

MOFs for capturing carbon dioxide after combustion

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Abstract. The expanding population and technological advancements are driving the energy demand. The overuse of conventional petroleum fossil fuels has resulted in large emissions of greenhouse gases, which cause global warming and other problems. Controlling carbon dioxide emissions is therefore essential to reducing greenhouse impact. Among the numerous benefits of metal-organic frameworks (MOFs) are their high porosity and vast interior surface area. They are now the most promising adsorbent materials and have a wide variety of applications in the adsorption and separation of gases, including carbon dioxide. To address the mechanical, chemical, thermal, and water stability of MOFs, this article first provides an overview of their structure and synthesis design techniques. Next, this article addresses the selectivity of MOFs for nitrogen and water as well as the adsorption process of CO₂ in MOFs. The techniques for modifying MOFs, such as pore size-controlled MOFs, targeted metal unit modification, and functional group modification to improve adsorption and separation performance, were highlighted last.

Keywords: MOFs, synthesis, CO₂, mechanism, capture.

1. Introduction

With the fast advancement of industrialization and urbanization in the 21st century, together with exponential increases in population growth, there has been an exponential rise in the energy needs of humans. The process of burning traditional fossil fuels releases many gases, including NO, CO₂, and SO₂. Among them, the significant emissions of CO₂ as a greenhouse gas have greatly intensified the greenhouse effect, leading to an increase in global warming and extreme weather. According to reports, the quantity of CO₂ in the atmosphere has grown from around 315 parts per million to 420 parts per million between 1960 and 2023 [1]. It is predictable that significant environmental problems on a worldwide scale will result from the ongoing growth in carbon emissions. It is crucial to investigate methods for mitigating the greenhouse effect in the face of these obstacles.

Reducing carbon dioxide emissions is now the primary strategy for mitigating the greenhouse impact. In general, there are a number of ways to lower carbon dioxide emissions, such as creating new energy sources, increasing the efficiency of combustion, and implementing CO₂ capture and storage technology. Of all the techniques, carbon capture is usually thought to be more economical.

Currently, available technologies for removing CO₂ from coal-fired power stations' flues include membrane separation procedures, electrochemical separation, solid adsorbents (such as zeolites and metal-organic frameworks), and water-based amine absorbents [1]. Because of their huge surface area and high capacity, MOFs are among the most effective CO₂ adsorbents available, and they have been the subject of extensive research in recent years.

The three primary phases of carbon dioxide emissions from coal-fired power plants—before combustion, during combustion, and after combustion—all include the usage of solid adsorbents. The post-combustion capture method exhibits a more intricate trapping environment and a reduced partial pressure of CO₂ when compared to the other two methods. However, the primary advantage of post-combustion capture lies in its direct applicability to existing coal-fired power plants without requiring any re-routing or pre-processing. The cost advantages of post-combustion capture are evident.

2. The basic characteristics of MOFs

2.1. Structural Feature

MOFs are porous materials with three dimensions that are made of organic ligands and metal ions. Typically, the structure consists of a metal atom in the center, to which a polydentate organic ligand with oxygen or nitrogen bound is connected. Coordinate bonds bind the ligand and the core metal atom together. The porous structure and abundant adsorption sites of MOFs render them highly effective as CO₂ adsorbents. MOFs are highly adjustable, and there exists a robust interaction between metal ions and organic ligands. Thereby, MOFs have many excellent properties, including large specific surface area, diverse structural variations, high porosity, large storage capacity, versatile characteristics, and facile recovery.

