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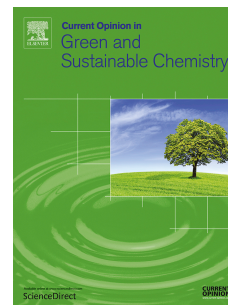
Recent progress on direct air capture of carbon dioxide

Jialiang Sun [‡,1,2], Meng Zhao[‡,1,2], Liang Huang[1,2], Tianyu Zhang[1,2], Qiang Wang[1,2,*]

[‡]Jialiang Sun and Meng Zhao contributed equally.

[1]Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

[2]Engineering Research Center for Water Pollution Source Control & Eco-remediation, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

*Corresponding author:

E-mail: qiangwang@bjfu.edu.cn (Q. Wang)

Abstract

Direct air capture (DAC) has received tremendous attention as a negative carbon emission technology that could facilitate the addressing of global climate change. In this work, we systematically summarized the latest progress on the development of direct air capture and comprehensively reviewed the properties and performance of DAC adsorbents, which are categorized as physisorption and chemisorption according to sorption mechanisms. The unresolved issues and possible improvements of traditional DAC adsorbents for CO_2 capture are pointed out. We highlight the potential of novel MMO-supported solid amine materials for DAC due to its excellent CO_2 adsorption capacity, superior regenerability, and ease for scaled up. This review paves the way for the understanding of the intrinsic mechanism and the practical development of DAC technology.

Keywords: direct air capture, adsorbents, physical materials, chemisorption materials, amine-functionalized materials, mixed metal oxides.

Introduction

During the past few years, we have witnessed a dramatic increase of CO_2 concentration in the atmosphere from a preindustrial level of 280 ppm to 416 ppm [1]. The unprecedentedly increased CO_2 emission has caused a serious greenhouse effect, leading to severe global warming accompanied by natural disasters such as glaciers melting, extreme weather, and desertification, which pose a considerable threat to the environment and human life [2]. To realize the Paris Agreement's goal of keeping the global average temperature increase to within 1.5 °C, in addition to reducing CO_2 emissions from industrial sources, it is necessary to eliminate the CO_2 released into the atmosphere [3]. In this regard, carbon capture utilization and storage (CCUS) showed great potential application for both industrial and atmospheric CO_2 reduction and was considered an indispensable technology for carbon neutrality [4].

Different from the traditional CO_2 capture techniques, direct air capture (DAC) is a typical "negative emission" technology that could remove CO_2 directly from the air and is currently under widespread consideration as an option for realizing negative carbon emission (**Figure 1)** [5]. The DAC technology has various advantages, such as flexibility in location and convenience for CO_2 transfer. Due the low concentration of CO_2 in air, the cost of DAC is very high, so this technology has high requirements for the adsorption performance of CO_2 capture materials [6].

Reports on various DAC adsorption materials have increased rapidly in the past two decades. A comprehensive understanding of the recent development of DAC adsorbents, including the emerging MMO-based amine-functionalized DAC adsorbent,

needs a fresh assessment. In this work, we critically reviewed the CO_2 capture capacity, regenerability, and mechanism of all DAC materials. Such efforts are expected to significantly assist the development of DAC from fundamental research to large-scale applications.
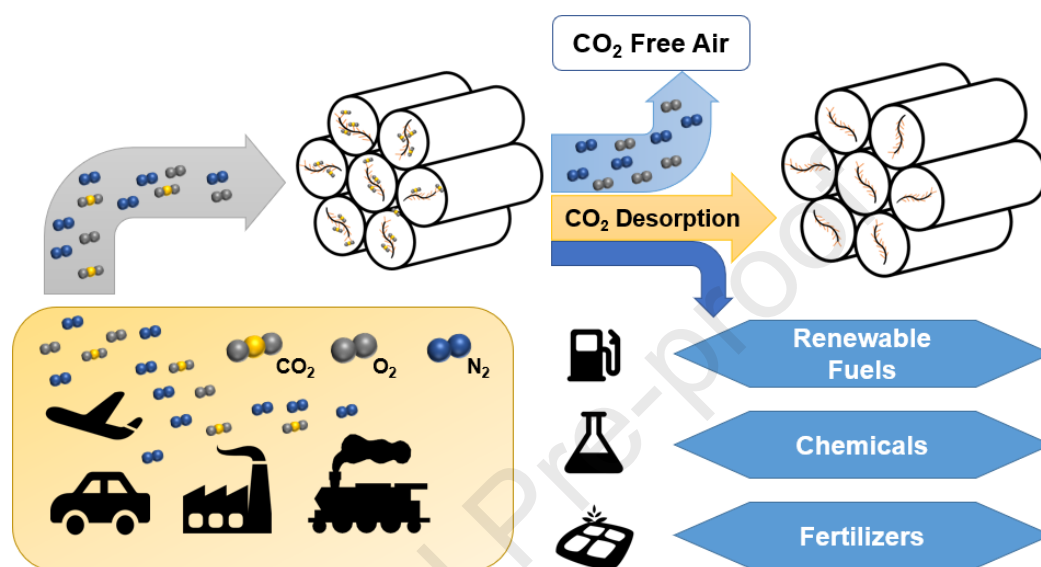
Figure 1. Scheme of DAC and subsequent utilization chain [7].

Adsorbent for CO_2 capture from air

In 1999, Lackner et al. [8] first put forward the concept of DAC. In the following two decades, DAC has been demonstrated as a promising technology for climate change mitigation, and a lot of research work has been carried out from the perspective of CO_2 capture from ambient air. To make a clear clarification of materials relevant to DAC, we have tried to categorize all adsorbents into two classes based on the adsorption mechanism, which included (1) physical adsorption materials and (2) chemical adsorption materials.

