremely low pressure, alkylamine-functionalized Mg_2(dobpdc) showed a very high affinity for CO_2. The CO_2 adsorption isotherm obtained under different temperatures conditions are shown in Figure 8b. At 25 °C and 390 ppm, the compound obtained a excellent adsorption capacity of 2.0 mmol g^{-1}， which was similar to that of the amine-functionalized silica adsorbent reported in literature [120], or even better than some adsorbents (such as triamine-grafted MCM-41 and silica gels) [101, 121]. In addition, amine-functionalization also appeared to increase the stability of MOF, since no similar degradation of mmen-Mg_2(dobpdc) was observed after one week of exposure to air. Based on mmen-functionalized M_2(dobpdc) showing high CO_2 uptake in ultra-diluted CO_2 streams. Subsequently, Hong et al.[122] further investigated the use of other amine functionalized M_2(dobpdc) to capture CO_2 from the ambient air (Figure 8c). A framework M_2(dobpdc) functionalized with ethylenediamine (en) has a capacity of 2.83 mmol g^{-1} at 390 ppm and 25 °C, which is much higher than that of mmen-M_2(dobpdc). The main reason for this result may be that the adsorption heat of primary amine is higher than that of secondary amine, CO_2 is more accessible in the presence of primary amines. The adsorption-desorption cycle test showed that the adsorption capacity only decreased by 6% after 5 cycles. The CO_2 capacity remained the same even when exposed to moisture. Darunte et al.[123] loaded different amines on MIL-101(Cr) to study the CO_2 adsorption performance, kinetics and stability of different amine-functionalized MIL-101(Cr). Studied have shown that TREN can effectively improve the CO_2 absorption and amine efficiency, but the cycling performance of TREN may be poor due to its relatively high volatility. The CO_2 adsorption capacity of PEI-functionalized MIL-101(Cr) increased with the increase of PEI load, but with the increase of PEI load, the time needed to reach the adsorption equilibrium also increased significantly. Therefore, the CO_2 adsorption and kinetic equilibrium of these materials need to be further optimized. Zhu et al.[124] synthesized a novel PEI-grafted HKUST-Type MOF/polyHIPE composite (PEI@PGD-H) in the presence of hydrophobic-modified CuO nanoparticles (Figure 8d). The material synthesized by them showed excellent CO_2 adsorption performance, and its adsorption capacity under ambient conditions was 1.8 mmol g^{-1}. Apart from this, it also exhibits excellent thermal stability, low desorption energy, good water resistance and reusability. Under simulated flue gas conditions, after 20 times adsorption-desorption cycles, the adsorption capacity decreased by only 5% for simulated flue gas, but unfortunately, the adsorption-desorption cycle test under environmental conditions was not carried out.

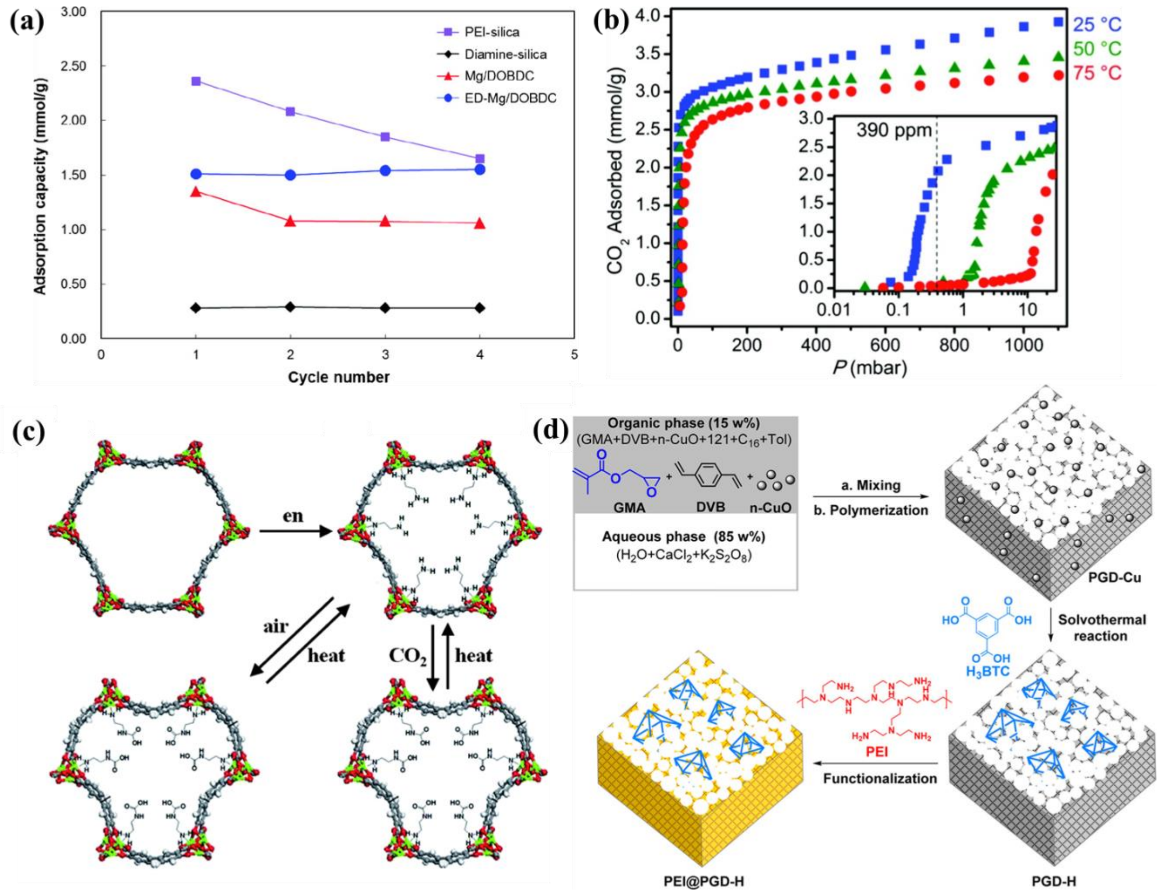

Figure 8. (a) Stability of the different hybrid adsorbents during the four-cycle tests.[109] (b) Adsorption of CO_2 in mmen-2 at 25 °C, 50 ℃, and 75 °C.[119] (c) Structures of activated Mg_2(dobpdc) (1), en-functionalized Mg_2(dobpdc) (1-en), CO_2 capture from ambient air, and CO_2 capture from flue gas. (d) CO_2 adsorption/desorption cycles of PEI70@PGD-H.[124]

3.2.3 The effect of the moisture

Another practical problem that affects the CO_2 adsorption performance of MOF-based adsorbents is moisture. Many people believe that the adsorption and selectivity of MOFs for CO_2 are significantly decreased in the presence of water vapor, which are mainly due to the competitive adsorption between water molecules and CO_2.[125-127] Zaworotko and his colleagues have demonstrated that the presence of water has a strong impact on the adsorption ability of MOFs.[111, 128] They studied a range of different types of adsorbents, including a variety of MOF-based adsorbents, and compared them with conventional zeolite and amine-modified silica materials. In addition to investigating the performance of adsorbent to capture CO_2 under the ambient air, experimental studies on the stability of the samples exposed to water vapor were conducted. All the physical adsorbents studied showed strong adsorption performance, but their CO_2 adsorption performance was reduced in the presence of water vapor. Therefore, physical adsorbents can compete with chemical adsorbents under dry conditions, but the adsorption performance of physical adsorbents in DAC will be reduced due to the competition with water vapor. If physical adsorbents are to compete with chemical absorbents, it is necessary to further solve the problem of controlling pore size and pore chemistry to enhance the stability of adsorbents in the presence of water molecules or develop novel hydrophobic materials. In order to solve the above problems, Eddaoudi et al.[114] constructed a hydrolytically stable MOF NbOFFIVE-1-Ni by replacing $(SiF_6)^{2-}$ with a bulkier and relatively nucleophilic inorganic pillar $(NbOF_5)^{2-}$, and its adsorption capacity can reach up 1.3 mmol g^{-1} at 400 ppm of CO_2 and 25 ℃ (Figure 9a). In the cyclic CO_2 column breakthrough experiments, the adsorbent did not significantly change the CO_2 breakthrough time at the presence of humidity (75% RH) (Figure 9b). It is worth noting that the adsorption of water does not significantly limit the CO_2 capture capacity of NbOFFIVE-1-Ni, which indicates that compared with most MOFs and zeolites,[111] the rare simultaneous adsorption of water and CO_2.

Moreover, introducing suitable groups (such as alkyl groups) into the pores can also decrease the hydrophilicity of the MOF.[129] Mukherjee et al.[130] proposed a SIFSIX-18-Ni-β synthesized by a crystal engineering method controlled by pore size and void chemistry (strong electrostatic interaction of inorganic anions and hydrophobic coupling of methyl groups), which exhibits extraordinary CO_2 selective. Moreover, compared with NbOFFIVE-1-Ni, SIFSIX-18-Ni-β is much less affected by water vapor at all levels from 1000 to 10000 ppm (Figure 9c), but its CO_2 capture capacity at 500 ppm level does not seem to be ideal, with a adsorption capacity of only 0.4 mmol g^{-1}.[130]

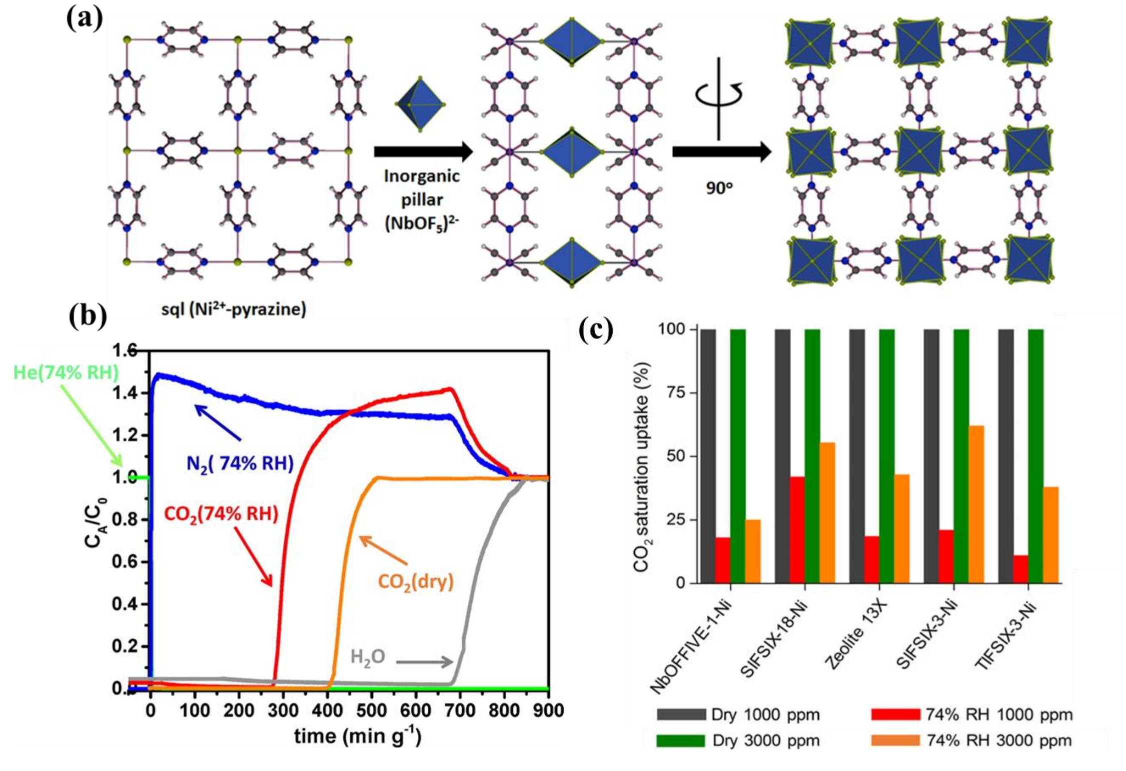

Figure 9. (a) Structural characterization of NbOFFIVE-1-Ni.[114] (b) Column breakthrough tests for NbOFFIVE-1-Ni under both dry and humid conditions.[114] (c) Comparison of CO_2 adsorption curves of different MOF materials at low pressure.[130]

3.2.3 Summary and outlook of MOF-based adsorbents

The stability of MOF to water vapor is a major consideration in practical applications.[126] Developing MOF with hydrophobic characteristics is a huge challenge for DAC systems. Most of the amine-functionalized MOF materials studied at present have good adsorption properties under experimental conditions, but their long-term stability under water vapor and oxygen conditions has not been verified.[122, 123, 128] It is also necessary to further investigate the long-term cycling stability and antioxidant capacity of the developed amine-functionalized MOF adsorbents under wet conditions. Studies have shown that hydroxyl functional groups are crucial for enhancing the performance of CO_2 capture under wet conditions, and the strong interaction between water molecules and hydroxyl functions can make more CO_2 be captured effectively.[131] Therefore, the introduction of hydroxyl functional group into amine functional group MOF material may improve the stability of CO_2 capture in air.