2.2. Synthesis of MOFs

A modular technique is often used in the synthesis of MOFs. In this method, metal precursors are combined with appropriate ligands under moderate conditions to produce a crystalline porosity network. Solvents are often eliminated from the synthesis process by using a vacuum, heating, or swapping with volatile molecules to produce large guest molecules accessible surface areas. Common synthesis procedures include the diffusion method, solvothermal synthesis, microwave synthesis, sonication synthesis, and mechanochemical synthesis. The synthesis process has a major impact on both the pore size and the size of the final particle. In laboratory settings, the solvothermal technique has been widely used to synthesize well-known MOFs such as MOF-5, HKUST-1, and ZIF-8. When it comes to cost and practicality, the synthesis techniques used for the large-scale industrial manufacture of MOFs should be low-cost, low-toxicity, and have high yields.

For CO₂ adsorbable MOFs, the structure and pore characteristics can be adjusted by selecting appropriate metal ions and organic ligands to improve their CO₂ adsorption capacity. As an alternative, the adsorption capacity and selectivity of CO₂ can be increased by adding polar functional groups including fluorine, bromine, chlorine, hydroxyl, and carboxyl. To accomplish effective CO₂ collection, parameters including hydrophobicity, hybrid structure, and metal site saturation of MOFs must be taken into account during the design and synthesizing process.

2.3. Stability of MOFs

The stability of the adsorbent material must be guaranteed for the CO₂ capture method after combustion. Because corrosive solutions, high humidity, and high temperatures are common problems in the working environment following combustion. To solve these problems, MOFs with high temperature characteristics must be developed.

2.3.1 Mechanical stability

The capacity of MOFs to sustain mechanical stresses is known as their mechanical stability, and a major factor influencing this stability is their underlying structure. The partial collapse of pores or phase transitions inside MOFs is frequently caused by the mechanical instability of MOFs with high porosity. The greater coordination numbers linked to tetravalent and trivalent metals improve the mechanical stability of zirconium-based MOFs in multivalent (trivalent or tetravalent) forms [1].

2.3.2 Chemical stability

Chemical stability refers to the ability of MOFs to maintain their structure and adsorption properties unchanged or with little change in acidic and alkaline solutions. The chemical stability of MOFs can be assessed using PXRD and TGA techniques. When MOFs with limited stability are exposed to acidic or alkaline environments, their surface undergoes collapse or expansion, leading to alterations in surface area and subsequent reduction in adsorption capacity. The chemical stability of various MOFs in acid, base, H₂O₂, H₂O, and air at 3 days and 2 months was investigated by Leus et al. [2], as presented in Figure 1. Notably, MIL-101 (Cr) and NH₂-UiO-66 exhibited remarkable

resistance to acidic conditions with pH values of 0 and 4, demonstrating excellent acid-base chemical stability that persisted for two months.

MOFs	XRD (3 days)						XRD (2 months)					
	pH = 0	pH = 4	pH = 12	H ₂ O ₂	H ₂ O	air	pH = 0	pH = 4	pH = 12	H ₂ O ₂	H ₂ O	air
MIL-101 (Cr)	LP	LP	LP	LP	LP	LP	LP	LP	LP	CD	LP	LP
NH ₂ -MIL-101 (Al)	CD	CD	CD	CD	PD	CD	CD	CD	CD	CD	CD	CD
MIL-53 (Al)	CD	LP	LP	PD	LP	LP	CD	PD	LP	PD	LP	LP
NH ₂ -MIL-53	PD	LP	LP	LP	LP	LP	CD	LP	LP	PD	LP	LP
UiO-66	LP	LP	LP	LP	LP	PD	LP	LP	LP	LP	LP	PD
NH ₂ -UiO-66	LP	LP	LP	LP	LP	LP	LP	LP	LP	LP	LP	LP
UiO-67	CD	LP	LP	CD	LP	LP	CD	PD	LP	CD	LP	LP
CuBTC	CD	PD	PD	LP	PD	LP	CD	PD	PD	CD	PD	LP
ZIF-8	CD	LP	LP	PD	LP	LP	CD	PD	PD	CD	PD	LP

Fig. 1 Stability of different MOFs in acid, base, H₂O₂, H₂O, and air [2].

