Research progress on MOFs for CO₂ separation and capture

Shanhan Zhou*
Ulink College of Shanghai, Shanghai, China
* Corresponding Author Email: shanhan.zhou@ulink.cn

Abstract. The world's population and economy have grown quickly, which has resulted in significant carbon dioxide emissions. People are concerned about the ensuing climate change and other problems. While there are now technologies that can lower alarming levels of greenhouse gas emissions, carbon dioxide capture is seen to be the most economical solution. Thus, it is essential to create efficient CO₂ capture systems. Metal-organic frameworks (MOFs) have been demonstrated to be the most successful materials for CO₂ collection and adsorption due to their microporous structure and advantageous properties, making them the most promising materials currently on the market. The basic properties of MOFs, such as their large surface area, chemical stability, adjustable pores, and porous structure, are initially outlined in this article. Next, the features of MOFs for separation were presented, particularly how well they could separate CO₂ from gases like hydrogen, natural gas, and flue gas. Lastly, this research highlights the use of chemical functionalization, doping metals, and unsaturated metal centers to improve MOFs' adsorption and CO₂ storage capabilities.

Keywords: MOFs, gas separation, CO₂ capture, improvements.

1. Introduction

Industrialization is growing as science and technology advance. Carbon dioxide emissions from the combustion of conventional fossil fuels like coal and oil are substantial. This has made carbon dioxide emissions worse, along with a fast-expanding population. It is a greenhouse gas that causes global warming, disrupts the natural ecosystem's equilibrium, has an adverse effect on human health, and may potentially endanger the existence of the human race. It is therefore important that the development of renewable energy technologies be accompanied by the promotion of carbon capture and storage systems that effectively absorb carbon dioxide. The extensive use of fossil fuels is accompanied by an increase in CO₂ emissions, which are close to 40 Gt CO₂ annually. As a result, the average global temperature rises, and the quantity of CO₂ in the atmosphere rises beyond 400 parts per million (ppm), raising serious concerns among the public [1].

There are several ways to lower carbon dioxide emissions, such as increasing productivity, switching to other energy sources in place of fossil fuels, and developing CO₂ collection technology. CO₂ capture technology is one of them that can lower CO₂ emissions and aid in addressing the problems caused by climate change. Additionally, it can lessen reliance on scarce resources while still providing energy demands. Sustainable economic growth may also be aided by the production of new goods using carbon dioxide collected. A novel kind of material called MOFs effectively absorbs CO₂. They feature a large surface area, a variety of compositions and architectures, high porosity, and a large volume of storage voids. Under high pressure, MOFs may hold 10-12 times more CO₂ than empty containers [2]. Other molecules may absorb CO₂ and store it in the pores and channels of MOFs once it has been caught. Thus, this page primarily outlines the fundamental properties of MOFs, describes how they separate CO₂ from various gasses and offers techniques for enhancing their CO₂ adsorption.

2. Basic characteristics of MOFs

2.1. Porous Structure and High Surface Area

MOFs, often referred to as coordination polymers or hybrid porous solids, are composed of inorganic fragments joined by ligands, which are organic linker molecules. There are many other
shapes that the inorganic pieces might adopt, such as single polyhedra, chains, clusters, and layers. Organic ligands bind these pieces together to create a framework structure. MOFs can display a crystalline structure and crystallize into a variety of particle sizes, ranging from larger single crystals (>150 µm) to microcrystalline powders (particles smaller than 1 µm). In comparison to amorphous porous carbon and silica, which may have a less well-defined pore structure, MOFs' crystalline nature creates a well-defined and well-ordered pore system throughout the material, improving reproducibility and uniformity of adsorption properties. The homogeneity of the pores allows for exact control of the size and shape of molecules that may be adsorbed or segregated inside the material. The well-defined pore system in MOFs offers benefits in their adsorption capabilities and applications. Because of their tunability and repeatability, MOFs are helpful in applications involving the storage, separation, and purification of gases where exact control over the adsorption characteristics is crucial. Larger materials can adsorb larger amounts of a given substance because the interaction between the adsorbed substance and the adsorbent surface is typically much stronger than that between the guest substance itself. Surface area is also an important characteristic of porous solids when it comes to adsorption and separation processes. The high surface area of MOFs is advantageous in gas storage for several reasons. First, a larger surface area facilitates the adsorption of more gas molecules, increasing storage capacity. Secondly, a large surface area offers more sites for selective adsorption during separation, enabling the effective separation of various components.