Further pilot-scale studies are also necessary to assess the possibility of using MOFs for capturing CO_2 in large-scale DAC systems. Thornton et al.[132] performed a pilot-scale demonstration of MOF nanocomposites that capture CO_2 directly from the ambient air. The renewable energy consumption of the demonstration project can be as low as 1.6 kWh kg CO_2^{-1}, and the CO_2 purity obtained is 70%-80%. During pilot-scale testing, a total of 8 kg of CO_2 was captured over 2,680 cycles. The capture cost of CO_2 was about \$35~350 tonCO_2^{-1}. This will be used to provide accurate capital and operating cost estimates for commercial deployments. In summary, the application of MOF materials to large-scale DAC systems is still a long way off. In the future, it should continue to explore better performance of MOF materials and further reduce the cost of DAC. The CO_2 capture performance of MOF-based adsorbents are shown in Table 3.

Table 3. Summary of CO_2 capture performance of MOF-based adsorbents.

Sorbent	CO_2 uptake	Adsorption condition	Ref
SIFSIX-3-Cu	1.24 mmol g^{-1}	25 °C, 400 ppm	[110]
SIFSIX-3-Zn	0.13 mmol g^{-1}	25 °C, 400 ppm	[110]
SIFSIX-2-Cu-i	0.07 mmol g^{-1}	25 °C, 400 ppm	[110]
NbOFFIVE-1-Ni	1.30 mmol g^{-1}	25 °C, 400 ppm	[114]
Mg-MOF-74	0.05 mmol g^{-1}	25 °C, 500 ppm	[130]
SIFSIX-18-Ni-β	0.40 mmol g^{-1}	25 °C, 500 ppm	[130]
SIFSIX-3-Ni	0.40 mmol g^{-1}	25 °C, 500 ppm	[130]
TIFSIX-3-Ni	1.20 mmol g^{-1}	25 °C, 500 ppm	[130]
ZU-16-Co	1.05 mmol g^{-1}	25 °C, 400 ppm	[112]
Mg/DOBDC	1.35 mmol g^{-1}	25 °C, 400 ppm	[109]
ED-Mg/DOBDC	1.51 mmol g^{-1}	25 °C, 400 ppm	[109]
mmen-Mg_2(dobpdc)	2.00 mmol g^{-1}	25 °C, 390 ppm	[119]
1-en-Mg_2(dobpdc)	2.83 mmol g^{-1}	25 °C, 390 ppm	[122]
PEI70@PGD-H	1.80 mmol g^{-1}	25 °C, 400 ppm	[124]

3.3 Zeolite-based adsorbents

Zeolite is a kind of aluminosilicate with special ordered microporous structure, which is considered as a physical adsorbent with good CO_2 capture performance. Since the early 1980s, Na-X is already used industrially to capture CO_2 from the air.[133, 134] Its adsorption efficiency is mainly affected by the chemical composition of zeolite, pore size, Si/Al ratio and the type and distribution of cations.[135-137] Zeolites usually have very high CO_2 adsorption rates at low pressure due to their alkalinity and the polarity field in their cavities.[138] In general, changing the framework structure and composition of zeolite is an effective way to enhance its adsorption ability.

3.3.1 Cation exchange modification

Some studies have proved that the adsorption capacity of zeolite for CO_2 will be significantly reduced under wet conditions, and the CO_2/N_2 selectivity of zeolite is poor.[139] To improve the adsorption performance of zeolite for CO_2, cation exchange is a feasible method. The adsorption of CO_2 by zeolite largely depends on cation concentration and ion radius. Therefore, these cation types will affect the CO_2 adsorption performance of zeolite. Stuckert et al.[140] studied the ability of a series of cationic LSX zeolites to capture CO_2 under environmental conditions. The CO_2 adsorption capacity of Li-LSX (1.34 mmol g^{-1}) was three that of zeolite NaX (0.41mmol g^{-1}) at 395 ppm and 25℃, which was also higher than that of all other zeolites reported, and was the zeolite-based adsorbent with the highest CO_2 loading capacity so far. Under dry conditions, zeolites showed exceptionally good adsorption performance. However, when the relative humidity of the gas mixture increases to 80%, almost all the adsorption capacity is lost.[140] Therefore, the development of hydrophobic zeolite with good adsorption performance is also the focus of future research. Another weakness of zeolite in capturing CO_2 is its poor selectivity to CO_2/N_2.[113] The proportion of N_2 in the atmosphere is 78%, so it is necessary to study the selectivity of zeolite for CO_2/N_2. The zeolite NaEST-4 studied by Santori and his colleagues is highly selective compared to zeolite 13X under environmental conditions, with a selectivity value of about 2060 and a regeneration temperature of only 95 ℃, thus achieving higher CO_2 purity with lower energy consumption.[88] In addition， zeolites with low Si/Al ratios are also promising adsorbents for CO_2 capture. Because they have more exoskeleton cations, they can promote adsorption through charge-quadrupole interactions. Wilson et al.[141] showed that using faujasite zeolite with low Si/Al ratio (Figure 10a), such as APG-III, to capture CO_2 from environmental concentration, has high CO_2 adsorption (up to 0.42 mmol g^{-1}) and high CO_2/N_2 selectivity. However, the high temperature (~200℃) of desorption of CO_2 and the need to remove water before capturing CO_2 are two major challenges in capturing CO_2 directly from the air using faujasite zeolites with a low Si/Al ratio.

3.3.2 Amine modification

Another important strategy to enhance the adsorption performance of zeolite is to modify zeolite with amine groups. At present, some researchers have started to modify zeolites by impregnation and grafting amine groups to further improve the CO_2 absorption capacity of zeolites. For example， Lee et al.[142] developed amine-impregnated zeolites Y and evaluated their ability to remove CO_2 from indoor. Moreover, Thakkar and his colleagues developed several inexpensive bimodal pore-network zeolites (e. g. ZSM-5, Zeolite Y and SAPO-34) from kaolin and applied them to capture

CO_2 from the air, further increasing their CO_2 capacity by functioning these molecular sieves with amine groups.[143] The successful impregnation of TEPA into the zeolite framework and the further increase of its CO_2 capacity depends largely on the pore size of the zeolite. Therefore, kaolin-based zeolite with large mesopore is suitable for impregnation of amine to improve the adsorption performance. In addition, TEPA-ZY (1.09 mmol g^{-1}) had a higher CO_2 capacity than kaolin-based zeolite (0.90 mmol g^{-1}) without amine modification, and showed stable performance in the adsorption-desorption cycle (Figure 10b).

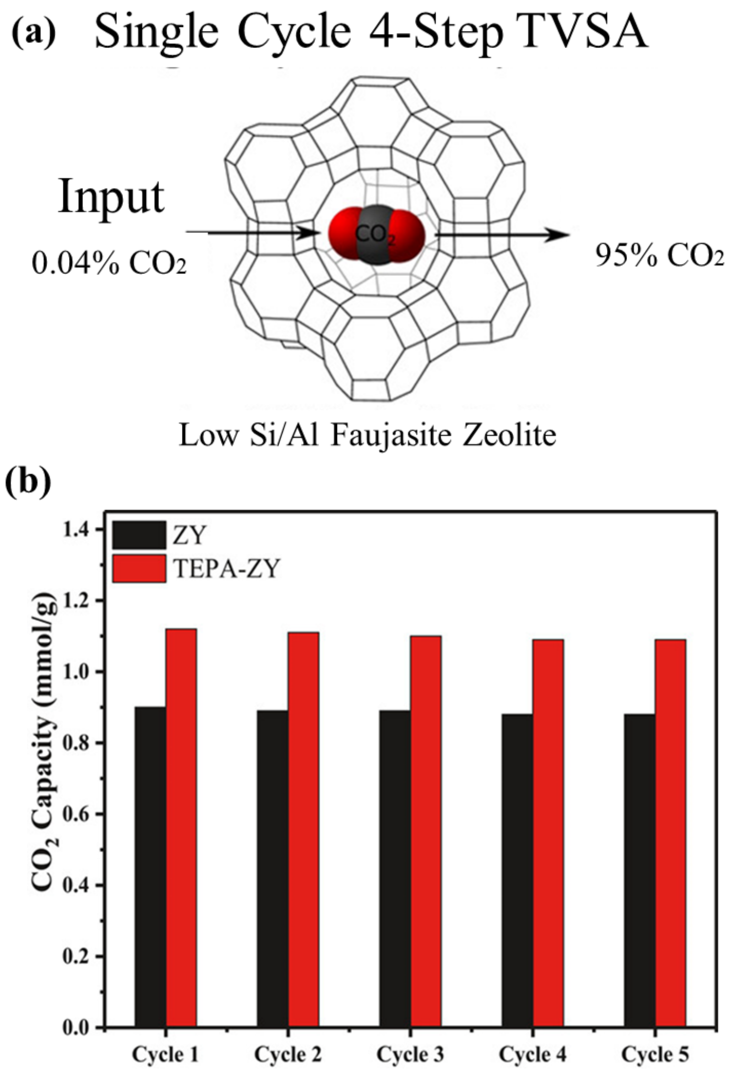

Figure 10. (a) CO_2 capture by low Si/Al faujasite zeolites.[141] (b) Cyclic adsorption capacity measurements of ZY and TEPA-ZY.[143]

3.3.2 Summary and outlook of zeolite-based adsorbents

In general, there are few studies on the application of zeolite in the field of DAC, mainly because of the instability of zeolite capturing CO_2 from the air.[137] Water vapor is a very critical factor affecting the CO_2 adsorption performance by zeolite, as it may compete with CO_2 for the active adsorption sites.[144] At present, many researchers have reported a series of zeolites with better CO_2 capture performance based on cation exchange and amine modification. The CO_2 adsorption ability of zeolite can be enhanced by introducing cations to influence the electric field in the pore and pore volume.[140] So far, the highest CO_2 adsorption capacity of cationic modified zeolite in DAC is 1.34 mmol g^{-1}.[140] The application of amine modified zeolite in DAC needs further research. To date, there is only one study on the capture of CO_2 by amine-modified zeolite in the diluted CO_2 stream, and the concentration of CO_2 used in the experiment is much higher than that in the air. Hence, a more extensive study of the performance of amine-modified zeolite for capturing CO_2 from the air is warranted. The CO_2 capture performance of zeolite-based adsorbents are summarized in Table 4.

Table 4. Summary of CO_2 capture performance of zeolite-based adsorbents.