2.3.3 Thermal stability

Heating at high temperatures can degrade MOFs, causing structural damage and deactivation. Therefore, to prevent influencing the CO₂ adsorption performance, it is required to increase thermal stability during structural design and modification. According to a study, adding trivalent metal centers to MOFs may strengthen their bonds with organic ligands and increase their thermal stability. The thermal stability of MOFs was greatly increased by the preparation of zirconium-based UiF-66 (Zr), which was made by using zirconium as the metal center and functionalizing its surface with various functional groups (such as amino, carboxyl, carboxyl lithium, etc.). The thermogravimetric analysis also supported this conclusion, as seen in Figure 2 [3].

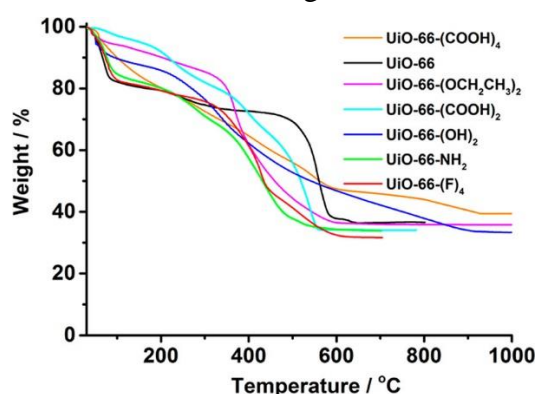


Fig. 2 Stability of different MOFs [3].

Furthermore, MOFs have very poor stability in humid environments. This is mostly because of their weak coordination bond strength, which readily breaks in the presence of water vapor and causes the skeleton to collapse. In addition to being very hot, the smoke produced following fuel burning also has a significant concentration of water vapor. Consequently, it is also required to increase MOFs' stability in humid conditions based on their strong thermal stability. Shi et al. recently published a paper on modified MOFs. By altering the amino groups on their surface, MOFs may be made to endure temperatures as high as 440 °C and to show good chemical and water stability in alkaline or acidic water vapor [4].

3. MOFs in CO₂ post-combustion capture

3.1. CO₂ adsorption mechanism in MOFs

MOFs have three different ways of absorbing carbon dioxide. The first is the thermodynamic separation process, in which certain MOF channel adsorption sites absorb CO₂. Metal ions, metal clusters, and organic ligand functional groups are examples of adsorption sites. The second method

is molecular sieve analysis, which primarily uses the length of the organic ligand to filter out other gas molecules according to their kinetic diameter and pore size. The third way for achieving separation is called kinetic separation, which takes advantage of the variations in the diffusion rates of various molecules within the pore. It is worth noting that flexible MOFs have entered the research scope because of their excellent properties and unique adsorption mechanisms. Flexible MOFs exhibit unique structural flexibility and can undergo reversible transformations in response to external stimuli. Flexible MOFs produce breathing only when stimulated by a specific external pressure, opening the valve in a structural rearrangement to transition to an open and porous phase. Since the pressure of each gas fluctuates, the valve may only be opened when the specified pressure is attained or exceeded. This makes it possible for the selective adsorption process to be completed after structural modification. Figure 3 illustrates how a flexible MOF's structure may vary and its pore size can alter during the adsorption process to provide selective adsorption [2].

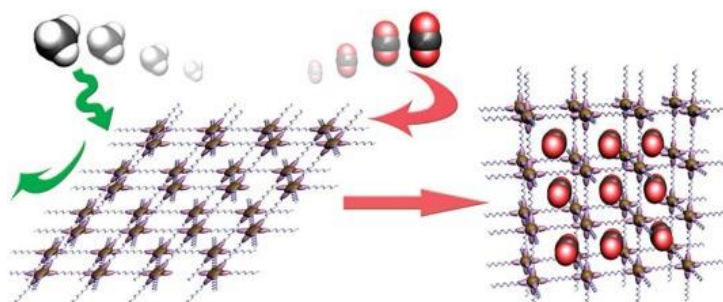


Fig. 3 Schematic illustration of selective gas adsorption in a flexible MOF [2].