2.2. Thermal Stability

MOFs are prone to degradation at high temperatures as well as in humid, acidic, alkaline, or reactive environments. This degradation raises the probability of an organic ligand structural collapse or breakdown. Several factors, including the pore size, the particular organic ligand employed, and the coordination geometry of the metal ions, affect MOF's thermal stability. One famous example of a MOF that exhibits remarkable thermal stability is MOF-5. Its ability to withstand temperatures as high as 523 K (250 °C) without breaking down even after prolonged immersion in boiling water serves [3].

2.3. Tunable properties

The tunability of MOF materials both during and after production is one of its primary benefits. Functional groups can be included in MOFs to modify the metal cations that make up the framework and to alter the pore size while preserving the particular topology of the framework. The isometric St. determines this tunability. Because of their adaptability, Andrews porous materials, like STA-12 (Ni) and STA-16 (Co), have a honeycomb-like structure that makes it possible to modify MOFs to fit specific applications. For instance, adding amino groups to hydrophobic organic connecting molecules can make pore systems that were previously restricted by them hydrophilic. In conclusion, the many uses of porous solids—including MOFs—in gas storage, separation, and purification have piqued curiosity. Their key benefit over conventional materials like zeolites and porous carbon is their tunability, which lets them tailor their characteristics to suit certain requirements.

3. Gas Separation

3.1. CO₂ separation from flue gas

Two key factors in evaluating a membrane's efficacy for CO₂ capture from flue gases—which typically consist of a mixture of gases including H₂O, N₂, O₂, and CO₂—are CO₂ permeance and selectivity. When it comes to CO₂/N₂ separation, zeolite membranes are substantially more selective than MOF membranes. This is mainly because the crystal structure of zeolite gives it the function of a molecular sieve. On the other hand, because of the organic linkers, MOFs have a flexible structure that creates a breathing effect. This effect restricts the occurrence of molecular sieving phenomena in MOFs. Therefore, MOF membranes exhibit relatively lower selectivity. However, the CO₂ permeability of MOF membranes which is computed by multiplying the permeance by the thickness
of the membrane is often higher, this is because of their flexible framework nature and larger surface areas, which result in a higher CO$_2$ permeability.

Currently, common methods for separating natural gas and CO$_2$ include cryogenic separation, absorption, and membrane separation. The low temperature separation method requires a large amount of energy consumption. The absorption method usually uses alcohol and amine solution to absorb CO$_2$, but the alcohol and amine solution has certain corrosives, that cut regeneration energy consumption. The membrane separation method still lacks economic and durable high-performance membrane materials. MOFs have received wide attention because of their novel structure and unique properties. In recent years, MOFs have been better developed for the selective separation and adsorption of natural gas and CO$_2$. A large number of studies have shown that functional groups (e.g., carboxyl, amino, hydroxyl, etc.) functional site modification or the formation of ionic MOFs can effectively improve the interaction between CO$_2$ and backbone. For example, NOTT-101 modified with functional group nitro exhibited higher CO$_2$ adsorption performance (187 cm$^3$/g vs. 164 cm$^3$/g at 273 K/0.1 MPa for NOTT-101) and CO$_2$/CH$_4$ separation performance. This was mainly due to the functionalization of nitro and unsaturated copper sites that increased the polarization rate of CO$_2$, resulting in stronger electrostatic interactions between CO$_2$ and strands.