Sorbent	CO_2 uptake	Adsorption condition	Ref

Li-LSX	1.34 mmol g^{-1}	395 ppm, 25 ℃	[140]
Na-LSX	0.87 mmol g^{-1}	395 ppm, 25 ℃	[140]
K-LSX	0.67 mmol g^{-1}	395 ppm, 25 ℃	[140]
Ca-LSX	0.76 mmol g^{-1}	395 ppm, 25 ℃	[140]
NaX	0.41 mmol g^{-1}	395 ppm, 25 ℃	[140]
NaY	0.08 mmol g^{-1}	395 ppm, 25 ℃	[140]
CaY	0.14 mmol g^{-1}	395 ppm, 25 ℃	[140]
Zeolite 13X	0.4 mmol g^{-1}	500 ppm, 25 ℃	[130]
APG-III	0.42 mmol g^{-1}	400 ppm, 22 ℃	[141]
TEPA-ZSM-5	0.15 mmol g^{-1}	5000 ppm, 25 ℃	[143]
TEPA-ZY	1.09 mmol g^{-1}	5000 ppm, 25 ℃	[143]
ZY	0.90 mmol g^{-1}	5000 ppm, 25 ℃	[143]
TEPA-SAPO-34	0.45 mmol g^{-1}	5000 ppm, 25 ℃	[143]

3.4 Alkali metal carbonate-based adsorbents

3.4.1 Progress on alkali metal carbonate-based adsorbents

Alkali-metal carbonate-based adsorbents are mainly K_2CO_3 and Na_2CO_3, which are widely studied for capturing CO_2 due to their excellent adsorption ability and low cost.[145, 146] The alkali metal carbonate can capture CO_2 to form sodium bicarbonate or potassium bicarbonate in the presence of water at temperatures below 100 ℃.[147-149] The principle of CO_2 adsorption is as follows:

$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$ （1）

$K_2CO_3 + H_2O + CO_2 = 2KHCO_3$ （2）

Regeneration of sodium bicarbonate or potassium bicarbonate formed during the adsorption process usually takes place at temperatures of 120-200 °C, which requires a large amount of energy. In addition, there are also problems such as low carbonation rate and poor durability of alkali metal carbonate-based adsorbents. In order to solve these problems, K_2CO_3/Na_2CO_3 has been tried to load on porous carriers, such as Al_2O_3, AC, ZrO_2, etc.[4, 150] The $K_2CO_3/\gamma\text{-}Al_2O_3$ complex has been shown to be a potential candidate for capturing CO_2 from air.[151] When the potassium loading is equivalent to 21~23 wt.% K_2CO_3 or 31~33 wt.% $KHCO_3$, the CO_2 adsorption capacity of $K_2CO_3/\gamma\text{-}Al_2O_3$ composite material exposed to air is as high as 0.98~1.2 mmol g^{-1}, and the utilization efficiency of K_2CO_3 is 55%~71%. The $K_2CO_3/\gamma\text{-}Al_2O_3$ sorbent adsorbs CO_2 through two ways of crystalline $KHCO_3$ phase and nano-dispersed $KAlCO_3(OH)_2$ on the surface of alumina. When the regeneration temperature increases from 150-200 °C to 250-300 °C, the CO_2 adsorption capacity increases (Figure 11a). This is due to the decomposition of the nano-dispersed $KAlCO_3(OH)_2$ on the alumina surface, which causes the extra CO_2 to be desorbed. The regeneration temperature is in the range of 250-300 °C, and the composite material shows good stability over 80 times CO_2 adsorption-desorption cycles. In 2018, they developed a new method that combines K_2CO_3/Al_2O_3 composite sorbent to capture CO_2 directly from the ambient air and CO_2 methanation in the presence of 4%Ru/Al_2O_3.[152-154] The results shown that at the temperature range of 325 °C to 400 °C, the desorption CO_2 can be converted to methane with a conversion rate of > 98% using Ru/Al_2O_3 as catalyst.

Studies have shown that the dynamic CO_2 adsorption performance of composite adsorbents is highly dependent on the chemical properties and porous structure of the matrix.[40] As a support material, Y_2O_3 also showed many attractive properties. CaO and Y_2O_3 composites exhibit very stable CO_2 capacity in multiple adsorption-desorption cycles.[155] Okunev and his colleagues synthesized the K_2CO_3/Y_2O_3 composite by impregnation method and investigated its ability to capture CO_2 from the ambient air.[156] The maximum CO_2 adsorption capacity of Y_2O_3 containing 26.2 wt.% K_2CO_3 was 0.64 mmol g^{-1} at the regeneration temperature of 150-250 °C, but when the regeneration temperature increased to 300-350°C, its CO_2 capture capacity decreases significantly. This is due to the difference in thermal stability between the mixed K-Al and K-Y phases, and the decomposition of K-Y begins above 460 °C. Although the K_2CO_3 loading amount of Y_2O_3 is higher than that of γ-Al_2O_3, the CO_2 capture capacity of K_2CO_3/Y_2O_3 is slightly lower than that of K_2CO_3/γ-Al_2O_3. From the perspective of long-term stability and CO_2 adsorption performance, Al_2O_3 seems to be more suitable than Y_2O_3 as the support for K_2CO_3 to directly capture CO_2 from ambient air.

K_2CO_3 supported on AC is also considered as a potential CO_2 adsorbent， which exhibited good CO_2 adsorption capacity and ~~rapid~~ carbonation reaction rate among various alkaline metal-based adsorbents.[157, 158] Lu et al.[159] studied the carbonization behavior of K_2CO_3/AC with different K_2CO_3 loading at different concentrations of CO_2 and humidity and at low reaction temperatures. The results indicated that the CO_2 capture process of K_2CO_3/AC can be compartmentalized into two stages: hydration reaction and conversion of unstable intermediate to $KHCO_3$. For adsorbents loaded with low $KHCO_3$ or at low humidity and high reaction temperature more K_2CO_3 will be converted to $KHCO_3$. In addition, the study also showed that the effect of moisture on the process of K_2CO_3/AC CO_2 capture was more significant, mainly because the hydration reaction was the rate control step in the process of CO_2 capture. The concentration of CO_2 in the experiment ranged from 1%~4%, which was still much higher than the concentration of CO_2 in the ambient air. Rodríguez-Mosqueda et al.[160] studied the ability of K_2CO_3 loaded on AC honeycomb to capture CO_2 from the air after pretreatment with H_2O. Pretreatment with water before adsorption makes the surface of the adsorbent formed a layer of aqueous solution capable of capturing CO_2, thereby enhancing its adsorption performance. AC with 5.58% K_2CO_3 content could obtain the highest capture capacity of 0.25 mmol g^{-1} at 500 ppm and 20 °C. Due to the physical degradation of the support under higher loads, the support K_2CO_3 content remained quite low. Therefore, increasing the salt load of the support and finding a support with a higher salt load are the focus of future work.

In order to design a regenerative adsorbent which can be regenerated at the temperature ≤200 °C, it is very important to find a new support for the synthesis of K_2CO_3-based composite adsorbent. Recent studies have shown that K_2CO_3 and ZrO_2 composites are promising adsorbents for direct removal of CO_2 from the air.[161] K_2CO_3 was loaded onto the ZrO_2 support by impregnation method. When the K_2CO_3 content increased from 9% to 23%, the CO_2 adsorption capacity increased from 0.09 mmol g^{-1} to 1.045 mmol g^{-1}, while, the further increase of the load resulted in a decrease in the adsorption capacity. In addition, the 23% K_2CO_3/ZrO_2 composite adsorbent showed good regeneration stability, and the amount of CO_2 adsorption hardly decreased after 14 times adsorption-desorption cycles at regeneration temperature of 200 °C.

According to the adsorption performance of the carbonate composite adsorbents summarized above, it is found that the performance of the support greatly affects the dispersion and sorption performance of the active adsorbent. To this end, Lu et al.[150] studied the effect of K_2CO_3 impregnation on different supports on the CO_2 sorption performance under the conditions of ambient temperature and CO_2 concentration of 500 ppm. The results shown that the CO_2 adsorption capacity of AC, alumina, zeolite 5A, zeolite 13X and silica aerogel was improved after K_2CO_3 loading. The K_2CO_3/AC showed the highest carbonation conversion rate (K_2CO_3 utilization rate was close to 100%) and could be completely regenerated below 200 ℃ (Figure 11b) The presence of water would cause the loss of CO_2 adsorption ability of K_2CO_3/zeolite. During the impregnation, the microstructure of silica aerogel was destroyed, resulting in the loss of its CO_2 adsorption capacity. In general, among the five supports, K_2CO_3/AC may be more suitable as adsorbent to capture CO_2 from dilute CO_2 stream.

The active component is also the key to affect the adsorption performance of adsorbent. Among the existing research results, more studies have been conducted on K_2CO_3 as the active component loaded onto porous supports to study its CO_2 capture performance from ambient air. In addition to K_2CO_3, Na_2CO_3 is also a commonly used alkali metal adsorbent to capture CO_2 from flue gas. Nevertheless, in terms of CO_2 adsorption capacity and adsorption kinetics, K_2CO_3 is usually better than Na_2CO_3.[5] The pathway of Na_2CO_3 carbonization process is shown in the Figure 11(c). One way is that the carbonation reaction occurs on the interface between $NaHCO_3$ and Na_2CO_3, and CO_2 and H_2O molecules diffuse through the $NaHCO_3$ layer, and the other is that the carbonation reaction occurs on the surface of $NaHCO_3$.[162] Rodríguez-Mosqueda et al.[163] studied the performance of a composite adsorbents consisting of Na_2CO_3 and AC honeycombs to capture CO_2 from dilute CO_2 stream. Under the experimental conditions of 500 ppm and 20 ℃, the maximum adsorption capacity of 0.17 mmol g^{-1} was obtained. It is feasible to regenerate the adsorbent with a mild temperature at 65 ℃ and humidity swing. However, compared with K_2CO_3/AC, Na_2CO_3/AC was not competitive for capturing CO_2 from the ambient air under the same conditions.

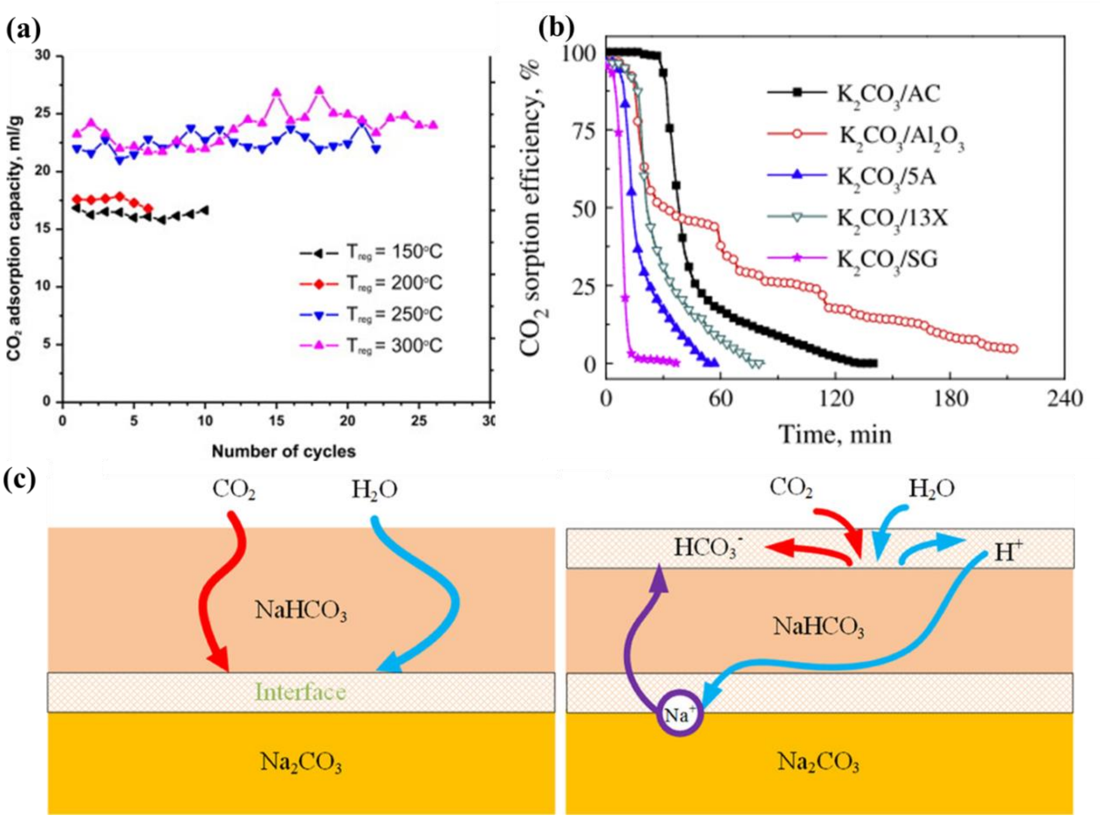

Figure 11. (a) CO_2 absorption capacity and cycling performance of $K_2CO_3/\gamma\text{-}Al_2O_3$ at different regeneration temperatures.[151] (b) CO_2 sorption performances of different sorbents.[150] (c) Two possible mechanisms for diffusion control of the Na_2CO_3 carbonation reaction.[162]

3.4.2 Summary and outlook of alkali metal carbonate-based adsorbents

Alkali metal carbonate-based adsorbents have been widely studied for CO_2 capture because of their high adsorption, low cost and low operating temperature.[145] But such adsorbents usually need to be fully regenerated at temperatures of more than 120 °C or higher, a process that consumes a lot of energy.[105] Therefore, high regeneration temperature is the main consideration of alkali metal carbonate-based composites in practical application. At present, there are few studies on the adsorption of CO_2 from ambient air by using the composite adsorbents of alkali metal carbonates and porous materials. Most studies only study a single matrix and active component. Therefore, in order to better understand the adsorption performance of supported alkali metal carbonate adsorbents, more comparative studies on composite adsorbents with low CO_2 concentration are very necessary. The CO_2 capture performance of the alkali metal carbonate-based adsorbent are shown in Table 5.