Physical adsorption materials

Physical adsorption materials have a great variety of adsorbents with stable

structures and ease of preparation but usually exhibit poor adsorption properties, including carbon-based materials, zeolites, and metal-organic frameworks (MOF).

Carbon-based materials are desirable adsorbents for CO_2 extraction caused of their ultrahigh specific surface area and inexpensive cost. It is believed that the excellent carbon-based CO_2 adsorption capacity can be obtained by tuning the textural properties by activating agents. Sevilla et al. [9] synthesized a porous carbon adsorbent and exhibited a high CO_2 capture capacity of 4.8 mmol g^{-1} in a pure CO_2 stream. The abundant micropores generated during chemical activation using KOH play an essential role in achieving high CO_2 uptake.

Nonetheless, carbon materials always exhibit a small capacity at low CO_2 partial pressure. For instance, the carbon monolith prepared by Lee et al. [10] showed a low CO_2 uptake of 0.00137 mmol g^{-1} in 3000 ppm of CO_2 at 30 °C. Furthermore, poor selectivity over N_2 and moisture significantly hinders their performance of CO_2 capture from air [11].

Zeolites could interact with CO_2 depending on the alkali cation on the surface and possess better performance at low CO_2 partial pressure compared to carbon-based adsorbents [12]. However, shortcomings of low CO_2 selectivity are the most challenging obstacle for zeolites to overcome [13]. A series of modification methodologies that are beneficial for improving the CO_2 selectivity of zeolites have been reported. For instance, Chen et al. [14] modified 13X zeolite with extra framework cation and obtained polymetallic cation-exchanged LiPdAgX zeolite that exhibited higher CO_2 selectivity than 13X and LiX-80 zeolites.

MOF is a new kind of nanocrystalline porous material that is composed of transition metal nodes that are connected by bridging organic ligands, exhibiting promising potential for CO_2 capture due to its high flexibility in chemical composition,

5

pore structure, and surface properties, which differs from zeolites and carbon-based materials [15]. Many studies about various types of MOF-based adsorbents have been developed for CO_2 removal at room temperature since MOF-177 with ultrahigh specific surface areas was reported by Millward et al. [16], demonstrating excellent CO_2 adsorption capacity at room temperature in 2005.

In addition to the specific surface area and pore structure, the adsorption capacity of CO_2 is also greatly associated with the content of unsaturated metal sites, NH_2 groups, and other adsorption sites that can strongly immobilize CO_2. For instance, Britt et al. [17] prepared Mg-MOF-74 with rich unsaturated Mg sites on the surface and yielded a high CO_2 uptake of 8.3 mmol g^{-1} at 25 °C and 1 bar, and 87% of the initial adsorption capacity can be maintained in temperature swing regeneration process.

However, the presence of water vapor in air can significantly reduce the adsorption capacity of MOF by competing for adsorption sites with CO_2. Kumar et al. [18] synthesized HKUST-1 and Mg-MOF-74 materials and found that both adsorbents showed a decrease in CO_2 adsorption capacity after exposure to a humid environment for 1, 7, and 14 days, with 23.9%, 26.9% and 33.6% uptake loss for HKUST-1, and 23%, 41% and 60.4% uptake loss for Mg-MOF74, respectively.

The main drawback of physical adsorption materials rests in their small uptake and slow CO_2 sorption kinetics from ambient air. Furthermore, most physical adsorbents will be subject to a significant selectivity decrease when temperature increases or in the presence of H_2O, which must be improved in future [19].

Chemisorption Materials

Alkali carbonate-based adsorbents

Alkali metal and alkaline earth metal oxides and hydroxides, such as CaO, NaOH,

and $Ca(OH)_2$, have a strong affinity for CO_2 and can be used to realize the cyclic adsorption-desorption of CO_2 through a reversible chemical reaction of carbonation reaction [20]. The CO_2 capture of CaO and $Ca(OH)_2$ at 200-450 °C was investigated by Nikulshina et al. [21]. His group reported that the carbonation reaction on $Ca(OH)_2$ was less hindered compared to CaO. On this basis, the direct capture of CO_2 from ambient air using $Ca(OH)_2$ was systematically investigated by Samari et al. [22]. The effects of pre-hydration of adsorbents and humidity in the inlet air on the observed breakthrough curve and global reaction rate over adsorption/desorption cycles was examined. Their results showed that the best adsorption performance was obtained when the $Ca(OH)_2$ was pre-hydrated for 3 h and the inlet air was humidified to 55% relative humidity, providing a facile strategy for further deployment of the DAC system.

However, one of the most significant factors limiting the application of such materials on a large scale is the expensive capture cost due to the high regeneration temperature. For example, $CaCO_3$, the product of the CaO carbonation reaction, requires a high temperature of 800-875 °C for a complete decomposition, which allows the CO_2 desorption and the regeneration of adsorbent [23]. Even if it is possible to be combined solar energy technologies to provide the required energy consumption for the adsorption process in future, the expensive cost and complex capture devices will pose a great challenge to the large-scale application of this technology [24].