3.2. CO₂/N₂ selectivity

Flue gas also has a large amount of N₂. In post-combustion carbon capture, methods to improve nitrogen selectivity and the competitive adsorption of CO₂ and N₂ by MOFs are important factors to take into account. At low CO₂ partial pressures, MOFs with high adsorption selectivity should interact strongly with CO₂, but less so with N₂ and other gases. The selectivity of MOFs to N₂ can be improved by adjusting the structure of MOFs. Due to the small kinetic diameter of CO₂ molecules, micropores typically possess an inherent advantage over mesoporous and/or macroporous pores in terms of enhancing the adsorption capacity and selectivity for CO₂. In addition, the selectivity of MOF to N₂ can be improved by introducing different functional groups. Isabel et al. successfully prepared two novel ultraporous MOFs, MUV-26 α and MUV-26 β , which have small pores, contain pyridine unit overhang, and point towards the pore space. Both materials exhibit almost unlimited CO₂/N₂ selectivity (Calculation of the dynamic selectivity value > 1000), maintain good working ability in high temperature and low concentration CO₂ mixtures, and are fully renewable at room temperature and ambient pressure [5].

3.3. CO₂/H₂O selectivity

The primary challenge associated with CO₂ capture in MOFs post-combustion lies in the presence of 5.7% H₂O within the flue gas. However, a majority of MOFs exhibit inadequate stability under high humidity conditions. The increased adsorption of water on the MOFs' surfaces could impede the adsorption of carbon dioxide, lowering the MOF's ability to adsorb the target gas. Because water has a greater affinity for metal ions than many of the metals utilized in MOFs adsorbents, this hydrolysis causes structural damage to the network [6]. The hydrolysis process not only causes structural damage but also leads to the release of metal ions from the network, which can contaminate the surrounding environment or interfere with desired chemical reactions occurring within the MOFs due to water's high affinity for these ions. It is important to note that different metals exhibit varying degrees of sensitivity towards hydrolysis reactions, as some metals form stronger chemical bonds with water molecules and are more prone to such reactions than others. Therefore, careful selection of metal composition in MOFs adsorbents is crucial for ensuring long-term stability and performance.

4. Strategies for enhancing CO₂ adsorption in MOFs

4.1. MOFs based on pore size control

The porosity of MOFs has a great influence on their CO₂ adsorption. Their highest separation efficiency applies only to the pore size of a particular molecule. To achieve optimal CO₂ adsorption and superior N₂(3.64 Å) separation, MOF pore sizes should be in close proximity to the CO₂ kinetic diameter (3.3 Å). DICRO-3-Ni-i ([M(L)₂(Cr₂O₇)_n], M^{1/4}Ni²⁺; 1,40 azopyridine) was synthesized effectively by Scott et al. [7]. This MOF structure exhibits twofold interpenetration, yielding pore sizes of 3.0 to 3.4 Å and 4.4 to 5.8 Å, respectively. The results of the investigation demonstrated that the material's ability to trap CO₂ could be greatly enhanced by adjusting its porosity, with a capacity of 40.26 cm³ g⁻¹ (CO₂/N₂, 1 bar, 293 K).

Furthermore, Ding et al. [8] provided a case study on pore engineering in MOFs to control their pore size, surface chemistry, polarity, hydrophobicity, and flexibility to promote CO₂ adsorption under low pressure circumstances to conduct a systematic investigation of porosity's influence on the trapping efficacy of MOFs.