Table 5. Summary of CO_2 capture performance of alkali carbonate-based CO_2 adsorbent.

Sorbents	CO_2 uptake	Adsorption condition	Ref
$K_2CO_3/\gamma\text{-}Al_2O_3$	1.20 mmol g^{-1}	ambient air	[151]

K_2CO_3/Y_2O_3	0.64 mmol g^{-1}	ambient air	[156]
K_2CO_3/AC	0.87 mmol g^{-1}	5000 ppm, 20 ℃	[150]
K_2CO_3/5A	0.34 mmol g^{-1}	5000 ppm, 20 ℃	[150]
K_2CO_3/13X	0.53 mmol g^{-1}	5000 ppm, 20 ℃	[150]
K_2CO_3/SG	0.15 mmol g^{-1}	5000 ppm, 20 ℃	[150]
Na_2CO_3/ACH	0.17 mmol/g	500 ppm, 20 ℃	[163]
K_2CO_3/ACH	0.25 mmol g^{-1}	500 ppm, 20 ℃	[160]
K_2CO_3/ZrO_2	1.04 mmol g^{-1}	450 ppm, 25 ℃	[161]

3.5 Silica-based adsorbents

Silica has attracted extensive attention in the field of CO_2 capture due to its high surface area, pore volume and good regeneration stability.[105] In recent years, the use of cost-effective porous silica materials in the DAC field has been investigated in depth. In DAC, silica was mainly used as supports to capture CO_2 by loading amines. The amine-impregnated silica system is currently the most widely studied adsorbent used to capture CO_2 from the ambient air.[8, 102] But the problem of poor circulation performance caused by amine leaching is a major problem to be solved urgently in amine impregnation system.[164] So as to improve the adsorption performance of adsorbents, the current research on silica loading amine mainly focuses on the selection of amines, the preparation of silica substrates with different pore size structures and the introduction of additives to enhance the stability of adsorbents.

3.5.1 Preparation of silica-based hybrid composites

In recent years, silica materials with low cost, high specific surface area and large pore volume have been widely used as support materials for CO_2 capture.[165] At present, the silica supports studied mainly include mesoporous silica, macroporous silica, fumed silica, silica aerogel and silica nanotubes, etc. Different types of silicon have different morphologies and pore structures, and a better pore structure can promote gas diffusion in porous CO_2 adsorbents and improve amine efficiency. Most papers of amine-based silica adsorbents exhibit excellent CO_2 removal efficiency from pure CO_2, but there is a lack of research on capturing CO_2 from ambient air.[166, 167] PEI is widely used in preparing CO_2 adsorbent due to its high efficiency in capture CO_2.[168] PEI-impregnated silica systems have been investigated by many researchers to capture CO_2 directly from a dilute CO_2 stream. Goeppert et al.[120, 169] evaluated the performance of PEI-impregnated silica adsorbent to capture CO_2 from the air. The adsorbent prepared by impregnating fumed silica with a low molecular weight PEI has a CO_2 capture capacity of up to 2.4 mmol g^{-1} at 400 ppm and 25 °C, while high molecular weight PEI impregnated fumed silica can only obtain 1.71 mmol g^{-1}. Subsequently, Wijesiri et al.[170] assessed the CO_2 capture performance of PEI-impregnated mesocellular foamed silica adsorbent at 420 ppm CO_2 under dry and humid conditions. At 46℃, 420 ppm and 2% mol-H_2O, the highest adsorption capacity of 2.52 mmol g^{-1} can be obtained, but higher humidity is not conducive to its CO_2 capture. Moreover, Kwon et al.[171] reported that hierarchical silica with bimodal meso/macroporosity as support loaded amine provides a significant advantage for the practical CO_2 capture from ambient air (Figure 12 a-d). The PEI-impregnated hierarchical silica showed impressive CO_2 capture capability at 400 ppm and 30 ℃, with the highest CO_2 capture capacity of 3.4 mmol g^{-1}. However, the cycle test shows that the presence of water vapor in the feed stream will significantly reduce the cycle stability of the adsorbent during the five cycle tests (Figure 12 e-f).

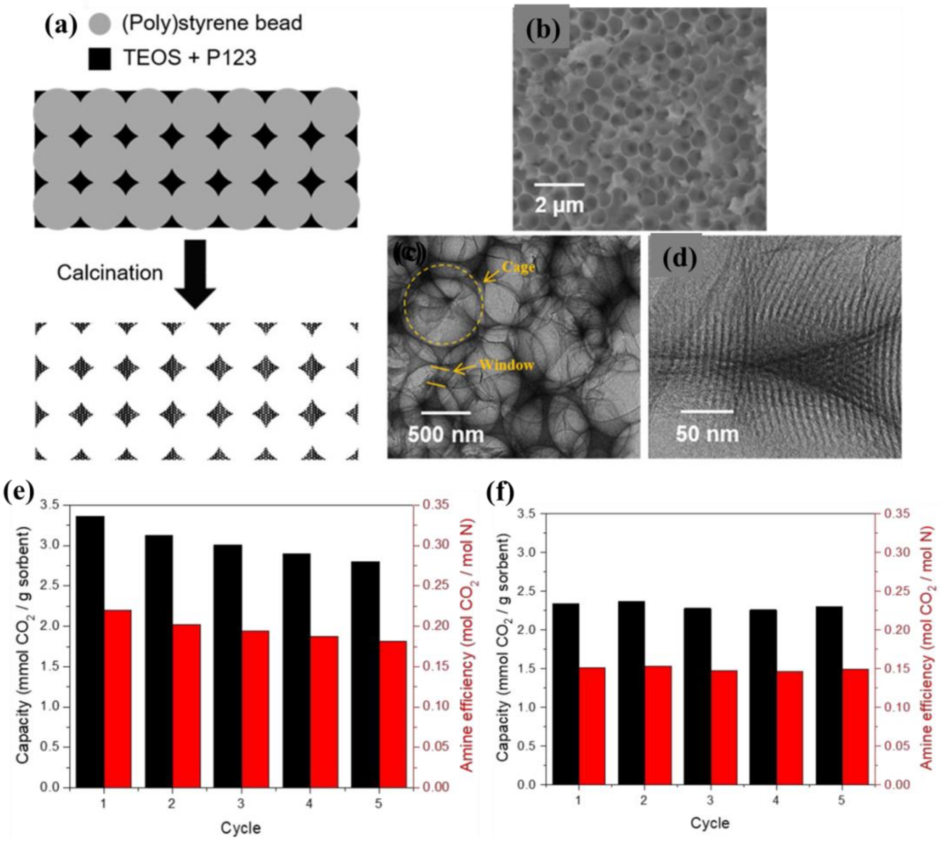

Figure 12. (a) Schematic diagram of structure synthesis for a hierarchical silica. (b) SEM image of the hierarchical structure. (c) and (d) TEM image of the hierarchical structure. (e) Cyclic adsorption performance under humid and (f) dry conditions at 400 ppm and 30℃. [171]

Most studies have shown that although the impregnated samples have a high CO_2 capture capacity, the problem of amine leaching in multiple cycles limits their development as CO_2

adsorbents.[164] The problem of amine leaching can be alleviated or solved by direct condensation or in-situ polymerization amine to supports surface.[4] Sayari et al.[101] have prepared triamine grafted pore-expanded mesoporous silica for the first time to directly remove CO_2 from ambient air, and its CO_2 capture capacity was 0.98 mmol g^{-1} at low CO_2 concentration. Yang et al.[121] reported that the capacity of the triamine grafted low-cost silica gels were comparable to that of the MCM-type materials[101], with a CO_2 adsorption capacity of 1.10 mmol g^{-1} under humid environmental conditions. Subsequently, Jones and his colleagues prepared a series of adsorbents through in-situ ring-opening polymerization, and made breakthrough progress in this field. They prepared a poly(L-lysine) brush–mesoporous silica hybrids material by in-situ ring-opening polymerization, and studied its performance as a biomolecule-based adsorbent to capture CO_2 from the ambient air.[172] The CO_2 adsorption capacity was only 0.6 mmol g^{-1} at 400 ppm and 25 °C, but it showed excellent stability in multiple cycles test. Subsequently, they also synthesized a hyperbranched aminosilica material (HAS).[173] Due to the large number of amine groups in these HAS materials, these adsorbents exhibit high CO_2 adsorption capacities (up to 1.72 mmol g^{-1}) and excellent renewability over continuous operations.[173] In addition, Kong et al.[174] prepared amine hybrid titania/silsesquioxane composite aerogel (AHTSA) by sol-gel method combined with supercritical drying, with a CO_2 capacity of 1.64 mmol g^{-1}. Since AHTSA is a hybrid precursor fabricated by in-situ polymerization, the amine in AHTSA was bonded to the aerogel chemically and remains good stable during the 15-cycle test. Morever, Saraladevi et al.[174] synthesized a functionalized polysilsesquioxane-based hybrid silica materials with easy regeneration and high thermal stability by a simple and efficient co-condensation method as a solid amine adsorbent to directly capture CO_2 from the air. It showed good stability during 50 cycles test and could be completely regenerated at 80 ℃. The CO_2 capture capacity could reach 1.68 mmol g^{-1} within 50 min. Recently, Liu et al.[175] prepared a adsorbent for CO_2 capture from the ambient air by encapsulating PEI in ethane-silica nanotubes with a diameter of less than 10 nm. But its CO_2 capture ability was not high, only 1.0 mmol g^{-1} at 400 ppm, 25 ℃

In addition, O_2 is one of the oxidants capable of oxidizing organic polymer compounds. Thence, it is also necessary to explore the effect of O_2 on the adsorption capacity in the process of swing temperature adsorption-desorption cycle.[176, 177] The rapid degradation of amines in the presence of O_2 is the biggest obstacle to the application of amine-based solid adsorbents.[5] Wang et al.[178] showed that the presence of O_2 would reduce the adsorption capacity of the adsorbent, but would not affect its circulation capacity. In 2018, Pang et al.[179] synthesized an oxidation-stable linear PPI/SBA-15 composite with a CO_2 adsorption capacity of 1.25 mmol g^{-1} that maintained a CO_2 capacity of 65~83% after exposure to harsh oxidation treatments, compared to a retention rate of only 20~40% for linear PEI. In addition, linear PPI adsorbents maintained long-term stability over 50 cycles of adsorption/desorption without loss of performance.

The water vapor content in the air is about 5%, so the influence of water vapor on the adsorption performance of the adsorbent is also not negligible. The presence of water has shown significant improvement in the stability of amine-based solid adsorbents by avoiding the formation of urea.[180] Many studies have shown that water can promote the adsorption of CO_2.[170, 178, 181]

Kumar et al.[182] prepared alkyl-aryl amine-rich small molecules (Ph-X-YY) by nucleophilic substitution method, and the analysis of TGA and DSC showed that these adsorbents had a relatively stable adsorption performance (Figure 13). Under dry conditions, the CO_2 adsorption capacity of Ph-3-ED can get 1.9 mmol g^{-1}, while under wet conditions with relative humidity of 30%, the CO_2 adsorption capacity can reach 2.9 mmol g^{-1}. On the contrary, some researchers claim that water has a negative effect on adsorption, believing that most amines are hydrophilic, which block some amines from entering the support.[169] Based on this contradiction, it is necessary to further research the effect of water molecules on the adsorption performance of amine-based solid adsorbents, such as the promotion or reduction mechanism.

