Recent Advances in Post-Combustion CO2 Capture via Adsorption Methods

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Abstract. In order to alleviate the environmental problems associated with increasing CO2 emissions, efficient CO2 capture technologies are urgently needed. Nowadays, there are several main kinds of capture methods, such as absorption, membrane, cryogenic and adsorption etc. The principle, advantages and disadvantages of each method have been summarized. Due to its high adsorption rate, low regeneration energy, good selectivity, high stability and gentle operation condition, adsorption has been regarded as the most promising method for industrial application. Additionally, the core of adsorption is to develop good adsorption materials with low-cost and high-efficiency, and some typical materials, including carbonaceous adsorbents, silica gel, zeolite molecular sieve, and metal-organic frameworks (MOFs), have also been introduced. As a new type of material, MOFs are popular with many researchers depending on functionalizing pore surface, permanent and highly adjustable porosity. As more and more potential mechanisms and raw materials have been discovered, MOFs may speed up the process of application of adsorption methods in the industry.

Keywords: CO2 capture, adsorption, MOFs.

1. Introduction

Since the mid to late twentieth century, CO2 levels in the atmosphere have continued to rise worldwide, and the relevant data from 2017 to 2022 and from 1980 to 2022 have been shown in Fig. 1 (a) and (b). The resulting environmental problems, such as global warming, melting glaciers and rising sea levels, have become increasingly serious, causing serious damage to global resources and the sustainable development of the world economy. In fact, CO2 plays an important role in the preservation of agricultural products, supercritical CO2 oil flooding technology, CO2 extraction technology and other fields. Within the last twenty years, especially under the background of carbon peaking and carbon neutrality goals, carbon capture, utilization and storage (CCUS) has made great progress, and many scholars have taken CO2 as a carbon resource for further research.

In the development of CO2-related technologies, carbon capture is the premise and foundation of capture utilization and storage. Generally, there are three main carbon capture processes, namely oxy-combustion CO2 capture, pre-combustion CO2 capture and post-combustion CO2 capture. Among them, pre-combustion CO2 capture has a lower cost, while low efficiency and high-temperature requirements have been the limitations of its industrial application [1]. Oxy-combustion CO2 capture requires specific materials of pure oxygen combustion equipment and air separation systems, which will significantly increase the investment in carbon capture. At present, large-scale pure oxygen combustion technology is still in the research stage. As for post-combustion CO2, it is a mature technology with a wide range of applications, simple system principles and good inheritance to existing power plants. Due to these advantages, this method has been seen as the most promising industrialized technology. This paper will briefly discuss four ways of post-combustion CO2 capture, absorption, membrane separation, cryogenic separation and adsorption, respectively. Depending on a series of merits and more and more newly developed materials, adsorption has become a favorable method for many researchers, and the distribution of typical articles published in four fields during the past decade has been shown in Fig. 2, and Fig. 3 introduces several common adsorption materials. Additionally, metal-organic frameworks (MOFs), as a kind of adsorption material, bringing a new mechanism and perspective for CO2 adsorption separation, maybe provide those power plants with a viable option.
Figure 1. (a) Recent global monthly mean CO₂(2017-2022), (b) Global monthly mean CO₂(1980-2022) [2]

Figure 2. Number of publications related to CO₂ capture methods in the last decade(2012-2022)

Figure 3. Several common porous adsorption materials

2. Post-combustion adsorption methods in CO₂ capture

2.1. Absorption method

Absorption is a method that takes advantage of the difference in solubility of CO₂ in solution from that of other components in gas mixture to separate CO₂ as shown in Fig. 4. When the absorbent reaches saturation, the separation of absorbents from CO₂ is achieved by heating, which provides energy to decompose physical or chemical bonds. Due to low input costs, good separation effects,
stable operation and relatively mature technology, this method has been extensively used in the chemical and food industries.