To reduce energy consumption in the regeneration process, Nikulshina et al. [25] reported a Na-based adsorbent for DAC. Although the energy consumption of Na-based adsorbent materials was decreased compared to Ca-based materials, it was still relatively high. The complete thermal decomposition of Na_2CO_3 to Na_2O and CO_2 requires high temperatures of 1000-1400 °C, which hindered the further promotion and application of Na-based adsorbent materials. Recently, Veselovskaya et al. [26]

performed the direct CO_2 capture from ambient air using a K_2CO_3/Al_2O_3 composite adsorbent followed by CO_2 methanation in the presence of 4% Ru/Al_2O_3 catalyst, and the CO_2 uptake capacity of the composite adsorbent was 22 ± 2 mL CO_2 g^{-1}, showed great potential in the application for DAC. In particular, the regeneration of the composite adsorbent could occur at 325 °C, which decreases energy-demanding compared to Na-based and Ca-based adsorbents.

Solid amine-based adsorbents

Amine-modified solid materials have shown great potential in DAC applications due to their high CO_2 adsorption capacity, fast kinetics, and low energy consumption [1]. These adsorbents can be classified into three categories according to the preparation methods as shown in **Figure 2**, which are named: class 1 adsorbents (physically impregnated amine-modified materials), class 2 adsorbents (chemically grafted amine-modified materials), and class 3 adsorbents (in-situ polymerized amine-modified materials). The amine type chosen is an important factor influencing the adsorption performance. For example, linear PEI, which mainly consists of secondary amines, has high oxidative resistance but low CO_2 uptake, while small amines like TEPA exhibited excellent capture performance but poor cyclic stability. The molecular structures of the most well studied amines are presented in **Figure 3**. Among the amines mentioned above, PEI has received the most attention cause of its high amine density and good thermal stability [27].
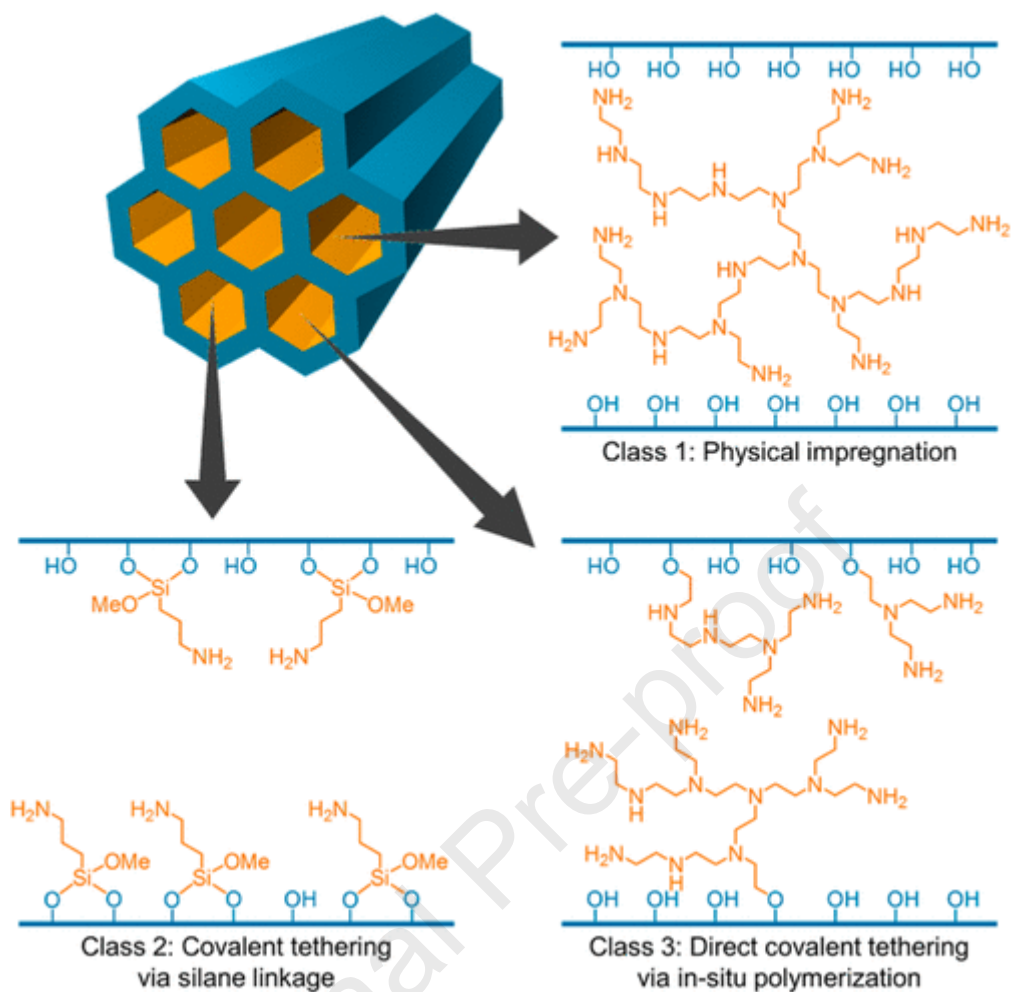
Figure 2. Three categories of solid amine-based adsorbents. Class 1 adsorbent: physically impregnated amine-modified materials. Class 2 adsorbent: chemically grafted amine-modified materials. Class 3 adsorbent: in-situ polymerized amine-modified materials [27].
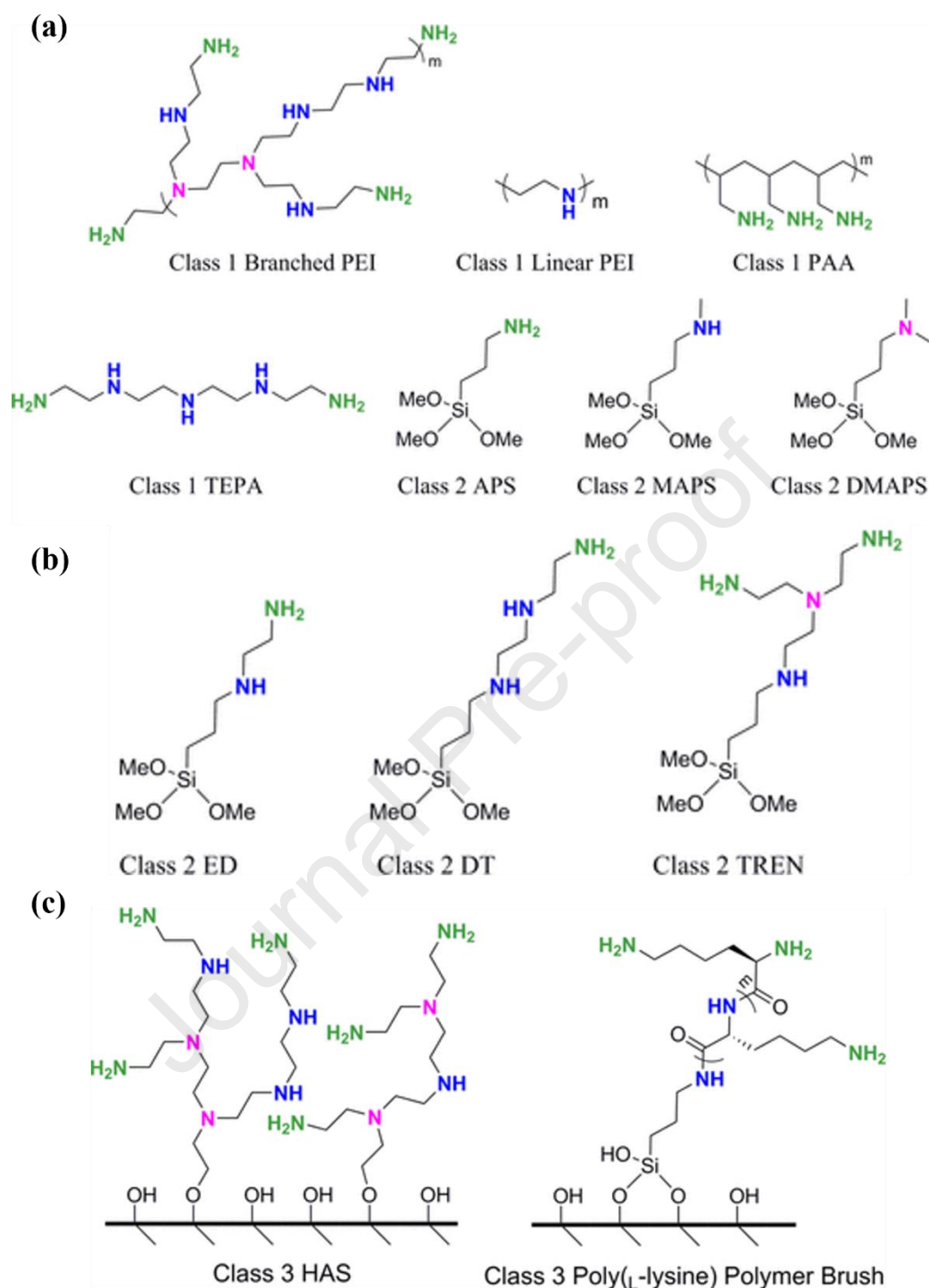
Figure 3. Structures of well-studied solid amines for DAC adsorbents: (a) class 1, (b) class 2, (3) class 3 [20].