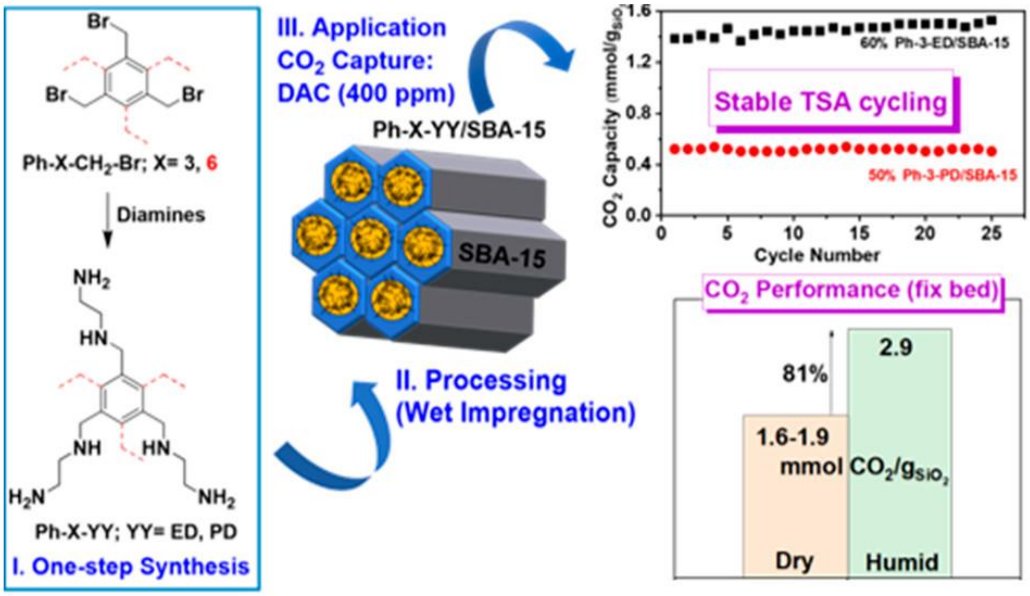

Figure 13. Synthesis of Ph-X-YY CO_2 adsorbent and adsorption performance.[182]

3.5.2 Introducing additives to improve adsorbent performance

It was found that adding additives to polymer amines such as PEI supported by porous silica is an effective strategy to enhance the stable properties of the adsorbents. In previous studies, Wang et al.[178] showed that the addition of additives (e.g. CTAB and PEG) could effectively improve the adsorption capacity and cycling performance of the adsorbent. A similar study was conducted by Sakwa-Novak and Song et al.[183, 184] Sakwa-Novak et al.[183] systematically studied the influence of several additives ~~(CTAB, PEG200, PEG1000)~~ on the adsorption performance of PEI/SBA-15 under thr simulated ambient air condition. They found that additive molecules, especially low-molecular weight PEG, significantly increased the amine efficiency of PEI/SBA-15 in adsorbing CO_2 from simulated air by 60% (0.1~0.16 mol CO_2/mol N). The hydrogen bond interaction between PEG and PEI made it have better stability in the adsorption process. Due to the lack of hydrogen bonding sites, CTAB might not interact well with PEI. The properties of the additives led to the inhomogeneity of the deposition of organic on the interior and exterior of the particles, which was mainly caused by the interaction between the additives and PEI molecules. Song et al.[184] investigated the mechanism by which PEG promoted the adsorption of CO_2 by PEI loaded on molecular basket. Their results showed that there may be two promotion mechanisms of PEG. Normally, 1 mol CO_2 reacts with 2 mol amines to form carbamate, but the introduction of PEG provides hydroxyl groups that allow 1 mol CO_2 to react with 1mol amines, resulting in higher CO2 adsorption capacity. Another possibility is that the interaction between PEG and PEI molecules makes PEI molecules more separated and promotes the diffusion of CO_2 in PEI layer, leading to the increase of CO_2 adsorption capacity. Figure 14a visually illustrates how PEG separates PEI molecules. The branches of PEI would be entangled through intramolecular and intermolecular interactions without PEG. More intermolecular interactions will occur between PEI and PEG when PEG is present, thereby reducing the intramolecular and intermolecular interactions between branched PEI molecules and making the PEI molecules more separated. Morever, Choi et al.[185] prepared two novel modified PEI-based silica adsorbents by impregnation method, which were 3-aminopropyltrimethoxysilane (A-PEI/silica) or tetraethyl orthotitanate (T-PEI/silica) to modify PEI. The modified adsorbent has relatively excellent CO_2 adsorption capacity, which was more than 2.0 mmol g^{-1} under simulated ambient air conditions. Compared with conventional PEI-impregnated silica adsorbent, the adsorption kinetics is enhanced. Moreover, the novel adsorbent showed good stability during the cyclic test. After four cycles of experiments, the adsorption capacity of PEI/SiO_2 decreased by 30%, while the A-PEI /SiO_2 adsorption capacity decreased by 9%, and the loss of T-PEI/SiO_2 adsorption capacity was less than 2%. In addition, the epoxide modified polyamine impregnated SiO_2 adsorbent prepared by Goeppert et al.[186] can effectively absorb CO_2 and can be regenerated under relatively mild conditions (50-85 °C). Compared with unmodified adsorbents, they show higher stability, especially under oxidizing conditions. At 400 ppm, 25 ℃, during the 15 adsorption-desorption cycle tests, the adsorption performance of the adsorbent is almost no loss.

The adjustment of silica matrix structure is also an method to improve the stability of the material. For instance, by introducing heteroatoms (e.g. Al, Ti and Zr) into the silica matrix directly or after synthesis, a tunable porous solid can be produced.[7, 187, 188] The electrophilic/nucleophilic sites generated in this way can be used as CO_2 or amine activation sites to play a role in CO_2

adsorption. The study by Kuwahara et al.[189] showed that it is possible to change the acidity/basicity of the support by incorporating heteroatoms such as zirconium into the silica support to significantly enhance the adsorption of CO_2. Similar results were also reported by Zhou et al.[190], as shown in Figure 14b, zirconium ions were introduced into the SBA-15 supports. These novel adsorbents significantly increase the CO_2 adsorption capacity, improve adsorption kinetics, and enhance thermal stability and reproducibility compared with traditional PEI/SBA-15 materials. The CO_2 adsorption capacity (0.19~0.85mmol g^{-1}) of PEI/Zr7-SBA-15 (Zr/Si $\approx$ 0.07) was increased by four times compared with the PEI-SBA-15, and the adsorption capacity decreased by only 2% during the 4-cycles test.[189] However, the PEI-MCM-41 synthesized by Sayari et al. with abundant surface cetyltrimethylammonium ($CTMA^+$) cations can obtain excellent CO_2 capacity and stability.[3] They found that $CTMA^+$ cations can effectively change the dispersion of PEI on the surface of silica, thus increasing the efficiency of amines. Under a humid with 400 ppm CO_2, the CO_2 capacity of 40 wt% PEI/PME can reach 2.92 mmol g^{-1}, and its working capacity is only reduced by 2% during the 20-cycle test. This work demonstrates the critical role of material design in improving CO_2 capture capability.

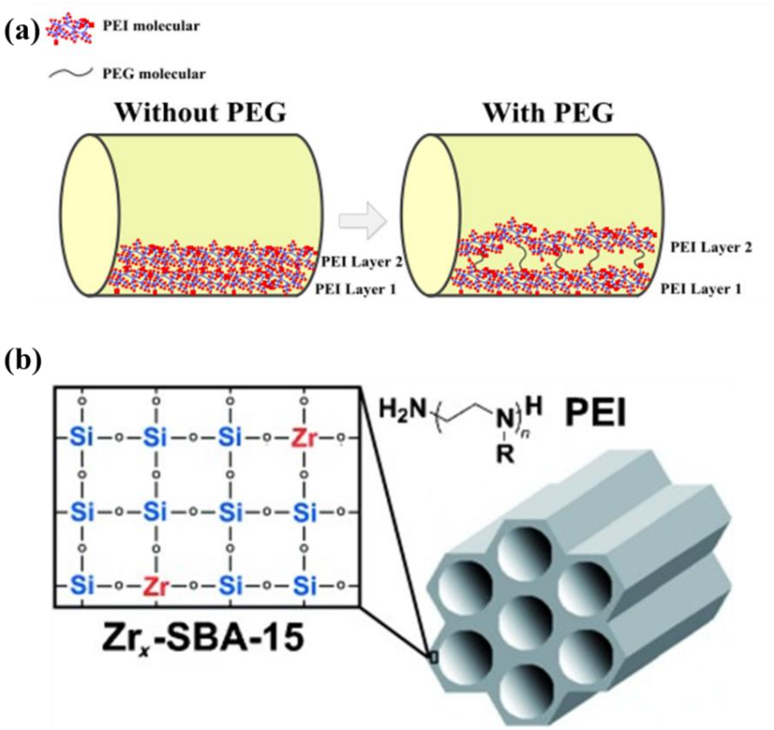

Figure 14. (a) PEI layer model of MBSs doping or without doping PEG.[184] (b) Schematic diagram of SBA-15 incorporated with zirconium ions and dopped with PEI.[190]

3.5.3 Summary and outlook of silica-based adsorbents

Overall, many researchers have explored most types of SiO_2-loaded amine adsorbents for capturing CO_2 from ambient air. Studies have also shown that most silica-based adsorbents are effective in removing CO_2 from simulated air and are easily regenerated under relatively mild conditions. At present, the most mature DAC technology is the CO_2 capture technology of alkali metal hydroxide solution, which has been used to capture CO_2 in air in a large scale. In addition, the most extensive research is amine-modified silica materials, but it is still limited to laboratory research, and there are still significant unknown factors in practical application, mainly focusing on the long-term stability of adsorbents under long-term practical operating conditions. However, due to the weak physical adsorption connection between amine and porous support, the stability of impregnation system is often poor, but it can usually obtain a higher adsorption capacity. Therefore, the mechanism of active additives in adsorbents can be further studied to improve the stability of adsorbents. In addition, O_2 and other impurities coexisting in the air will reduce the adsorption capacity or stability of the adsorbent, so it is necessary to study the antioxidant properties of the adsorbent. The CO_2 capture performance of silica-based adsorbents are shown in Table 6.

Table 6. Summary of CO_2 capture performance of silica-based and other types of adsorbents.

Silica types	Surface modifications	CO_2 uptake	Adsorption condition	Ref
PE-MCM-41	Triamine-grafted	0.98 mmol g^{-1}	400 ppm, 25 °C	[101]
Fumed silica	PEI(25000)-impregnated	1.71 mmol g^{-1}	420 ppm, 25 °C	[169]
	PEI(800)- impregnated	2.40 mmol g^{-1}	400 ppm, 25 °C	[120]
Silica gels	Triamine-grafted	1.10 mmol g^{-1}	415 ppm, 25 °C	[121]
AHTSA		1.64 mmol g^{-1}	400 ppm, 25 °C	[174]
Hierarchical silica	PEI-impregnated	3.40 mmol g^{-1}	400 ppm, 30 °C	[171]
Ethane-silica	PEI modified	1.00 mmol g^{-1}	400 ppm, 30 °C	[175]

nanotubes				
HAS		1.72 mmol g^{-1}	400 ppm, 25 °C	[173]
SBA-15	Poly (L-lysine) modified	0.60 mmol g^{-1}	400 ppm, 25 °C	[172]
	linear PPI modified	1.25 mmol g^{-1}	400 ppm, 35 °C	[179]
	Ph-X-YY-impregnated	2.90 mmol g^{-1}	400 ppm, 35 °C	[182]
	PEI(800)-impregnated	0.19 mmol g^{-1}	400 ppm, 25 °C	[189]
	PEI/Zr7 modified	0.85 mmol g^{-1}	400 ppm, 25 °C	[189]
MAHSM	co-condensation of AS and VS	1.68 mmol g^{-1}	400ppm, 30 °C	[191]
PME	PEI-impregnated	2.92 mmol g^{-1}	400 ppm, 25 °C	[3]
CaO/SiO_2		2.00 mmol g^{-1}	500 ppm, 364°C	[192]
CaO	Ethanol treatment	10.00 mmol g^{-1}	air	[193]
	Wastewater treatments	17.00 mmol g^{-1}	air	[193]
	Ethanol/alkaline wastewater treatments	15.90 mmol g^{-1}	air	[193]
TiO_2		0.06 mmol g^{-1}	2000 ppm, 20°C	[194]
	NH_4OH and KOH	0.53 mmol g^{-1}	2000 ppm, 20°C	[194]
LDHs	PEI impregnated MMOs	2.27 mmol g^{-1}	400 ppm, 25 °C	[195]
	TRI treatment	1.05 mmol g^{-1}	400 ppm, 25 °C	[196]