![Diagram of absorption-stripping process](image)

**Figure 4.** Simplified technological process of absorption-stripping in CO$_2$ capture [3]

2.1.1. Physical absorption method.

The physical absorption method refers to the process that which CO$_2$ dissolves in the absorption solution, but does not react with the absorption solution. The principle is to use the characteristic of larger solubility of CO$_2$ in absorption solution while other gas components have smaller solubility to achieve separation effect. Since the solubility of solutes varies with pressure and temperature, solutes can be absorbed in solution via low temperature or high pressure and be separated via the inverse process. At present, the developed technologies include the low-temperature methanol method and propylene carbonate method [4].

2.1.2. Chemical absorption method.

The operation of chemical absorption takes advantage of the reversible chemical reaction between alkaline absorbent and CO$_2$ in the mixture to generate unstable salts, such as carbonate, bicarbonate, and carbamate. Then these types of salt will decompose under extreme conditions such as high temperature and release CO$_2$ to achieve capture and separation of CO$_2$. Popular adsorbents include ammonia absorbent, ammonium salt absorbent, potassium carbonate absorbent, etc. Now the mixed amine absorbent, phase change absorbent, ionic liquid absorbent, nanofluid absorbent and other new absorbents are also getting more and more attention from researchers [5].

2.2. Membrane separation method

Membrane made of polymer materials has different permeability to different kinds of gases, which is the principle of the membrane absorption method. The driving force of this method is the pressure difference between two sides of the membrane. The gas components with higher permeability have priority through the membrane to the outlet side, while gases with lower permeability stay at the inlet side of the membrane. Subsequently, the two groups of gases will be divided into the respective side of the membrane to get the target gas separated. Typical membrane materials are cellulose acetate butyrate, cellulose acetate, polyamide, polyimide, polysulfone, polyethersulfone, polyethylene oxide, etc [6].
2.3. Cryogenic method

Due to their different condensing temperatures, the diverse gases can be separated at a specific temperature in a gradual cooling system. According to the different refrigeration systems providing cooling capacity, the low-temperature separation method can be divided into the direct expansion refrigeration method, the external cold source refrigeration method and the mixed refrigeration method [7]. These methods need large equipment and high energy consumption, so they are generally rarely used. Oil field mining site mainly uses this way to separate and recover CO$_2$ from Semi-gas in the Oilfield and enhance the oil recovery rate [8].

2.4. Adsorption method

Some porous materials have a strong binding ability to a certain component of mixed gas under certain conditions, allowing them to absorb the gas components on a solid surface while the rest remain in the air phase. Adsorption achieves gas separation by this principle, and the simple adsorption process is shown in Fig. 5. There are physical adsorption and chemical adsorption on the basis of different adsorption. The former is dominated by van der Waals intermolecular interaction force, whereas the latter is dominated by a chemical bond due to the binding force. Generally, physical adsorption can be multilayer adsorption with low selectivity; chemical adsorption is only monolayer adsorption with higher selectivity [4]. According to different operations, adsorption can be divided into thermal swing adsorption (TSA), pressure swing adsorption (PSA), vacuum swing adsorption (VSA) and electric swing adsorption (ESA). This article briefly introduces the first two ways.

![Figure 5. Brief schematic diagram of CO$_2$ separation by adsorption [9]](image)

The process of TSA is that adsorption materials absorb gases at low temperatures and desorbs gases at high temperatures. Due to the low thermal conductivity of common adsorbents, heating and cooling time is relatively long, often taking several hours. So its equipment is usually large, and it needs corresponding heating and cooling equipment, of which energy consumption and investment are relatively high. Therefore, TSA is not so widely used as PSA and is only suitable for occasions where the impurity component in mixture gas is low, and the requirement for recovery rate is very high.

PSA utilizes the character varying with pressure to get CO$_2$ captured and separated, which adsorbs CO$_2$ at high pressure and desorbs CO$_2$ at low pressure. PSA has three mechanisms: the steric hindrance effect, kinetic effect, and equilibrium effect. The steric hindrance effect is mainly applicable to the screening effect of zeolite molecular sieves. For kinetic effect, the required condition is that the pore size of the adsorbent is located between the two gases waiting to separate. As for the equilibrium effect, the principle of the design and selection of adsorbents is based on the basic physical properties of adsorbed components, such as polarization, magnetization coefficient, magnetism, quadrupole moment and permanent dipole moment [4]. In comparison, because the PSA productions have high purity, a high degree of automation and long service life of adsorbents, it is a method valued by many researchers [10].
In the above four methods, the absorption method has a better effect but has not been widely used in industry because of complicated operation, low utilization of absorbents and high energy consumption. Although the membrane separation method has made great progress in the laboratory, considering the cost of the membrane, there are many difficulties to be overcome in the way of industrialization. And the cryogenic method has less suitable occasions, which has been explained before. In comparison, adsorption has many advantages over other materials. Some advantages and disadvantages have been summarized in Table 1. However, whatever the principle, the core research direction of adsorption is the study of adsorbent materials.