4.2. Targeted modifications to the metal unit

Unsaturated metal sites in the MOF structure are responsible for the MOFs' affinity for CO₂ molecules. These sites also act as a major driving factor for CO₂ adsorption onto MOFs by facilitating the adsorption heat (Q_{st}) of CO₂. According to some findings, metal ions may be added to MOF materials to effectively increase the CO₂ adsorption efficiency of MOFs. Currently, there are three methods available for adding metal ions: metal chelation, metal alkoxylation, and direct metal doping. For instance, to create MFM-300(Ga_{1.87}Fe_{0.13}), Krap et al. [9] doped Fe ions into [Ga₂(OH)₂(L)]. The findings showed that at 293 K and 1 bar, the adsorption capacity of MFM-300 rose from 2.15 mmol g⁻¹ to 2.36 mmol/g. In the case of identical metal ion radii, it is discovered through the initial single crystal diffraction investigation that Fe doping causes an increase in the porosity of the material. This indicates that the adsorption capability of CO₂ is positively impacted by the MOF material MFM-300 combined with Fe ions. In addition, the influence of different elements mixed into MOFs materials is different. Alkali metal is more advantageous than transition metal ions. Because alkali metals have higher affinity and lower polarization, especially lithium ions. Using DFT, Liu et al. [10] examined the benefits of lithium ions and found that doped Li atoms and O atoms in CO₂ are separated by 2.638 Å. Li doping has a positive effect on CO₂ adsorption, as evidenced by the predicted adsorption energy rising to 24.76 kJ mol⁻¹.

4.3. Functional group modification

Modifying the functional group of MOFs is one way to enhance their CO₂ capacity. The CO₂ adsorption capacity and selectivity of MOFs can be enhanced by modifying their pore structure and surface characteristics by the introduction of distinct functional groups. Functional groups like amino, hydroxyl, carboxyl, and so forth are frequently added. Due to their strong polarity and nucleophilicity, amine modifications are the most often employed of these. The primary method of producing carbamate or bicarbonate through the Lewis acid-base interaction between amine and CO₂ is used to produce the adsorption effect. Currently, there are two primary techniques for functionalizing MOFs with amines: (1) grafting the amine onto the unsaturated metal site, or (2) synthesizing the amine directly via bridging ligands that include terminal amino groups. Dinda et al. employed in-situ grafting to integrate two polydentines, namely diethylenetriamine and tetraethylenepentamine, into ZrFu MOF structures. The findings indicated that the original ZrFu had a CO₂ adsorption capability of 73 g CO₂/kg adsorbent. The greatest adsorption capacity of DETA-modified ZrFu in amine-modified MOFs was 86 g CO₂/kg adsorbent [11].

5. Conclusion

In the past few decades, a significant amount of CO₂ has been emitted by human activities, resulting in the intensification of the greenhouse effect. Carbon capture and storage technology is widely acknowledged as an effective means to mitigate greenhouse gas emissions. MOFs, a new type of porous organic compound, show promise as pre-combustion carbon capture adsorbents. This paper summarized several methods commonly used for MOFs modification. The selective adsorption efficiency of CO₂ can be effectively improved by controlling the pore size. The CO₂ capture capacity and selectivity of MOFs can be improved by adding lithium ions in alkali metals to MOFs or by modifying them with amine functionalization.

The use of MOFs in post-combustion CO₂ collection still faces significant difficulties. Three points are presented in this work that may be relevant to future research: (1) Keep improving MOFs' water vapor selectivity and water stability. Creating MOFs with low hydrophilicity and high selectivity is an important area of study for post-combustion flue gas that contains a significant quantity of water. (2) Increase MOFs adsorbent's capacity for recycling and lengthen its service life. (3) Lower the price of the materials for MOFs. Most MOFs are more expensive, especially those using more expensive precious metals. This is also the reason why MOFs are currently not as widely used as zeolite adsorbents. In conclusion, despite the presence of numerous formidable challenges, the remarkable performance of MOFs in terms of their high capacity and adjustability remains highly valuable. The rapid advancement of computer simulations coupled with the relentless endeavors of researchers will pave the way for a promising future in carbon capture based on MOFs.

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