DFM	0.20 mmol g^{-1}	air	[197]

3.6 Other type of solid adsorbents for CO_2 capture from the air

Recently, a series of new solid adsorbents have been reported for DAC of CO_2. Many natural sources of alkalinity such as CaO and MgO have also been studied in recent years for DAC of CO_2[198, 199] CaO has attracted extensive attention due to its high theoretical adsorption capacity and low cost.[200] The research on CO_2 capture by CaO in post-combustion flue gas has been relatively mature, but the research on the capture of CO_2 from ambient air by CaO is still scarce. Steinfeld et al.[192] initially studied the thermodynamics, kinetics and thermogravimetric analysis of CaO and $Ca(OH)_2$ in capturing CO_2 from ambient air in 2009. The carbonation rates of CaO and $Ca(OH)_2$ in the presence of water vapor and the effect of water vapor on the carbonation rates were studied at 500 ppm CO_2 concentration. The carbonation step of CaO was carried out at 365-400 °C, and the calcination step was carried out at 800-875 °C. In each carbonation step of 600s, CO_2 can be completely removed from the ambient air stream in 1.3s, and in the calcination step, CO_2 can be completely released in about 500s. In addition, the addition of water vapor helps to increase the rate of carbonation. The degree of carbonation reached 80% after 100 min in the presence of water vapor. Similar results were also reported by Samari et al.[201] and Erans et al.[202] These series of studies show that under environmental conditions, humidity plays a very important role in the carbonization of CaO. Besides, the method of adding solvents or surfactants to reduce the particle size of CaO and increase its specific surface area is also an effective method to increase its carbonation conversion rate. Gerven et al.[193] researched the carbonation mechanism of solvochemical carbonation of CaO using ethanol and investigated different options for increasing the conversion of carbonation. The results showed that the carbonation occurred after the evaporation of ethanol solvent, and the treatment of CaO by ethanol increased the specific surface area of the particles. Moreover, increasing exposure time to the atmosphere, increasing the liquid-to-solid ratio, or grinding the ethanol-CaO slurry before exposure to the atmosphere can increase carbonation conversion. In addition, the use of alkaline wastewater is also an effective method to increase the yield of carbonation. Wilcox et al.[199] studied direct exposure of MgO to weathering environments to remove CO_2 from the ambient air. The CO_2 capture cost is approximately \$46-\$159 t CO_2^{-1}, which is roughly the same as the cost of the potassium hydroxide and calcium oxide process estimated by Keith et al.[41]

Moreover, many other metal oxides have also been used to capture CO_2 from ambient air. Titanium-based materials with high specific surface area and ion-exchange capacity show exciting CO_2 adsorption potential. Unmodified TiO_2 absorbs CO_2 mainly through physical adsorption, so the adsorption performance of the raw TiO_2 is usually relatively poor, about 0.06 mmol g^{-1}.[194] Kapica-kozar et al.[194] prepared a novel type of TiO_2 adsorbent with high CO_2 capture performance by modifying TiO_2 with different concentrations of alkaline liquid. The total adsorption capacity of the modified TiO_2 was increased by 88%. Yanase et al.[203] synthesized β-$NaFeO_2$ to remove CO_2 from the air by heating a mixture of α-Fe_2O_3 and $NaNO_3$ at 800 °C. Its CO_2 uptake can get 2.5 mmol g^{-1} In the presence of water vapor. The results also showed that as the relative humidity in the air increasing, the ability of β-$NaFeO_2$ to capture CO_2 from the air increased. This is mainly because the water vapor adsorbed on the surface of β-$NaFeO_2$ forms an alkaline water film, which promotes β-$NaFeO_2$ to absorb CO_2 from the air. While, Farrauto and his colleagues reported the feasibility of using dual function materials to directly capture CO_2 from ambient air and then convert it into methane.[197] The results showed that DMF could capture 0.2 mmol g^{-1} from the diluted CO_2 streams and selectively convert the captured CO_2 into methane after the introduction of H_2.

In addition, the LDH-derived mixed metal oxides (MMO) possess abundant basic sites and high specific surface area, which is beneficial to the absorption of acidic CO_2 in the temperature range of 200-400 °C.[204, 205] Therefore, MMO are considered to be an important intermediate-temperature CO_2 adsorbents. Although LDHs as CO_2 adsorbents have been studied for decades, their first application in DAC is reported in 2020.[195] Wang et al[195]. prepared a novel DAC adsorbent by impregnating branched PEI onto MMOs, which showed surprising CO_2 adsorption capacity, rapid kinetics, and cyclic stability, with the adsorption capacity up to 2.27 mmol g^{-1} at 25 °C, 400 ppm. The materials they prepared have a rich slit-like mesoporous structure that provided a loose framework for loading a large amount of PEI. The huge specific surface area of the MMO nanosheets also ensures that CO_2 can fully contact the active sites. However, the MMO materials synthesized by them are not commercially viable from an economic point of view. Current studies have shown that improving the cycle stability and adsorption kinetics of the adsorbent have great potential in reducing the energy consumption of the DAC process and increasing the CO_2 productivity.[206, 207] Recently, they reported that aminosilane monolayers were loaded on LDH-derived nanosheets for removing CO_2 from the ambient air (Figure 15).[196] Compared with PEI-impregnated MMOs, aminosilane monolayers-grafted LDHs showed excellent kinetic and cyclic stability. TRI-grafted LDHs can reach as high as 70% of adsorption value within 30 min, and the adsorption value was stable at 0.91 mmol g^{-1} during a 50 adsorption-desorption cycle test.

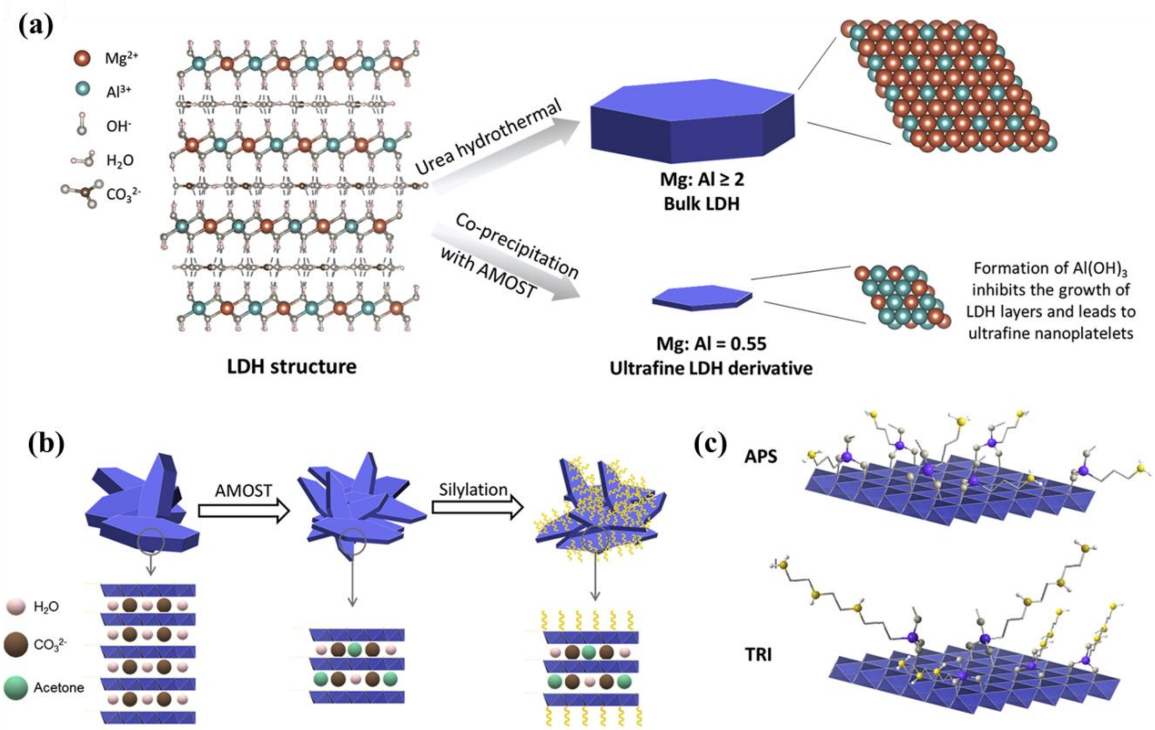

Figure 15. Preparation of amine monolayer grafted MgAl-LDHs.[196]

4 Moisture-swing CO_2 adsorbent

Moisture swing adsorption provides a new method for the regeneration of CO_2 adsorbents. The consumption of water replaces the heat input in thermal swing or the mechanical energy in pressure swing, and the evaporation of water provides free energy to drive the adsorbent adsorption-desorption cycle. The use of wet-driven cycles provides new opportunities to decrease energy consumption. In order to reduce the capture cost of DAC, in 2009, Lackner first proposed the technology of using moisture swing adsorbents to capture CO_2 from ambient air.[28] Moisture swing adsorbents usually contain fixed quaternary ammonium groups and movable anions in their molecular chains, such as OH^- or CO_3^{2-} ions. The CO_3^{2-} ions can be hydrolyzed to produce OH^- ions, and basic OH^- react with CO_2 to form HCO_3^-, thereby fixing CO_2 from the air.[208] Recently, Yang et al.[209] directly studied the moisture swing adsorption process using solid-state NMR. They found that CO_2 was absorbed to form HCO_3^- at low humidity levels. Bicarbonate was replaced by hydrated OH^- at high humidity levels and the adsorbed CO_2 was released. Due to the low price of water and no heat supply, the moisture-swing adsorbent can be compared with solid amines in terms of cost and energy consumption. Moisture swing adsorption seems to be a promising DAC technology.

Several moisture swing adsorbents have been reported, such as porous polymers, modified carbon black, quaternized bamboo fibers, quaternized chitosan aerogels and ion exchange resins. Among them, ion exchange resin is one of the most commonly used adsorbents in moisture swing adsorption, because it combines the low binding energy of carbonate to bicarbonate conversion with the known faster reaction kinetics from sodium hydroxide solution.[28] Wang et al.[210] studied the process of ion exchange resin capturing CO_2 from ambient air. They found that the amine-based anion exchange resin dispersed in polypropylene flakes could absorb CO_2 under dry conditions and release it under wet conditions. The measured resin was completely saturated with CO_2 when the water vapor concentration reached 0.5% under the condition of 23 °C, 400 ppm, and its capacity to capture CO_2 from ambient air was 0.82 mmol g^{-1}.[210] The reaction path of CO_2 adsorption and desorption is explained in Figure 16. Alternatively, the resin can also be exposed to liquid water to force the release of CO_2. But water swing would require clean water and can lead to higher water losses. Thermodynamic analysis showed that the water swing may be more advantageous than the moisture swing, which required an increase in temperature to produce water vapor, and the energy requirement of the water swing process was low.[211]

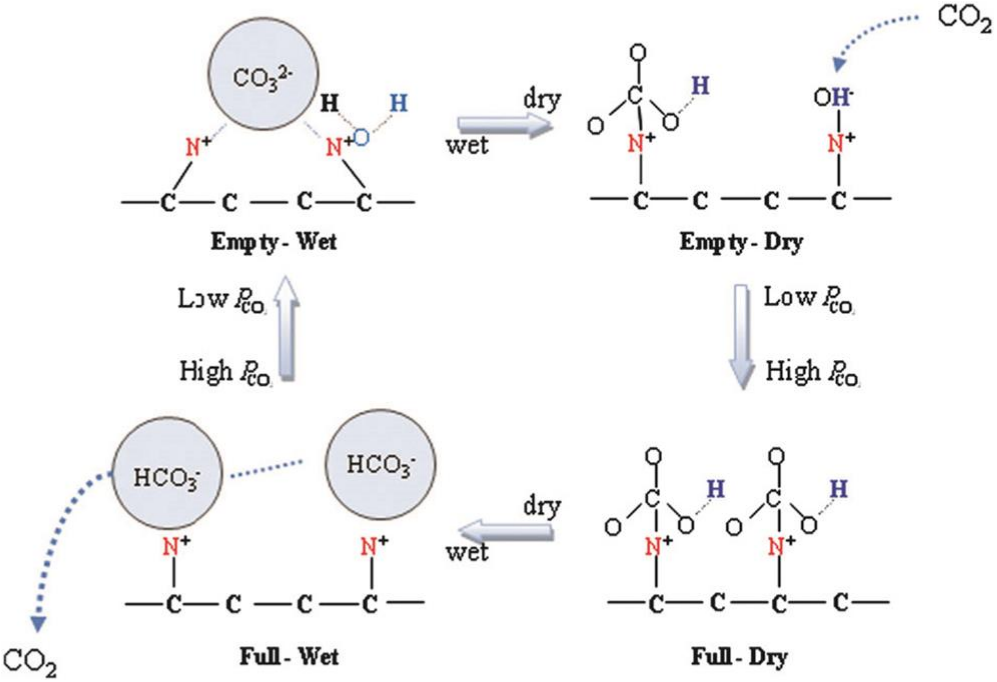

Figure 16. Schematic diagram of resin moisture swing process.[211]