Traditional amine-silica materials

Silica-based mesoporous materials such as SBA-15, MCM-41, SBA-16, KIT-6, etc., are usually formed by using organic molecules as templating agents. The assemblies are obtained from self-assembly of supramolecular or the synergy between

inorganic silicon source and template thin surface. Then the organic substances are removed by calcination or extraction to retain the inorganic skeleton and form mesoporous structures [28]. Researchers believe that surface chemical modification (functionalization with amine groups) of these mesoporous materials makes the modified adsorbent a promising carbon capture adsorbent due to the acid-base interaction between CO_2 and the modified basic sites, which greatly increases the adsorption capacity and selectivity for CO_2 [29].

Song's group [30] reported the study of CO_2 capture by amine-impregnated silica materials for the first time in 2002. This is a material obtained by loading polyethyleneimine (PEI) on MCM-41 zeolite. Since then, a variety of amine-based solid adsorbents have been synthesized via modifying porous supports with different amines, including PEI, pentaethylenehexamine (PEHA), and tetraethylenepentamine (TEPA) et al. Among them, low molecular weight PEI is commonly used for the preparation of class 1 adsorbents. For example, Choi et al. [31] conducted a study on the use of PEI-impregnated amine adsorbent for DAC. By loading 45.1% PEI on SiO_2, a CO_2 adsorption capacity of 2.36 mmol g^{-1} was obtained at 25 °C in a CO_2 concentration of 400 ppm. However, the cyclic stability of the material was poor, and the adsorption capacity decreased to 1.65 mmol g^{-1} after four cycles.

Since the class 1 adsorbents are prepared by impregnation method, the amine groups are only physically adsorbed instead of being chemically bonded on the surface of supports. Moreover, the relatively high regeneration temperature (>100 °C) resulted in a series of chemical stability issues containing urea species formation under the CO_2-rich regeneration environment and the oxidative degradation of amines under O_2-containing air [32]. Therefore, some strategies were proposed to retard the chemical deactivation by modifying the class 1 adsorbents. For example, Choi et al. [33] reported

that the 1,2-epoxybutane (EB) -functionalization can improve the oxidative stability and anti-urea properties of PEI, while it also resulted in an appreciable drop of CO_2 uptake, which limits the DAC application.