### Table 1. Advantages and disadvantages of dominant CO₂ capture methods.

<table>
<thead>
<tr>
<th>CO₂ capture methods</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Physical absorption</td>
<td>• Low energy consumption</td>
<td>• Low selectivity</td>
<td>[11][12]</td>
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<td></td>
<td>• High separation and recovery efficiency</td>
<td>• High processing cost</td>
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<td></td>
<td>• Available at high pressure</td>
<td>• Large plant footprints</td>
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<td></td>
<td>• Has been commercialized for many decades</td>
<td>• Low absorption rate</td>
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<td></td>
<td></td>
<td>• Fast degradation rate of absorption</td>
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<tr>
<td>Chemical absorption</td>
<td>• Suitable for existing power plants transformation</td>
<td>• Low CO₂ carrying capacity</td>
<td>[5][13]</td>
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<tr>
<td></td>
<td>• High purity of CO₂ flow</td>
<td>• High corrosiveness</td>
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<td></td>
<td></td>
<td>• Balance between permeability and selectivity</td>
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<td>Membrane</td>
<td>• Less energy-intensive</td>
<td>• High cost for membrane with good stability</td>
<td>[14]</td>
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<td></td>
<td>• Simple operation</td>
<td>• Require multiplied phases and recycle</td>
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<td></td>
<td>• No secondary pollution</td>
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<td></td>
<td>• Easy and modular design</td>
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<tr>
<td></td>
<td>• High CO₂ recovery and purity</td>
<td>• Blockage of other gas components</td>
<td></td>
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<tr>
<td></td>
<td>• No corrosion potential</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>• Separating in liquid</td>
<td>• High energy consumption</td>
<td>[15][16]</td>
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<td></td>
<td>• Low energy consumption of pressurization for transport</td>
<td>• High refrigeration demand</td>
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<td></td>
<td>• High adsorption rate</td>
<td>• Large equipment</td>
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<td></td>
<td>• Low regeneration energy</td>
<td>• Low adsorption capacities at low temperature</td>
<td>[13][17]</td>
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<tr>
<td></td>
<td>• Good selectivity</td>
<td>• influenced by water vapor and other gas components</td>
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<tr>
<td></td>
<td>• High stability</td>
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<tr>
<td></td>
<td>• Gentle operation condition</td>
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<tr>
<td>Adsorption</td>
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3. **Typical adsorption materials**

3.1. **Carbonaceous adsorbents**

There are abundant carbon resources in nature, and they are widely used in scientific research. Especially, carbon materials show some good performances in the field of adsorption, such as high specific surface area, good porosity, large pore volume, stable chemical properties and good electric properties [18]. Several simple carbon materials are shown in Fig. 6.
Mohd investigated that the principle of gas adsorption using biochar is mainly physical adsorption and pores on biochar surfaces are storage sites for gas molecules [19]. Najafabadi made carbonaceous adsorbents from cocoa shells and indicated that cocoa shell biochar has good stability after several cycles and has great potential as a biochar adsorbent [20]. In addition, he compared the properties between cocoa shell biochar and commercial activated carbon. The result indicated the higher equilibrium CO$_2$ uptake of the biochar, while the activated carbon has a faster adsorption rate.

Nowadays, scientists attempt to promote the adsorption properties of activated carbon (AC) by pore structure adjustment, AC-based composite adsorption, preparation of surface modification and nitrogen amine doping [21]. Boujibar successfully synthesized AC adsorbents from Moroccan coal [22]. The Coal-K-PM sample, which was chemically activated by KOH and prepared through physical mixing (PM), had a high pore volume of 1.34 cm$^3$/g and the highest surface area of 2934 m$^2$/g, whereas the Coal-K-Im (prepared using impregnation (Im) method) showed the best CO$_2$ adsorption capacity to 5.88 mmol/g at 25 ºC.

3.2. Silica gel

Silica gel is a kind of cheap adsorbent and has been widely used in many industrial fields, such as dehydration in cracked or natural gas and removal of oxidized or chlorinated organic matter from hydrogen. Researchers are currently committed to studying modified silica gel to improve its performance.

The most commonly used modification methods of silica gel are ionic liquid modification, organic amine modification and alkali metal ion modification [23]. Anyanwu et al. utilized organic amine modification to improve the adsorption properties of 150A silica gels (corresponding mesh sizes of 200-425) [24]. The improvement included the addition of water while grafting to increase the concentration of amine (N1-(3trimethoxysilylpropyl) diethylenetriamine). This action brought about a CO$_2$ adsorption capacity of 1.83 mmol/g at 0.15 bar and 75 ºC and 2.3 mmol/g at 1 bar and 75 ºC. The wet-amine-grafted adsorbent exhibited good amine efficiency, rapid uptake rates and cyclic stability, and due to its commercial feasibility and excellent performance, this kind of material has great application prospects.

Garip et al. used sol-gel method to synthesize silica-based aerogels with different components of ionic liquid (1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide (IL)) and 3-aminopropyltriethoxysilane (APTES) [25]. According to his research, the addition of APTES and IL both enhanced the CO$_2$ adsorption properties of silica gel. Among various experiment groups, the sample with mol ratios of APTES and IL are 0.24 and 0.28, respectively, showed favorable performance with 5.53 mmol/g (243.32 mg/g).

3.3. Zeolite molecular sieve

Zeolite molecular sieve is a natural or synthetic crystalline aluminosilicate containing alkali or alkaline earth metal oxides. Due to the large specific surface area and adjustable pore size, the zeolite molecular sieve is regarded as an excellent CO$_2$ solid adsorbent material [26]. The adsorption
mechanism of Zeolite molecular sieve is generally that molecular sieves with kinetic selectivity are easy to adsorb molecules with strong polarity or polarization. The molecular sieves framework and cations have strong polarity, which can attract each other with the heteroelectric center of polar molecules so that the polarization of molecules can be achieved via electrostatic induction [27].

Gabriele et al. used fly ash as raw material to synthesize X-type zeolite through the melting and hydrothermal method, and its adsorption capacity is 2.18 mmol/g [28]. Chao et al. performed a high-throughput grand canonical Monte Carlo (GCMC) simulation to foresee the CO$_2$ adsorption effect of 2625 aluminosilicate zeolite structures [29]. The consequences of simulation revealed that those models exhibited excellent performance in TSA and PSA processes, and some of them even exceeded the most efficient zeolite at present, the zeolite Na-X.

Runlin Han et al. prepared SSZ-13 via an unconventional process by adding Al(NO$_3$)$_3$ as the aluminum resource before the structure-directing agent and base. In this case, SSZ-13 was crystallized by an unconventional growth mechanism [30]. Based on the preparation of SSZ-13, the author also optimized the effects of aging time and the number of fluoride ions on the adsorption effect. The result showed that SSZ-13 had a bright application prospect. When the ratio of F/Si was 0.1, the product had the best adsorption performance, 2.74 mmol/g at 0.25 bar and 4.55 mmol/g at 1 bar, which was 54.8% and 20.4%, respectively, which is higher than that of SSZ-13 prepared by typical methods.

3.4. Metal-organic frameworks

MOFs are periodic and ordered crystal structures self-assembling via organic or inorganic linkers and metal-containing nodes (also known as Secondary Building Units or SBUs). They have functionalizing pore surface, permanent and highly adjustable porosity [31]. Because of the advantages of a rich source of raw materials, high stability in getting a high capacity of CO$_2$, and favorable selectivity, MOFs have been regarded as the most promising materials for industrialization.