3.2. CO$_2$ separation from natural gas

Compared to methane, CO$_2$ has a higher cubic moment and polarization rate. Usually, this leads to increased CO$_2$ and MOF interactions. Therefore, by modifying the pore size in the porous skeleton to include polar functional sites and open metal sites, the selective separation of CO$_2$ and CH$_4$ may be further enhanced. Overall, the majority of rigid MOFs used to selectively remove CO$_2$ from CH$_4$ fall under the molecular sieve separation effect and are influenced by synergistic interactions like kinetic-driven separation or thermodynamic equilibrium separation, which are based on the intrinsic characteristics of both the MOFs and the molecules of CH$_4$. CO$_2$ may more readily diffuse in MOFs using molecular sieving, which efficiently achieves separation by accurately altering the size of the holes utilizing the difference between the kinetic diameters of CH$_4$ and CO$_2$ molecules [3].

By solid interactions between CO$_2$ and functional groups/sites immobilized inside the framework of the MOFs, some stiff MOFs were separated by CO$_2$ adsorption. Kinetic-driven separation or thermodynamic equilibrium serves as the primary basis for the separation. That is to say, the adsorption characteristics of these materials are influenced by the MOFs’ pore surface characteristics in addition to the chemical and physical characteristics of CO$_2$ and CH$_4$ (such as polarity and quadruple moments). MOFs functionalized with hydroxyl, methyl, and amino groups can produce greater host-guest interactions by adjusting the polarity and acidity of the porous environment, which in turn increases the relative adsorption of CO$_2$ in the presence of other gases, interactions between objects, resulting in increased CO$_2$ affinity.

Furthermore, to separate CO$_2$/CH$_4$ mixtures, flexible MOFs’ kinetic behavior and flexible structure are also regulated. Their reversible structural alterations often happen in reaction to variations in the outside environment, including pressure or temperature. While the exact sieving of CO$_2$ and CH$_4$ gasses by pore structure modifications is a straightforward and very efficient technique, the cost of the ligands remains high. Finding an adsorbent for MOFs with a strong sieving performance, high stability, cheap ligand cost, and a straightforward and safe production is therefore crucial.

4. Strategies to improve the CO$_2$ adsorption performance of MOFs

For MOF adsorbents to successfully collect CO$_2$, they must be very selective and have a high CO$_2$ capacity. It has been shown that three of these methods—using chemical functionalization, adding metal doping, and including unsaturated metal centers—work exceptionally effectively.
4.1. Incorporation of unsaturated metal centers (UMCs)

It is possible to eliminate the partial coordination that some metal atoms in MOFs show with solvent molecules by heating the material or applying a vacuum. Removing this coordination allows unsaturated metal sites to form inside the pores. Because unsaturated metal sites greatly increase the affinity of CO\textsubscript{2} molecules, these MOFs have a higher possibility of efficiently absorbing CO\textsubscript{2} even at low pressures.

2,5-dihydroxyterephthalic acid and metal salts react to form M-MOF-74 compounds; M might be Mg, Co, Fe, Zn, or Ni [4]. The compounds that are being examined have a notable prevalence of open metal sites within their structures. As a result, they ought should be able to collect carbon dioxide at low pressure. Recent studies have shown that Mg-MOF-74 displays the greatest CO\textsubscript{2} adsorption at 298 K and 1 bar of pressure (up to 8.0 mmol g\textsuperscript{-1}). Scientists have studied the CO\textsubscript{2} adsorption properties of two particular MOFs, M-BTT and M-MOF-74, theoretically to comprehend the CO\textsubscript{2} adsorption process of MOFs [5]. Nine divalent transition metal cations as well as calcium (Ca) and magnesium (Mg) were investigated. Of the two structures, the Ti and V-based MOFs exhibited the maximum CO\textsubscript{2} binding energy.

4.2. Doping Metals

Doping metals is another method for enhancing MOF performance. By adding foreign metal ions to MOFs during solvothermal crystallization, the CO\textsubscript{2} adsorption is improved. The validity of this notion is validated by computational simulations showing that MOFs containing Li\textsuperscript{+} ions increase the CO\textsubscript{2}/CH\textsubscript{4} selectivity. The CO\textsubscript{2} adsorption capability of lithium-doped MOF-5 is investigated using research [6]. The computed findings indicate that the distribution, intensity, and slope of the electrostatic potential within the pores are altered by the addition of lithium. As a result, the framework’s preferred adsorption sites are altered, increasing its capacity to absorb CO\textsubscript{2}.

Utilizing 2,4,6-tris-(4-carboxy-phenoxy)-1,3,5-triazine as a ligand was the subject of another study. In this work, a metal ion that bonded to a water molecule by coordination was used to replace the NH\textsubscript{2}(CH\textsubscript{3})\textsubscript{2} cation that was found in the pores of anionic SNU-100. Several SNU-100 compounds containing metal ions, including Li\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Co\textsuperscript{2+}, and Ni\textsuperscript{2+}, were formed as a result of the process [7]. The addition of metal ions to SNU-100 (M-SNU-100) materials has been shown computationally to improve their selectivity for CO\textsubscript{2}.

4.3. Chemical Functionalization

The quadrupole moments of N\textsubscript{2}, CH\textsubscript{4}, and H\textsubscript{2} are quite noticeable, while CO\textsubscript{2} is either nonpolar or somewhat polar. This difference may be used to selectively separate CO\textsubscript{2} from other gases by adding polar functional groups, which are particularly attracted to CO\textsubscript{2}, into the pores of metal-organic frameworks (MOFs). MOFs can absorb CO\textsubscript{2} more effectively.

One method is to include ligands with amine functions into MOFs. For the MOFs Cd-ANIC-1 and Co-ANIC-1, which employ 2-amino isonicotinic acid (ANIC) as a ligand, CO\textsubscript{2} adsorption shows great promise [7]. Second, (Me\textsubscript{2}NH\textsubscript{2})In(NH\textsubscript{2}BDC\textsubscript{2})-DMF-H\textsubscript{2}O, where NH\textsubscript{2}BDC denotes 2-aminoterephthalate, is the example. Because the microporous MOF has polar functional groups, it has a remarkable resistance to moisture and air. It exhibits good adsorption and has better selectivity for CO\textsubscript{2} than CH\textsubscript{4} [9].

Moreover, the hydroxyl group functions as an additional polar group that may intensify the attraction to CO\textsubscript{2}. Because the hydroxyl group was added, MAC-4-OH’s CO\textsubscript{2} capacity and CO\textsubscript{2}/N\textsubscript{2} selectivity were greatly increased. Despite having a smaller surface area than MAC-4, the hydroxyl group exhibits more electrostatic interaction with the CO\textsubscript{2} molecule [10].

5. Conclusions

Recent developments have demonstrated that MOF membranes can facilitate effective CO\textsubscript{2} collection because of their advantageous properties for gas separation, which include large surface
area, chemical stability, and changeable pore size. A thorough discussion of these positive traits is given in this review. Since gases are frequently found in mixes, gas mixture conditions must be used in industrial activities. This article discusses and explains the process of separating CO$_2$ from flue gas and CH$_4$ using a MOF membrane. The field of MOF research has made significant strides that enhance CO$_2$'s capacity and selectivity over other gases. While there has been progress in creating MOFs with high selectivity or high capacity, there aren't many that have both of these advantageous qualities. There are methods for improving MOF membrane separation efficiency, including doping metals, adding unsaturated metal centers, and functionalizing MOFs to change their affinity for certain compounds.

However, MOFs still face some problems. Firstly, reproducibility is a major issue in practice when it comes to MOF membranes. A major problem with membrane regeneration is inconsistency. Secondly, there may be problems with chemical stability and durability. On the other hand, the resilience of membranes to real flue gas and natural gas conditions (e.g., the presence of pollutants and the effects of temperature and pressure) has not been well studied. Based on this, future research should focus on the modification of MOFs, including the introduction of functionalized functional groups into the molecular structure of MOFs and the modulation of the structural composition of MOFs. On the other hand, the CO$_2$ separation and storage properties of MOFs in real environments need to be further investigated. The selectivity and permeability of MOFs should be improved as much as possible by adjusting the microstructure of the materials. In addition, the synthetic routes of MOFs need to be optimised to develop cheaper and simpler MOFs. This could reduce the cost in practical applications and facilitate the industrial application of MOFs in CO$_2$ separation. With further research, MOFs will play a greater role in CO$_2$ separation and storage and help mitigate global warming.

References