For this reason, researchers proposed the preparation of composites by chemical grafting, hoping to obtain amine-modified adsorbents with more stable structures. Belmabkhout et al. [34] first proposed the preparation of triamine-grafted mesoporous silica (TRIPE-MCM-41), which exhibited better CO_2 adsorption capacity and higher CO_2 selectivity than physical adsorbents under both dry and humid air conditions. Nevertheless, the limited number of silicon hydroxyl groups on the surface of the class 2 adsorbents reduces the amount of grafted amino groups, and the CO_2 adsorption capacity is lower than that of class 1 adsorbents [35].

To overcome the shortcomings of the class 1 adsorbents and the class 2 adsorbents mentioned above, Choi et al. [36] synthesized hyperbranched aminosilica (HAS) materials by integrating polymeric amines into typical porous matrices through covalent bonding, which were known as class 3 amine adsorbents. Thanks to the higher number of amino groups, the CO_2 adsorption capacity of class 3 adsorbents is higher than that of class 2 amine adsorbents, and the materials exhibit good stability in the adsorption-desorption cycling tests because the amino groups rely on covalent bonding to the supports. The advantages of class 3 adsorbents are easy to manufacture, potentially cost-effective, and cyclic stability. The main challenges currently limiting the large-scale application of class 3 adsorbents are the excessive energy consumption and the cost of the regeneration process [29].

Amine-MOF composites

Modification with amines is one of the most common strategies to improve the CO_2 adsorption capacity of MOF, which could enhance the affinity between the

adsorption site with CO_2 molecules [37]. Several works impregnated different types of amines onto such MOFs as Mg-MOF-74, HKUST-1, UiO-66357, and ZIF-8. As expected, the resulting amine-modified composites exhibit excellent CO_2 capture performance even at low pressure. Darunte et al. [38] chose the branched PEI, which has a low molecular weight to modify MIL-101(Cr) and demonstrated that the optimal MIL-101(Cr)-PEI material has relatively good stability under laboratory-scale temperature fluctuation adsorption conditions and in the presence of water vapor.

However, a disadvantage of amine-MOF composites is that their relatively narrow pore size hinders the diffusion of amines into their pores and the mass transfer of CO_2 within the pore channels. To overcome this shortcoming, some researchers tried to expand the ligands to obtain MOFs with wider channels [39]. In future, more in-depth studies should be carried out on the stability of functional group modification, the selection of metal groups, and the improvement of CO_2 adsorption kinetics.

Amine-mixed metal oxide composites

Conventional amine-impregnated/grafted mesoporous silica-based DAC materials generally suffer from slow adsorption kinetics and poor thermal stability due to the poor bonding between the amine group and the silica-based carrier [40]. The qualitative properties and surface microstructure of the supports can influence the amine morphology and the gas-solid interactions [41]. To solve the above-mentioned drawbacks, it is crucial to investigate and develop supporting materials with proper morphology, high hydrothermal resistance, and strong binding to amino groups [42].

LDHs are compounds assembled from positively charged main laminates and interlayer anions through non-covalent bonding interactions and are widely used in catalytic and environmental applications due to the chemical composition of the main laminates, the type and number of interlayer anions, and the tunability of the particle

size and distribution of the intercalated assemblies [43]. During the synthesis and subsequent calcination, the LDH-derived mixed metal oxide (MMO) nanosheets formed spherical particles by self-assembly with abundant surface defects, which can retard the leakage of amine molecules during the regeneration process by stronger attraction [42].

A new class of amine-functionalized DAC adsorbents impregnated with branched PEI onto composite MMO nanosheets with excellent CO_2 adsorption properties was first reported by Zhu et al. [42]. Compared with mesoporous silica-based materials, PEI/MMO exhibits superior CO_2 adsorption (2.27 mmol g^{-1}) and CO_2 adsorption kinetics (1.1 mmol g^{-1} h^{-1}) and possesses good thermal and hydrothermal stability with little performance degradation after 20 adsorption/regeneration cycles. On this base, Zhao et al. [1] synthesized TEPA modified MMOs as a novel amine-functionalized DAC adsorbent, and the optimized $Mg_{0.55}Al-O-TEPA67\%$ achieved a saturation adsorption capacity of 3.00 mmol g^{-1} at 25 °C. The CO_2 adsorption decreased by only 9.2% after 80 cycles, suggesting its superior cyclic stability. The amine group adsorption energy for MMO and conventional SiO_2 was obtained by DFT calculation. The result showed that the MMO possesses a much larger binding energy with the amino group of -1.73 eV than SiO_2 (-0.30 eV). It also confirmed that the unique charge transfer interaction between the oxygen defects on the MMO and the amino group results in the strong binding force, which significantly inhibits amine leakage during cyclic regeneration of the material and substantially improves the stability of the material during CO_2 adsorption/desorption cycles. The CO_2 adsorption capacity and stabilization mechanism for MMOs supported solid amine have been summarized in **Figure 4**. It is worth mentioning that the synthesis process of MMO is simple and inexpensive, making it a suitable support for amine modified composites. As the