In 2008, Wang et al. used grand canonical Monte Carlo simulations to certify the feasibility of MOF Cu-BTC for gas separation in three kinds of binary mixtures (CO$_2$/CO, CO$_2$/CH$_4$, and C$_2$H$_4$/C$_2$H$_6$) through adsorption [32]. In addition, they also illuminated the potential adsorption mechanism of MOFs at a molecular level, which made a foundation for the later research in the fields of metal-organic frameworks in CO$_2$ capture.

Nowadays, researchers have taken a series of actions to promote the adsorption performance of MOFs. Table 2 summarizes some strengths and challenges of these strategies.

<table>
<thead>
<tr>
<th>Strategy</th>
<th>Strengths</th>
<th>Challenges</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>OMS construction (Open metal sites)</td>
<td>The porosity and robust nature of MOFs facilitate the introduction and properties of OMS.</td>
<td>Due to the limitation of the stability of metal frameworks, it is critical to developing highly robust MOFs. Solvents or water molecules often occupy the OMS of MOFs.</td>
<td>[33][34]</td>
</tr>
<tr>
<td>Functionalized surface modification</td>
<td>The introduction of ligands can improve the adsorption properties of MOFs without destroying their overall structure. Synergistic effect of multiple metals will improve the performance of MOFs, such as CO$_2$ capacity and selectivity.</td>
<td>The introduced ligands will occupy some void space which results in the reduction of porosity and brings some negative impacts. Many metal ions are difficult to be doped into the framework and the sites of doped metal ions are usually unclear.</td>
<td>[35][36]</td>
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Wang et al. took advantage of the mixed linkers method to synthesize highly stable amine-functionalized MIP-207-n (n stood for the different part of the H$_3$BTC ligand replaced with 5-NH$_2$-
H₂IPA) [37]. They showed that MIP-207-25% expressed the most excellent adsorption properties up to 3.96 and 2.91 mmol/g, 20.7% and 43.3% higher than those unmodified at 0 ºC and 25 ºC, respectively.

Hu et al. reported that incorporating heterocyclic ligands could remarkably improve the CO₂ adsorption amount [34]. They investigated UiO type MOFs comprising N, S, and O heterocyclic ligands, and the UiO-67 comprising O-heterocyclic performed the highest CO₂ adsorption amount, which was four times much than those without O-heterocyclic. These results validated that the introduction of heterocyclic was a useful method to enhance the performance of MOFs. Meanwhile, the author also pointed out that further study would pay attention to investigating the co-adsorption of CO₂ with other competitive gas components in MOFs with heterocyclic ligands.

In the field of mixed metal-organic frameworks, Li et al. reported that they immobilized alkali metal ions (K⁺) in MOFs and enhanced CO₂ skeleton affinity by 24% [38]. Gao et al. developed a kind of mixed metal-organic framework (M‘MOF), [Fe(pyz)Ni(CN)₄] (pyz=pyrazine), used for C₂H₂/CO₂ separation [39]. This material showed high C₂H₂ adsorption capacity up to 4.54 mol/L and favorable C₂H₂ selectivity of 24% at ambient temperature and pressure.

4. Conclusion and future perspective

In this work, the principle, advantages and drawbacks of four kinds of adsorption methods have been reviewed, and adsorption has a broad prospect in industrialized applications because of its advantages of mild operating conditions, low energy consumption and excellent stability. The research status of common adsorbents has also been summarized. Nowadays, CO₂ capture and separation are essential tasks of human beings, and a number of researchers have achieved good results in the laboratory stage. The existing problem is how to develop a kind of low-cost adsorption material that can be successfully applied in the adsorption industry. As far as the research is concerned, zeolite molecular sieve, one of the widely researched materials, may be applied in industry in the near future by virtue of stable chemical property and high selectivity. However, in recent years, with the deepening of MOFs research, new materials have been constantly developed, and the unique mechanism of MOFs has also been constantly explored. The current target is to enhance the adsorption performance of MOFs, especially in the field of functionalized surface modification. But there is no doubt that this approach is still a long way from industrialization.

References


[31] D. Lai, Engineering the pore size of ultra-microporous MOFs for kinetical separation of CO$_2$/CH$_4$ [master dissertation, Zhejiang University].