The kinetic characteristics are an important factor affecting the moisture swing CO_2 adsorbent. For the novel water-driven CO_2 adsorbent, kinetic improvement is also a strategy to significantly reduce its cost and energy consumption. Previous studies have shown that the use of improved binders can raise the partial pressure of CO_2 during the release process and increase the contact area between the adsorbent and air.[212-214] The higher pressure and large contact area decrease the operating cost of the system. Shi et al.[181] developed a novel moisture-swing CO_2 adsorbent using ion-exchange resin as the functional group and PVC as binder. Research results indicated that the CO_2 adsorption rate of this novel adsorbent was almost three times that of the raw ion exchange resin, and 3~10 times that of ordinary amine-based solid adsorbents. A large number of pores in the polyvinylchloride matrix and large narrow pores between the ion-exchange resin and the polyvinylchloride, which greatly promote the diffusion rate of H_2O and CO_2 in the adsorbent. The faster the diffusion of H_2O, the faster the desorbed CO_2 was released. Since then, Armstrong et al.[215] and Song et al.[216, 217] all reported that their newly developed adsorbent with a smaller half-time, that is, the time required to reach half of the asymptotic load. The study by Song et al.[216] also showed that higher temperature can also improve the adsorption peak rate of CO_2 and decrease the half-life of adsorption. The half-life provided a simple preliminary assessment of the kinetics of CO_2 adsorption. Recently, Wang et al.[43] reported the use of mesoporous resins functionalized with quaternary ammonium functional groups as moisture swing adsorbents to capture CO_2 from the air (Figure 17). However, its CO_2 adsorption capacity was not high, only about 0.26 mmol g^{-1} of adsorption cycle capacity. But their report showed that this adsorbent had ultra-high adsorption kinetics, with a half-life of 2.9 minutes under the atmosphere condition, which was the highest value currently reported among DAC adsorbents.

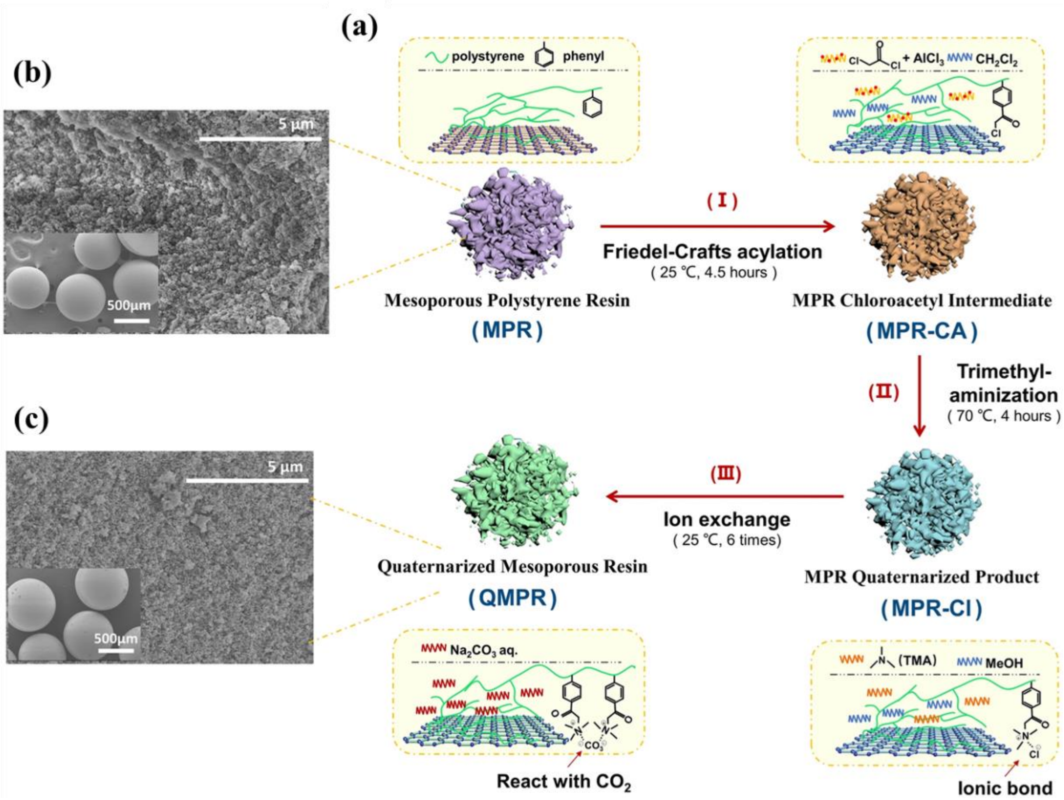

Figure 17. Fabrication and morphology of QMPRs.[43]

The prototype of the moisture-swing adsorbents are some commercial resins, which hinder the transfer of CO_2 due to insufficient porosity, thus resulting in poor kinetics. Optimizing the support structure or decreasing the size of the resin particles could effectively improve the kinetics. Matyjaszewski and his colleagues prepared three types of reversible CO_2 adsorption polymer materials such as cross-linked porous polymer templated by ordered colloidal crystals, polymers grafted from carbon black and high internal phase emulsion system, which all contain quaternary ammonium ions and hydroxide ions.[218] The synthetic route is shown in Figure 18. The resulting polymer was used as adsorbent to reversibly adsorb CO_2 from the air using moisture swing.

Compared with commercially materials with similar functional groups, the kinetic of the porous polymers during the adsorption/desorption process was significantly improved, and the swing size was also significantly improved. The performance of the high internal phase emulsion seemed to be better than the other two materials studied. The total rate of CO_2 capture and release was 12 times that of Excellion membrane, and the swing size was 3.8 times that of Excellion membrane. Although carbon black had a high specific surface area, compared with Excellion membrane, the material made by surface grafting does not seem to show excellent CO_2 adsorption/desorption performance. It maybe that the larger pore sizes and better interconnections improve the dynamics and swing sizes of colloidal crystal materials and HIPE materials. In order to obtain better CO_2 adsorption performance for the synthesized polymer, the effect of surface area, pore size and interconnection structure on the performance of the adsorbent should be further explored. Since then, the same group conducted more in-depth research on HIPE materials, and modified them by introducing quaternary ammonium hydroxide groups into the pore surface of the material network.[219] The results showed that the swing size of the prepared sample is 5.5 times that of Excellion membrane. The pore size and interconnected porous structure had a significant impact on the CO_2 adsorption and desorption performance. The use of organic carriers (like polystyrene or polymethyl methacrylate) for the synthesis of adsorbents is often complicated and expensive. Recently, Song et al.[217] and Hou et al.[220] reported the use of low-cost biomass materials to construct the moisture-swing CO_2 adsorbents. The research results showed that the quaternized cellulose synthesized by introducing quaternary ammonium groups on the natural lignocellulose support was hydrophobic, and it was not conducive to CO_2 capture at extremely low or high relative humidity. The maximum CO_2 adsorption capacity reached when the relative humidity was 66% was 0.19 mmol g^{-1}. At higher relative humidity, the adsorbent CO_2 capacity can maintain a mild response to moisture, which will facilitate the application of quaternized cellulose under working conditions.[220]

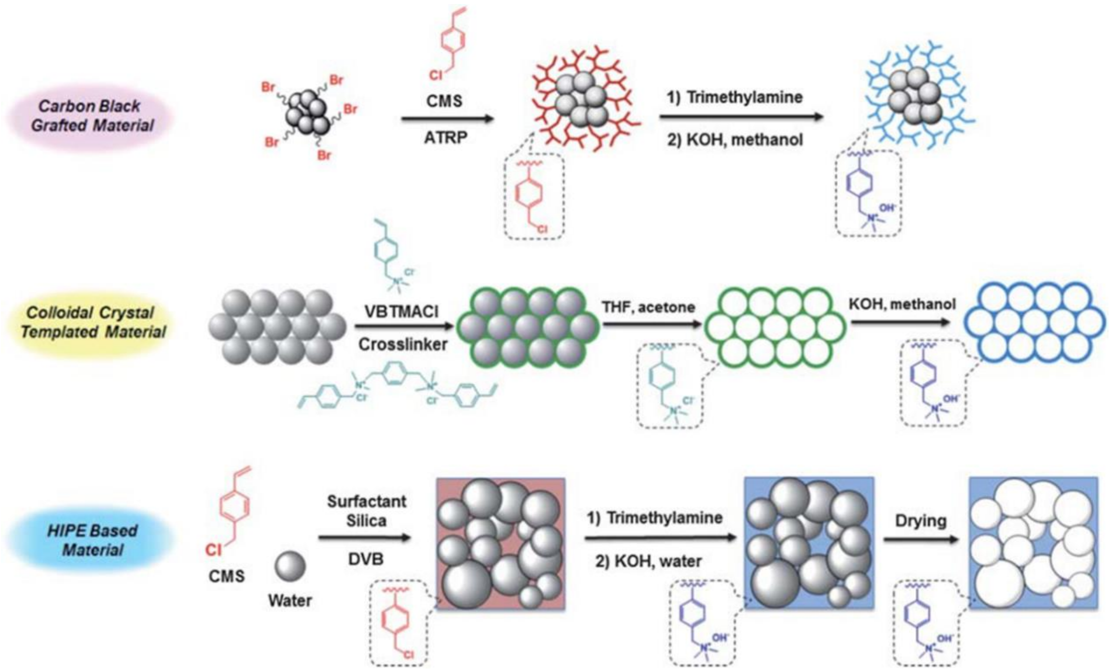

Figure 18. Synthetic diagram of the polymer-grafted carbon blacks , colloidal crystal templated material and HIPE based material.[218]

Moisture-swing adsorption involves the moisture swing drive of ion hydration and dehydration in iron-exchange resin. There is no simple mechanism to explain the behavior of adsorbents that absorb CO_2 at dry condition and release CO_2 at humidity condition. Shi et al.[221] theoretically clarified its mechanism by a computational modeling, and verified it through nanomaterials. The activity of water in the nanopores determines the ionic interactions on the adsorbent. The reduction in the number of water molecules in the pores promotes the hydrolysis of CO_3^{2-}. This finding indicates that moisture-driven CO_2 adsorption is not limited to ion exchange resins. In the future, we can further explore the possibility of other types of adsorption materials using water-drive CO_2 adsorption.

5 Technical and economic assessment

For the research of DAC technology, in addition to the development of high-efficiency CO_2 adsorbents, the technical and economic evaluation in practical applications is also a very important issue. Different groups have proposed different DAC approaches, ranging from hydroxide solutions to solid sorbents. Basic hydroxide solution is the earliest DAC adsorbent studied. Due to the early and immature stage of DAC technology, it is impossible to accurately estimate the cost. Lackner et al.[28] conducted a preliminary assessment of the cost of alkaline hydroxide solution in 2009, and predicted that its initial price would be \$200 per ton of CO_2. With the further improvement of DAC capture technology, its cost may be reduced to \$30 per ton of CO_2. Nikulshina et al.[36] estimated the CO_2 capture price would be \$176~\$220 per ton of CO_2 by using a $Ca(OH)_2$ absorbent combined with a solar calcination system. Moreover, Stolaroff et al.[35] evaluated the feasibility of using a sodium hydroxide spray contactor in an air capture system and estimated costs ranging from \$53 to \$127 per ton of CO_2. Carbon Engineering Corporation has been developing the aqueous DAC system since 2009 and has established the first 1t-CO_2/day pilot plant. In a recent paper, they reported that the cost of carbon engineering process with KOH solution as the main adsorbent has been between \$94~\$232 per ton of CO_2 since 2015.[41] In addition, Feron et al.[51] studied the technical performance of the traditional amine capture CO_2 process from ambient air, and found the total cost ranges from \$273 to \$1227 per ton of CO_2. Since they have carried out traditional packed column as absorbers, this may not be the optimal design for the DAC. It is found that using Carbon Engineering's cooling tower excitation system, the cost of the absorber can be reduced by about 80%. [222] However, the corrosion of amines will also increase the cost of carbon capture. For liquid absorbent, in order to further reduce costs, it is essential to use novel inexpensive contactors that operate at a lower liquid-to-gas ratio.

For solid absorbent, in 2018, the NAS estimated that the potential cost of DAC using solid adsorbents would be \$88~228 per ton of CO_2 within the next decade.[223] Both Sholl et al.[224] and Kawajiri et al.[225] provided a technical and economic assessment of the use of solid adsorbents to capture CO_2 from ambient air. Sayari et al.[101] developed a model of the Temperature Swing Adsorption (TSA) process using the silica-based adsorbent of TRI-PEMCM-41. One method is to use diurnal cooling and heating to minimize the energy input of the TSA cycle. Another method is to use steam as a heat source and sweep gas to create conditions conducive to the adsorption of the adsorbent surface. Both processes have been evaluated for different adsorption conditions, and the estimated capture price was \$100 per ton of CO_2, excluding capital expenses.[207] Moreover, Kawajiri et al.[225] proposed a Temperature Vacuum Swing Adsorption process(TVSA), using MOF adsorbent coated as films on monolithic contactors, and using steam as a stripping agent during the desorption process. The process uses two different MOF adsorbents, MIL-101(Cr)-PEI-800 and mmen-Mg_2(dobpdc), for modeling research and economic assessment of DAC. The results showed that the estimated cost of MIL-101(Cr)-PEI-800 is \$75~\$140 per ton of CO_2, and the estimated cost of mmen-Mg_2(dobpdc) is \$60~\$190 per ton of CO_2. A pilot-scale demonstration of DAC process using MOF-polymer nanocomposites as adsorbent was reported by Sadip et al.[132] The optimal regeneration temperature of the adsorbent was 80℃, and the adsorbent had strong CO_2 adsorption and repellence of water vapor during the adsorption process. During the pilot scale trial, the demonstrator captured a total of 8 kg of CO_2 during 2680 cycles at an operating cost of us \$35~\$350 per tonne of CO_2. Recently, Sabatino et al.[226] performed a comparative techno-economic assessment of CO_2 removal from the ambient air by two aqueous-scrubbing processes and one solid adsorbent process. The results showed that all three processes cost less than \$200 /tCO_2, but the absorption-based process generally has poorer performance than the solid adsorbent process. The productivity of alkali and amine-scrubbing processes is 0.18-0.45 $kg_{CO_2}\ m^{-3}\ h^{-1}$ and 0.75-1.07 $kg_{CO_2}\ m^{-3}\ h^{-1}$ respectively, while for solid sorbent processes it can vary from 3.8-10.6 $kg_{CO_2}\ m^{-3}\ h^{-1}$. The costs have been estimated for a range of electricity, heat and contactor prices. The high productivity of the solid sorbent process (VTSA) makes its cost less dependent on the air contactor. Thus, it was proved to be the most promising process. Designing new contactors and new sorbents can be more expensive than existing adsorbents. Based on the above review, amine-based solid adsorbents seem to be more suitable for DAC process from a technical and economic point of view, but MOF materials with continuous optimization also have great potential for large-scale DAC applications.

According to our review above, in addition to aqueous DAC systems, solid adsorbents seem to have great potential for direct capturing CO_2 from ambient air. At present, more than 30 companies and scientific research institutions around the world are conducting research on DAC technology, and start-up companies have established 19 pilot plants to provide experimental data for research and revise the direction of research and development. Among them, Climeworks, Global Thermostat and Carbon Engineering have advanced technologies and have initially realized the commercialization of the DAC system. Carbon Engineering uses alkaline liquid adsorbents, and Climeworks and Global Thermostat use amine-based solid adsorbents, and their CO_2 capture costs are \$136, \$222 and \$223-800 per ton of CO_2, respectively.[41, 206, 227] Unlike Carbon Engineering, Climeworks and Global Thermostat have almost no data to describe their carbon capture processes in the public literature, and the technical data analysis of their processes would help promote the development of the DAC field. In addition, based on the actual operating costs of the company, the alkali-scrubbing process remains best suited for DAC applications. Although the solid adsorbent VTSA process from the experimental analysis is an attractive choice[226], there are still many problems to be deployed on a large scale, including adsorbent, adsorption/desorption kinetics and the affinity of the adsorbent for water, etc., have a great impact on VTSA process.

6 Summary and future perspectives

CCS technology has a great potential for reducing global carbon emissions. The DAC of CO_2 is an emerging technology to combat climate change. Compared with traditional carbon capture and storage technologies, only DAC can remove CO_2 from the air and decrease the CO_2 concentration in the global atmospheric environment. Although the advantages of DAC are obvious, it has not been widely used in industry. In order to better understand the technology, and further apply it to the industrial environment. This review provides a comprehensive overview of the current development status of DAC technology, which will help accelerate the development of DAC.

In this review, the latest developments in DAC materials are reviewed. All materials are divided into 3 categories according to their adsorbent properties, including liquid-based absorbents, solid adsorbents and moisture-swing adsorption. For liquid absorbents, there are currently four main types of research. Alkaline hydroxide is the most widely studied and most mature adsorbent, and it has been tried for pilot scale application. Amine scrubbing is widely used to capture CO_2 from industrial flue gas due to its low cost, easy-to-obtain and high capture capacity.[5, 228] In fact, alkanolamines have a high affinity for CO_2 and can capture it from the air.[28] Surprisingly, alkanolamines (such as MEA) were hardly considered for applications in DAC until 2016. Ionic liquid adsorbents and phase change adsorbents have also only been studied in the DAC field in recent years. In the literature that has been reported, phase-change adsorbents show better CO_2 adsorption performance compared with amine-based adsorbents and ionic liquid adsorbents. Compared with alkaline scrubbing process, the regeneration temperature of the solvent is lower.[78] However, further exploration is needed for its stability in capture, and its cost is also an obstacle that limits large-scale applications. Solid adsorbents are at the core of research on CO_2 capture from ambient air. Among the solid adsorbents studied, the solid amine-based adsorbent is the most widely studied, which mainly captures CO_2 from the air through the combined of the physical adsorption of the support and the chemical adsorption of the active component. The highest adsorption capacity of the previously studied solid amine adsorbent can reach 3.40 mmol g^{-1}.[171] Therefore, solid amine-based adsorbents show great potential for capturing CO_2 directly from ambient air. In order to make such adsorbents suitable for commercial applications, a lot of energy can be invested in future research to improve their hydrothermal stability, kinetics, etc. MOF is well known as a potential low-temperature CO_2 adsorbent. In addition to functionalizing the MOF material with amines to improve its adsorption performance, it is also a feasible method to adjust its structure by metal doping or anion modification. There are few studies on anion-modified MOF materials, and more research is needed for reference, so as to clarify whether the material can be applied to DAC. Like hydroxide adsorbents, the biggest obstacle to the application of alkali metal carbonates is also the high energy consumption of regeneration. In addition, the performance of alkali metal carbonates to capture CO_2 directly from ambient air does not seem to be as good as solid amine-based adsorbents. Moisture-swing adsorbent is an emerging DAC technology. Due to the low price of water and no heat supply, the moisture-swing adsorbent are comparable to solid amines in cost and energy consumption. However, water-driven moisture-swing adsorption needs to consume a lot of water resources in applications. It is estimated that 10 Gigatons of CO_2 can consume 100 km^3 of water.[229] Therefore, the adsorbent should be evaluated from various aspects such as adsorbent stability, adsorption kinetics, regeneration energy consumption and cost before practical application. If the CO_2 adsorbent is to be truly applied in practice, in addition to improving the adsorption performance of the adsorbent through technical methods, it is also very necessary to conduct a technical and economic evaluation of the adsorbent. At the end of the review, we also briefly reviewed the technical and economic evaluation of a series of CO_2 adsorbents in practical applications. All results indicate that the development of cost-effective CO_2 sorbents to remove CO_2 from the atmospheric environment to mitigate climate change is highly warranted.

In short, DAC technology is still in initial stage, and there is still huge room for improvement in the adsorbent and process technology developed. In future research, we should also focus on the development of new and efficient CO_2 capture agents and further improvements to the adsorbents that have been developed to enable them to have better CO_2 adsorption performance.

Acronyms

AC	Activated carbon
ACH	Activated carbon honeycombs
AS	3-aminopropyl triethoxy silane
AMP	2-Amino-2-methyl-1-propanol
AHTSA	Amine hybrid titania/silsesquioxane composite aerogel
BUMEA	2-(butylamino)ethanol
BTIG	Trichelating iminoguanidine ligand
BIGs	Bis(iminoguanidine)
CCUS	Carbon dioxide capture, utilization, and storage
CCU	Carbon capture and storage
CTAB	Cetyltrimethylammonium bromid
CTMA	Cetyltrimethylammonium
CE	Carbon Engineering
DAC	Direct air capture
DEA	Diethanolamine
DEGMEE	Diethylene glycol monoethyl ether
DGA	2-(2-aminoethoxy)ethanol
DMMEA	2-(dimethylamino)ethanol
DIPA	Bis(2-hydroxypropyl)amine
DSC	Differential scanning calorimetry

DFM	Dual Function Materials
EG	Ethylene glycol
EMEA	2-(ethylamino)ethanol
(EMPY)(BH_4)	1-ethyl-1-methylpyrrolidinium borohydride IL
ED	Eethylene diamine
Gly	Glycine
GlyGly	Glycylglycine
GBIG	Glyoxal-bis(iminoguanidine)
HIPE	High internal phase emulsion
HAS	Hyperbranched aminosilica
IPCC	Intergovernmental Panel on Climate Change
ILs	Ionic liquids
LSX	Low silica type X
LDH	Layered Double Hydroxide
MAHSM	Mono Amine based Hybrid Silica Material
M_2(dobpdc)	M = Mg, Mn, Fe, Co, Ni, Zn; dobpdc^{4-} = 4,4'-dioxido-3,3'-biphenyldicarboxylate
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
MCM-41	Mesoporous material with a hierarchical structure
MSA	Moisture swing adsorbents
MOF	Metal organic framework
MBS	Molecular basket sorbent
MMOs	Mixed metal oxides
Mmen	N,N′-dimethylethylenediamine
NAS	National Academy of Sciences
NOAA	National Oceanic and Atmospheric Administration
NMR	Nuclear magnetic resonance
PEHA	Pentaethylenehexamine
PrOH	1-propanol
PyBIG	2,6-pyridinebis(iminoguanidine)
PPI	Poly(propylenimine)
PEI	Poly(ethylenimine)
Ph-X-YY	Aryl-Alkyl amine reach molecules
PEG	Polyethylene glycol
PME	Pore-expanded MCM-41 with a surface CTMA$^+$ layer
PVC	Polyvinylchloride
PEI@PGD-H	Polyethylenimine-Grafted HKUST-Type MOF/PolyHIPE Porous Composites

QMPRs	Quaternary ammonium functionalized mesoporous adsorbents
SBA-15	Mesoporous silica
Sar	Sarcosine
TBMEA	2-(tertbutylamino)ethanol
TEAB	Tetraethylammonium bromide
TPAB	Tetrapropylammonium bromide
TBAB	Tetra-n-butyl ammonium bromide
TRI-PE-MCM-41	Triamine-grafted pore-expanded mesoporous silica
TGA	Thermal gravimetric analyzer
TRI	3-(2-(2-Aminoethylamino)ethylamino)propyl-trimethoxysilane
TREN	Tris (2-amino ethyl) amine
TEPA	Tetraethylenepentamine
TSA	Temperature Swing Adsorption
TVSA	Temperature Vacuum Swing Adsorption
VS	Vinyl triethoxy silane
VTSA	Vacuum-pressure temperature swing adsorption

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Ethics declarations

Conflict of interest

The authors declare no competing interests.

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