observed oxidative degradation of most amine-functionalized adsorbents under realistic O_2-containing conditions could be correlated with regeneration temperature and amine ratio, much effort should be made to overcome this drawback for future industrial applications.
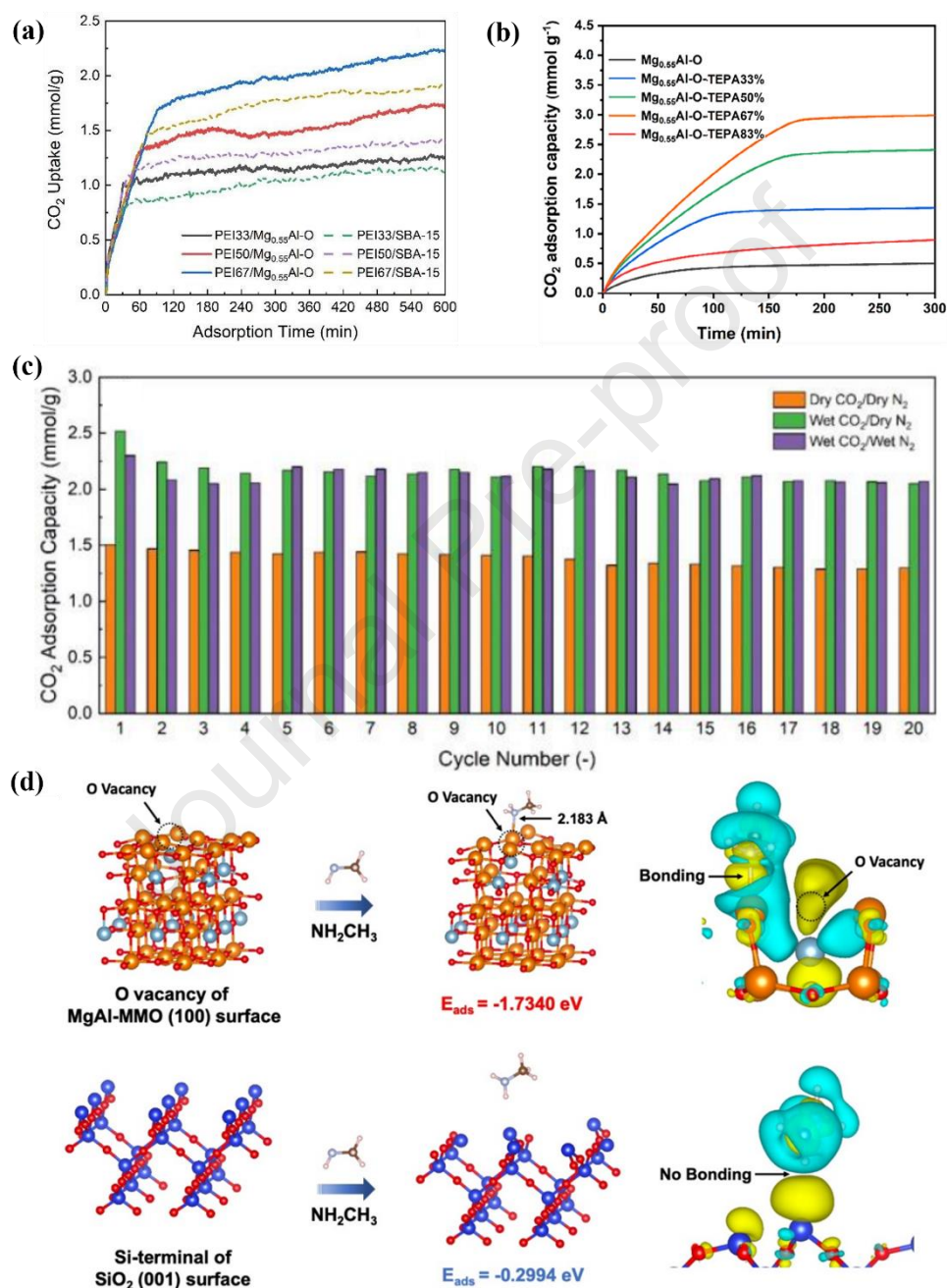
Figure 4. CO_2 adsorption performance and stabilization mechanism of Amine/poly(ethylenimine)-MMO composites used for DAC: CO_2 uptakes of (a) PEI/Mg$_{0.55}$Al-O composites [42] and (b) TEPA/Mg$_{0.55}$Al-O composites [1], (c) cyclic stability of PEI67/Mg$_{0.55}$Al-O [42], (d) The adsorption

energy of amine subunit (CH_3NH_2) over oxygen vacancy of Mg-Al MMO surface and SiO_2 surface [1].

Conclusions

DAC has been regarded as a promising approach to reducing carbon emissions and has been widely studied for the past two decades. In this mini-review, recent research advances in solid adsorbents for CO_2 capture from ambient air have been systematically summarized. So far, most of the adsorbents are far from ultimate industrial application owing to their high energy demands and stability drawbacks.

The poor uptake and low selectivity at low CO_2 partial pressure have always been the shortcomings for physical adsorbents. All of them need to be functionalized to chemisorb CO_2 due to their abundant porosity. Given the relatively high regeneration temperature, the resulting large energy consumption for the alkali solid capture techniques greatly hinders the DAC deployment. But, the operation cost of the capture system based on solid alkali carbonates adsorbents can be effectively decreased by loading alkali metal carbonates onto porous supports. The most popular solid-supported amine adsorbents synthesized through loading polyamines or amine onto SiO_2-support are currently suffering from irreversible decreases in CO_2 capture capacity during cycling. The thermal stability and chemical stability of the adsorbent under dry and humid CO_2 streams should be improved, which are essential for the long-term deployment of the capture system. Furthermore, a consistent benchmark or standard is required to better assess a novel adsorbent. Remarkably, MMO-based adsorbents and MOF-based adsorbents present higher CO_2 uptake and excellent regenerability, which

substantially addresses the extraordinary stability issues of solid amine materials.

In summary, the development of DAC materials is still in its infancy, and there is still much room for improvement. Further research about the design of a cost-effective DAC system and steam-assisted temperature swing process on these bases is needed to ultimately realize the deployment of such adsorbents.

References

1. ** Zhao M, J Xiao, W Gao, Q Wang: **Defect-rich Mg-Al MMOs supported TEPA with enhanced charge transfer for highly efficient and stable direct air capture**. *J Energy Chem* 2022, **68**:401-410.
(This study by Zhao et al. describes the preparation, characterization, and evaluation of TEPA/MMOs for DAC. This work first conducted a comprehensive investigation of the promotion mechanism of charge transfer between oxygen defects of MMO and amine groups.)

2. Gao W, T Zhou, Y Gao, B Louis, D O'Hare, Q Wang: **Molten salts-modified MgO-based adsorbents for intermediate-temperature CO_2 capture: A review**. *J Energy Chem* 2017, **26**:830-838.

3. Rajamani L, J Werksman: **The legal character and operational relevance of the Paris Agreement's temperature goal**. *Philos Trans A Math Phys Eng Sci* 2018, **376**.

4. Jiang K, P Ashworth, S Zhang, X Liang, Y Sun, D Angus: **China's carbon capture, utilization and storage (CCUS) policy: A critical review**. *Renewable Sustainable Energy Rev* 2020, **119**.

5. Custelcean R: **Direct air capture of CO_2 via crystal engineering**. *Chem Sci* 2021, **12**:12518-12528.

6. Deutz S, A Bardow: **Life-cycle assessment of an industrial direct air capture process based on temperature–vacuum swing adsorption**. *Nat Energy* 2021, **6**:203-213.

7. Cherevotan A, J Raj, S C Peter: **An overview of porous silica immobilized amines for direct air CO_2 capture**. *J Mater Chem A* 2021, **9**:27271-27303.

8. Lackner K, Ziock H J, G P.: **Carbon dioxide extraction From air: Is it an option?** *Los Alamos* 1999.

9. Sevilla M, A Fuertes: **Sustainable porous carbons with a superior performance for CO_2 capture**. *Energy Environ Sci* 2011, **4**:1765-1771.

10. Lee T S, J H Cho, S H Chi: **Carbon dioxide removal using carbon monolith as electric swing adsorption to improve indoor air quality**. *Build Sci* 2015, **92**:209-221.

11. Shen C, C A Grande, P Li, J Yu, A E Rodrigues: **Adsorption equilibria and kinetics of CO_2 and N_2 on activated carbon beads**. *Chem Eng J* 2010, **160**:398-407.

12. Divekar S, S Dasgupta, A Arya, P Gupta, S Singh, A Nanoti: **Improved CO_2 recovery from flue gas by layered bed Vacuum Swing Adsorption (VSA)**. *Sep Purif Technol* 2020, **234**.

13. Santori G, C Charalambous, M-C Ferrari, S Brandani: **Adsorption artificial tree for atmospheric carbon dioxide capture, purification and compression**. *Energy* 2018, **162**:1158-1168.

14. Chen S, M Zhu, Y Tang, Y Fu, W Li, B Xiao: **Molecular simulation and experimental investigation of CO_2 capture in a polymetallic cation-exchanged 13X zeolite**. *J Mater Chem A* 2018, **6**:19570-19583.

15. Gaikwad S, Y Kim, R Gaikwad, S Han: **Enhanced CO_2 capture capacity of amine-functionalized MOF-177 metal organic framework**. *J Environ Chem Eng* 2021, **9**.

16. Millward A, O Yaghi: **Metal-Organic Frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature**. *J Am Chem Soc* 2005, **127**:17998-17999.

17. Britt D, H Furukawa, B Wang, T Glover, O Yaghi: **Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites**. *Proc Natl Acad Sci U S A* 2009, **106**:20637-20640.

18. Kumar A, D G Madden, M Lusi, K J Chen, E A Daniels, T Curtin, J J t Perry, M J Zaworotko: **Direct air capture of CO_2 by physisorbent materials**. *Angew Chem Int Ed Engl* 2015, **54**:14372-14377.

19. Oschatz M, M Antonietti: **A search for selectivity to enable CO_2 capture with porous adsorbents**. *Energy Environ Sci* 2018, **11**:57-70.

20. ** Sanz-Perez E S, C R Murdock, S A Didas, C W Jones: **Direct capture of CO_2 from ambient air**. *Chem Rev* 2016, **116**:11840-11876.

(This work first conducted a historical overview of the field of DAC, along with an exhaustive description of the use of chemical adsorbents targeted at this application provided the fundamental basis for theoretical mechanism support of DAC adsorbents.)

21. Nikulshina V, M E Gálvez, A Steinfeld: **Kinetic analysis of the carbonation reactions for the capture of CO_2 from air via the $Ca(OH)_2$–$CaCO_3$–CaO solar thermochemical cycle**. *Chem Eng J* 2007, **129**:75-83.

22. M. Samari, F. Ridha, V. Manovic, A. Macchi, E.J. Anthony: **Direct capture of carbon dioxide from air via lime-based sorbents**. *Mitig. Adapt. Strateg. Glob. Change* 2020, **25**:25–41.

23. Nikulshina V, C Gebald, A Steinfeld: **CO_2 capture from atmospheric air via consecutive CaO-carbonation and $CaCO_3$-calcination cycles in a fluidized-bed solar reactor**. *Chem Eng J* 2009, **146**:244-248.

24. Liu R-S, S Xu, G-P Hao, A-H Lu: **Recent Advances of Porous Solids for Ultradilute CO_2 Capture**. *Chem Res Chin Univ* 2021, **38**:18-30.

25. Nikulshina V, N Ayesa, M E Gálvez, A Steinfeld: **Feasibility of Na-based thermochemical cycles for the capture of CO_2 from air—Thermodynamic and thermogravimetric analyses**. *Chem Eng J* 2008, **140**:62-70.

26. Veselovskaya J V, P D Parunin, O V Netskina, L S Kibis, A I Lysikov, A G Okunev: **Catalytic methanation of carbon dioxide captured from ambient air**. *Energy* 2018, **159**:766-773.

27. Didas S A, S Choi, W Chaikittisilp, C W Jones: **Amine-oxide hybrid materials for CO_2 capture from ambient air**. *Acc Chem Res* 2015, **48**:2680-2687.

28. Ahn C-I, Y Kwak, A-R Kim, M Jang, A Badakhsh, J Cha, Y Kim, Y S Jo, H Jeong, S H Choi, S W Nam, C W Yoon, H Sohn: **Dehydrogenation of homocyclic liquid organic hydrogen carriers (LOHCs) over Pt supported on an ordered pore structure of 3-D cubic mesoporous KIT-6 silica**. *Appl Catal B* 2022, **307**.

29. Shi X, H Xiao, H Azarabadi, J Song, X Wu, X Chen, K S Lackner: **Sorbents for the direct capture of CO_2 from ambient air**. *Angew Chem Int Ed* 2020, **59**:6984-7006.

30. Xu X, Song C, e a Andresen J M: **Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO_2 capture**. *Energy Fuels* 2002, **16**:1463-1469.

31. Choi S, M L Gray, C W Jones: **Amine-tethered solid adsorbents coupling high adsorption capacity and regenerability for CO₂ capture from ambient air**. *ChemSusChem* 2011, **4**:628-635.

32. ** Jahandar Lashaki M, S Khiavi, A Sayari: **Stability of amine-functionalized CO₂ adsorbents: a multifaceted puzzle**. *Chem Soc Rev* 2019, **48**:3320-3405.

(This review focuses on important stability issues facing amine-functionalized CO₂ adsorbents, including amine-grafted and amine-impregnated silicas, zeolites, metal-organic frameworks, and carbons, which could pave the way to implementing the next research on amine-functionalized CO₂ adsorbents.)

33. W. Choi, K. Min, C. Kim, Y. S. Ko, J. W. Jeon, H. Seo, Y.-K. Park and M. Choi: **Epoxide-functionalization of polyethyleneimine for synthesis of stable carbon dioxide adsorbent in temperature swing adsorption**. Nat. Commun 2016, **7**: 12640.

34. Belmabkhout Y, R Serna-Guerrero, A Sayari: **Amine-bearing mesoporous silica for CO₂ removal from dry and humid air**. *Chem Eng Sci* 2010, **65**:3695-3698.

35. Sanz-Pérez E S, A Fernández, A Arencibia, G Calleja, R Sanz: **Hybrid amine-silica materials: Determination of N content by 29Si NMR and application to direct CO₂ capture from air**. *Chem Eng J* 2019, **373**:1286-1294.

36. Choi S, J H Drese, P M Eisenberger, C W Jones: **Application of amine-tethered solid sorbents for direct CO₂ capture from the ambient air**. *Environ Sci Technol* 2011, **45**:2420-2427.

37. Piscopo C G, S Loebbecke: **Strategies to enhance carbon dioxide capture in Metal-Organic Frameworks**. *Chempluschem* 2020, **85**:538-547.

38. Darunte L A, A D Oetomo, K S Walton, D S Sholl, C W Jones: **Direct air capture of CO₂ using amine functionalized MIL-101(Cr)**. *ACS Sustainable Chem Eng* 2016, **4**:5761-5768.

39. Szczesniak B, J Choma, M Jaroniec: **Gas adsorption properties of hybrid graphene-MOF materials**. *J Colloid Interface Sci* 2018, **514**:801-813.

40. Chen C, J Kim, W-S Ahn: **CO₂ capture by amine-functionalized nanoporous materials: A review**. *Korean J Chem Eng* 2014, **31**:1919-1934.

41. Keshavarz L, M R Ghaani, J M D MacElroy, N J English: **A comprehensive review on the application of aerogels in CO₂-adsorption: Materials and characterisation**. *Chem Eng J* 2021, **412**.

42. ** Zhu X, T Ge, F Yang, M Lyu, C Chen, D O'Hare, R Wang: **Efficient CO₂ capture from ambient air with amine-functionalized Mg-Al mixed metal oxides**. *J Mater Chem A* 2020, **8**:16421-16428.

(A new family of PEI-functionalized Mg-Al MMO class 1 adsorbents was proposed in this work. the 67 wt.% PEI impregnated $Mg_{0.55}$Al-O MMO reaches the total CO₂ adsorption capacity of 2.27 mmol g^{-1} and the fast adsorption rate of 1.1 mmol g^{-1} h^{-1} within 90 min at 25 °C under 0.4 mbar CO₂.)

43. ** Wang Q, D O'Hare: **Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets**. *Chem Rev* 2012, **112**:4124-4155.

(This work summarized the current methods that have been developed for the synthesis of dispersed LDH nanosheets and reviewed the current literature in the areas of polymer/LDH nanocomposites, core−shell LDH materials, LDH thin films, nano

dispersed LDH catalysts, LDH electrode materials, LDH hybrid magnets, and bioinorganic hybrid materials, thus providing facile strategy and comprehensive theoretical mechanism support for future research about LDH materials.)

Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: