The Effect of MOFs on Carbon Dioxide Adsorption

Junze Wang *

College of Sino-German Engineering, Qingdao University of Science and Technology, Qingdao, 266000, China.

* Corresponding Author Email: 2017010117@mails.qust.edu.cn

Abstract. With the rapid increase in carbon dioxide emissions, the development of efficient treatment technologies is urgent. Metal organic frameworks (MOFs) are utilized in various fields, such as gas storage, gas adsorption, drug delivery, and more, making them a highly promising material. MOFs also play a crucial role in CO_2 adsorption. This article begins with a brief introduction to the principles of carbon dioxide adsorption, explaining the basic characteristics and fundamental adsorption mechanisms of MOFs. It then provides a more specific understanding of MOFs by discussing several aspects, including the synthesis methods, crystal structures, properties of various MOFs, and the influence of branch additions on their performance. This facilitates readers in gaining a more concrete impression and a better understanding of MOFs. However, despite the good performance of MOFs in carbon dioxide adsorption, there are still certain shortcomings in terms of stability, selectivity, and large-scale applications, which will be elaborated on in detail in the later prospects analysis.

Keywords: Carbon dioxide adsorption; MOFs; principles; properties.

1. Introduction

According to the report "World Energy Outlook 2021" published by the International Energy Agency [1], global energy demand increased significantly by 2.3% from 2018 to 2019, and it is projected to grow by 1.3% annually until 2040 [2]. This means that energy demand will continue to rise over time. Currently, using conventional energy sources undoubtedly generates carbon dioxide. For example, most people currently rely on fuels like oil, coal, and natural gas to produce energy. In other words, as time goes on, the amount of carbon dioxide generated will increase. Carbon dioxide is a greenhouse gas, and excessive emissions pose significant threats to the environment, such as ozone layer depletion, glacier melting, and more. According to IPCC statistics, it is estimated that by 2100, the atmospheric concentration of carbon dioxide could reach 980 ppm.

Therefore, it is evident that if the excessive carbon dioxide produced is not properly addressed and it will pose a serious threat to the human living environment. Throughout history, scientists have explored various methods for carbon dioxide mitigation, such as cooling and compression, combustion treatment, biological absorption, or underground burial. However, the effectiveness of these methods has been limited. Since the 20th century, carbon dioxide capture technologies have emerged, primarily categorized into precombustion, oxyfuel, and postcombustion capture. One more advanced technique is the use of MOFs for CO_2 capture. MOFs have some ideal properties, such as a large surface area. This makes them more advantageous in carbon dioxide capture compared with other methods. The specific details will be discussed in the following sections, including the principles of carbon dioxide adsorption, an introduction to MOF materials, and concluding remarks. This article will primarily discuss the principles of carbon dioxide adsorption, introduce MOF materials, and provide a summary and outlook.

2. Carbon Dioxide Adsorption

2.1. Concept

CO_2 adsorption is a physical action or chemical action that involves the absorption of carbon dioxide molecules from the air onto the surface of certain materials, resulting in the reduction or

removal of carbon dioxide. These materials are typically porous, such as MOFs, activated carbon, silica gel, and so on. The diameter of the hole and the chemistry of these porous materials enable them to selectively adsorb carbon dioxide while excluding other gases such as oxygen, nitrogen, and water vapor.

2.2. IUPAC Classification of Adsorption Isotherms

$$q = Q_m * K * C/(1 + K * C) \quad (1)$$

This is an equation that describes the physical phenomenon of gas or liquid adsorption on a solid surface. The equation depicts the adsorption equilibrium relationship between the solid surface and the adsorbate by studying the interactions between the adsorbent and the gas or liquid molecules.

IUPAC adsorption isotherms are commonly used to evaluate the adsorption capacity and other adsorption properties of adsorbent materials. It can be used to predict the adsorption amount of specific gases or liquids by adsorbent materials, thereby guiding the synthesis and selection of materials as well as the optimization design of adsorption processes. Therefore, its study on adsorption is very important. The following will introduce these six types of adsorption isotherms in detail. The specific situation can be seen in Figure 1.

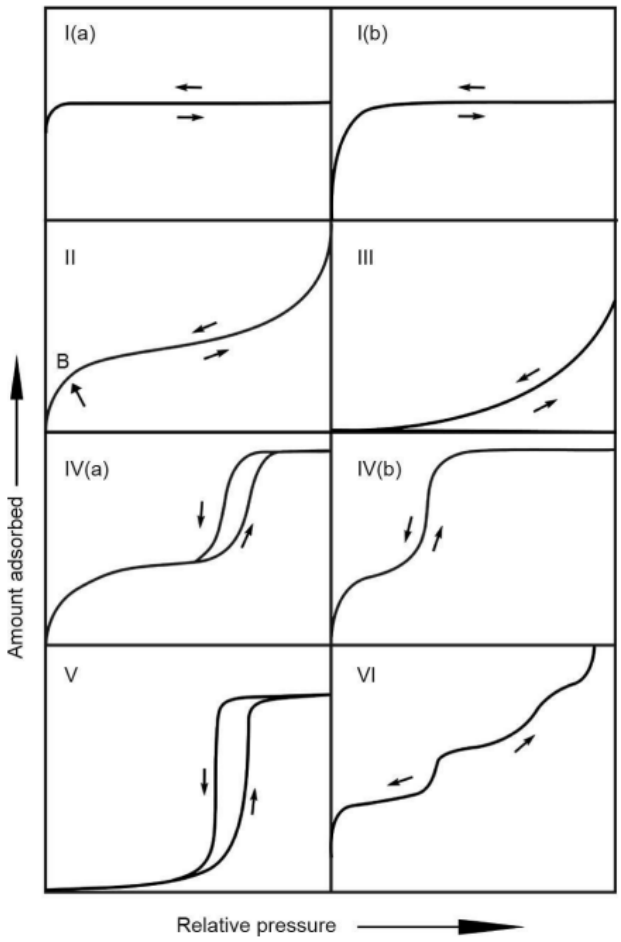

Fig 1. IUPAC classification of adsorption isotherms [3].

Type I is a chemisorption that is limited to monolayer adsorption. Its characteristic is that it exhibits near-saturation after a certain pressure. This is the Langmuir type. It is commonly used in adsorption in micropores, such as zeolites, some activated carbons, and MOFs. Type II is the most common type of adsorption isotherm. It represents multi-layer adsorption, and the adsorbate is mostly powders of non-porous particles. Type III is often used in cases where the adsorption is weak and the forces between the adsorbents are small. Type IV is similar to Type II, but the difference is that its adsorbate contains more mesopores. Capillary condensation easily occurs when approaching saturation vapor

pressure. In Type V, the adsorbent also contains more mesopores and capillary condensation is easily generated under certain pressure, such as water adsorption in hydrophobic MOFs. Type VI, also known as the stepwise isotherm, is gradually multi-layer adsorption on non-porous and non-uniform surfaces.

2.3. Adsorption Capacity and Enthalpy

Since adsorption capacity and adsorption enthalpy are two important factors to consider when evaluating CO_2 capture materials, the following will introduce these two aspects. The level of adsorption capacity directly determines whether the selected MOF material is suitable or whether the MOF material produced has good performance.

Extensive research has shown that the high internal surface area of MOFs provides an opportunity for the close packing of molecules on the pore surface [4], which can greatly enhance their adsorption capacity for carbon dioxide. For instance, at 35 bar, the volumetric CO_2 adsorption capacity of MOF-177 reaches 320 $cm^3_{(STP)}/cm^3$, which is higher than conventionally used materials zeolite 13X and MAXSORB, and is roughly 9 times higher than the amount stored at this pressure in a container without the MOF [5].

The adsorption enthalpy of CO_2 is a parameter that should be focused on when selecting adsorbent materials. The affinity of the pore surfaces is directly determined by the magnitude of adsorption enthalpy [4]. Moreover, in terms of regeneration, a too low adsorption enthalpy may make the material easier to regenerate, but it will reduce the adsorption selectivity and purity of the captured carbon dioxide, which is not worth the loss. Therefore, the adsorption enthalpy is a very important parameter for CO_2 capture materials.

3. Overview and Research Progress of MOFs

3.1. Introduction to MOFs

MOFs are porous materials composed of metal ions or clusters and organic ligands. MOFs have unique characteristics including structural tunability, enormous specific surface area, and rich pore structures. The structure of MOFs can be divided into the following parts: 1) metal clusters or ions, which are the most important components of MOFs and typically involve transition metals such as zinc, iron, and copper; 2) organic ligands, which act as ligands for metal ions and serve as bridges or connectors; 3) pores, which are formed by the assembly of organic ligands and metal ions and constitute cavities or gaps.

The adsorption of MOFs can be categorized into two groups from the viewpoint of mechanism: physical adsorption and chemical adsorption. Physical adsorption involves non-covalent interactions such as van der Waals forces and hydrogen bonds between gases or liquids and the surface of MOFs. In chemical adsorption, gases or liquids interact chemically with MOF surfaces to create covalently bonded chemical species. Additionally, the chosen metal and organic ligands, as well as the ways in which they are assembled, affect the physical and chemical characteristics of MOFs. MOFs offer a wide range of application prospects in adsorption separation, catalytic processes, and gas storage because of their great selectivity and tunability.

3.2. Research Progress of MOFs

Since the development of MOFs, their research fields have become very diverse, and a large amount of research has been published and applied in areas such as gas storage, drug transportation, electrochemical energy storage and conversion, and gas separation. In particular, attention has been paid to both general-level CO_2 capture and conversion technologies and individual technical approaches [6-9]. Figure 2 shows some research results of MOF adsorbents in the field of carbon capture, attached with a schematic diagram of the MOF structure [10].

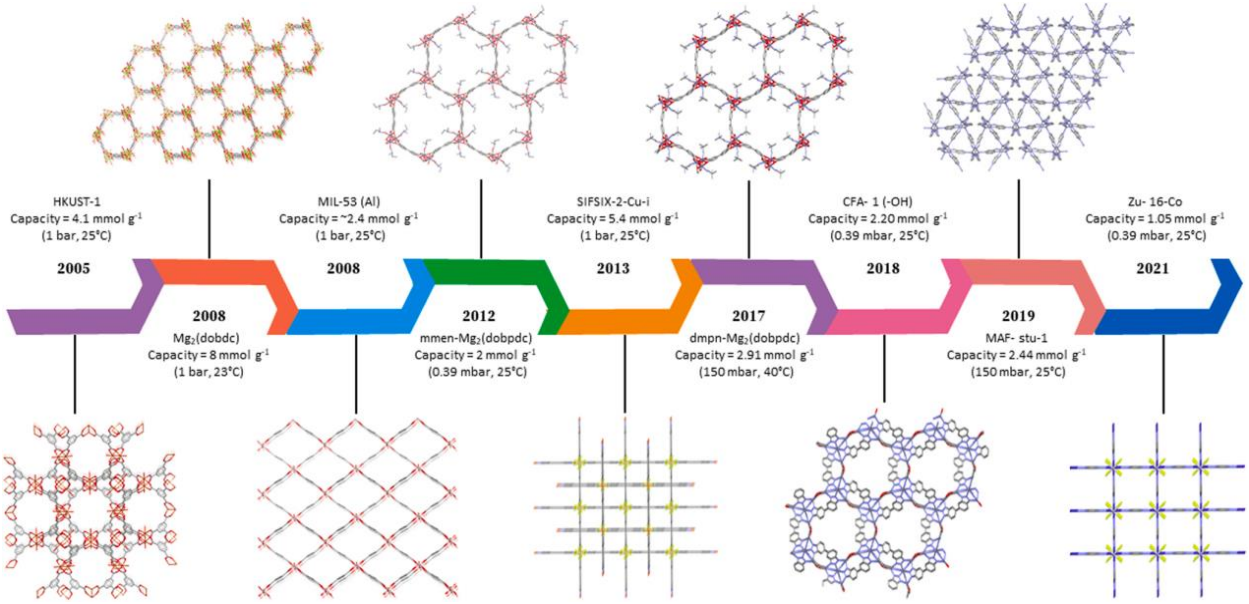

Fig 2. Research results of MOFs [10].

In addition to the single MOFs listed in the figure, scientists have been researching MOFs that are more efficient, adaptive, and show higher specificity under different conditions in recent years, as well as making improvements to existing MOFs. This will be discussed in the following sections.

4. Research Progress on MOFs and Modified MOFs

Due to the different scenarios for capturing CO_2, even if the same target is required, the performance of the necessary MOFs may vary. This requires the selection or development of efficient MOFs for capturing CO_2 for different scenarios and needs. The following will briefly introduce several MOFs and analyze their properties and compare their adsorption results.

4.1. Carbon Dioxide Adsorbent—Ni-Ade-TCPE

Ni-Ade-TCPE belonged to the system with the P21/n space group [11]. According to experimental measurements, its capturing mechanism could be referenced in Figure 3. The TCPE linker in Ni-Ade-TCPE could bind with Ni2 to form a two-dimensional layer (Figure 3c). The layers were bridged by one-dimensional chains to generate a three-dimensional framework (Figure 3d).

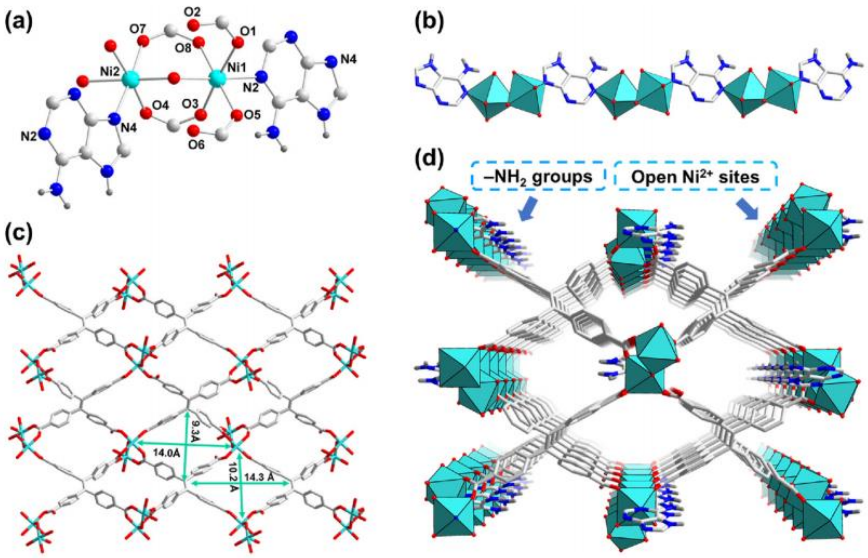

Fig 3. The spatial structure of Ni Ade TCPE [11].

The PXRD results showed that Ni-Ade-TCPE may perform effectively in a pure phase sample. It was clear through the consistency of the major peak in the PXRD pattern and the simulated pattern of the crystal structure that Ni-Ade-TCPE had good chemical stability within the pH range from 1 to 12. Then it was studied how well it catalyzed in the cycloaddition of epoxides and carbon dioxide. The experiment subsequently revealed that the ideal conversion temperature varied depending on the epoxide and that changes in pressure also had an impact on the outcomes. Its selectivity in the cycloaddition reaction between epoxides and CO_2 could reach more than 90% at 1 bar and 70 °C, which was extremely helpful for CO_2 capture. This indicated that suitable catalytic conditions needed to be selected in practical situations to achieve optimal effects.

Ni-Ade-TCPE was synthesized based on two mixed ligands. It had a 3D framework with 1D open channels, high chemical stability, and high adsorption capacity for carbon dioxide. Meanwhile, Ni-Ade-TCPE also had great development prospects, such as its use in the addition reaction with carbon dioxide under mild conditions.

4.2. Carbon Dioxide Adsorbent—Co-Ade-TCPE

The main synthetic process involved dissolving a certain amount of $Co(NO_3)_2 \cdot 6H_2O$, H4TCPE, and adenine in a spiral glass bottle containing a certain amount of deionized water. Then, a nitric acid solution was added. The mixture was heated and then cooled to room temperature, and the product was obtained after purification [11].

The specific structural diagram and capture mechanism are shown in Figure 4.

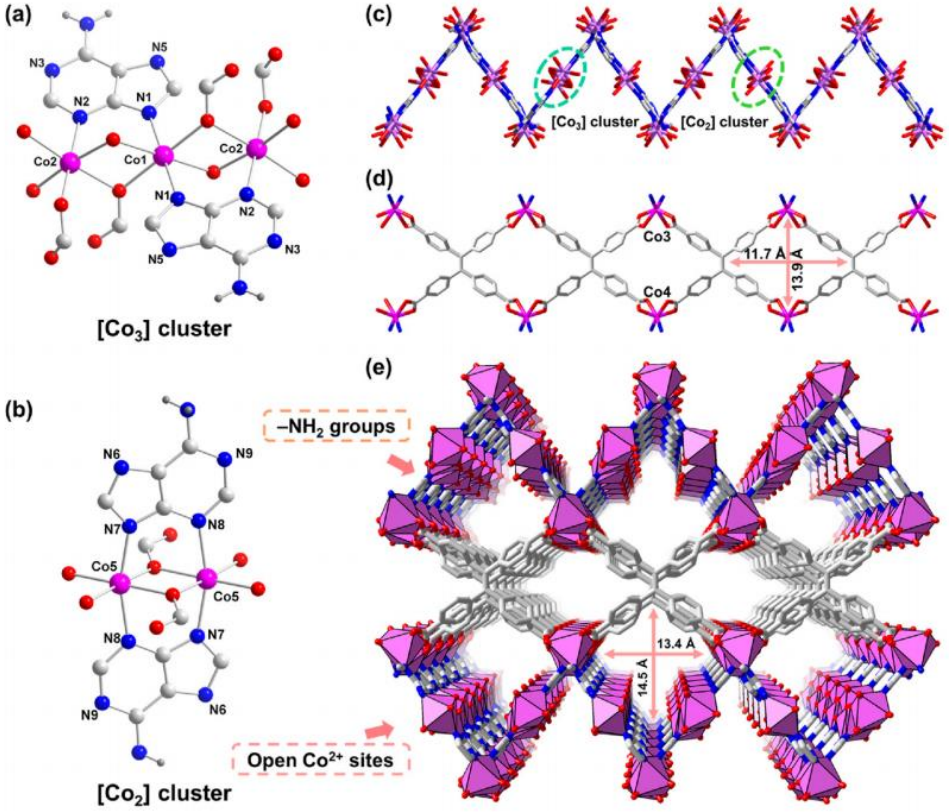

Fig 4. The spatial structure of Co-Ade-TCPE [11].

Similar to Ni-Ade-TCPE, PXRD indicated that Co-Ade-TCPE could be well replicated in pure phase samples. Within a certain pH range, Co-Ade-TCPE also had good chemical stability except for solutions with pH values of 11 and 12. In summary, Co-Ade-TCPE and Ni-Ade-TCPE both have three-dimensional frameworks with one-dimensional open channels and can be modified by unsaturated metal sites. They have good chemical stability within a certain pH range and exhibit excellent carbon dioxide adsorption capability.

4.3. MOF-808 and MOF-808 Modified by TEPA

MOF-808 is a Zr-based MOF with excellent CO_2 adsorption capacity at atmospheric pressure. However, in the field of selectively capturing carbon dioxide from waste gas, which is mostly carried out at low pressure, MOF-808 has not shown outstanding performance in terms of adsorption. Therefore, to find an efficient adsorbent that can selectively capture carbon dioxide at low pressure from waste gas, scientists have functionalized MOF-808 by modifying it with tetraethylenepentamine (TEPA), ethylenediamine (ED), and diethylenetriamine (DETA). As an example, different concentrations of triethylenetetraamine (TEPA) solution were prepared. The dried MOF-808 was then added to the prepared solution. The mixture was stirred under reflux conditions and subsequently separated through filtration. Finally, it was dried in an oven at 373 K to obtain MOF-808-TEPA. After experimental testing, the TEPA-modified MOF-808 showed stronger selective carbon dioxide capture ability at low pressure. Specific comparative data can be seen in Figure 5 [12].

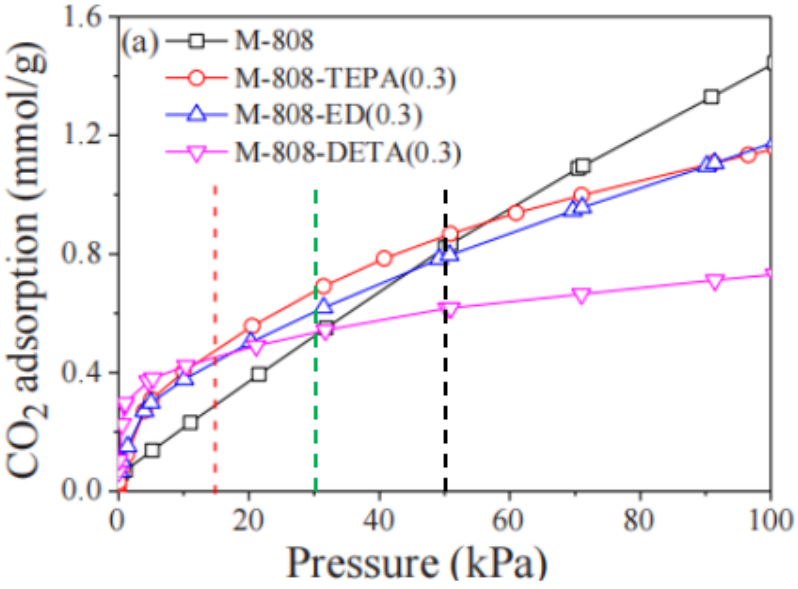

Fig 5. The spatial structure of Co-Ade-TCPE [12].

From Figure 5, it can be observed that for the same pressure, the CO_2 adsorption capacity often depended largely on the type of MOF-808, i.e., the CO_2 adsorption capacities of different branched MOF-808s at the same pressure were different. When the pressure was above 60 kPa, the CO_2 adsorption capacity of MOF-808 was the highest, and among the branched MOF-808s, MOF-808-TEPA had the largest CO_2 adsorption capacity, as shown by the red circle in the figure. When the pressure was 15-50 kPa, the CO_2 adsorption capacity of M-808-TEPA was the best. At lower pressures, approximately below 15 kPa, MOF-808-DETA performed well. At pressures lower than 30 kPa, the CO_2 adsorption capacities of the modified MOF-808s were superior to that of the single M-808.

In summary, modified M-808 has higher CO_2 adsorption capacities compared with single MOF-808 under low-pressure conditions, which is important for capturing CO_2 in waste gases. Meanwhile, experiments conducted by Hyeok Joon Jun et al. also show that an M-808 modified with sufficient TEPA exhibits significant performance in CO_2 adsorption approximately seven times that of the original M-808 [12]. Of course, this applies to using it for CO_2 adsorption or removal under low-pressure conditions.

5. Conclusion

In summary, in terms of both structure and performance, MOFs have significant advantages and promising prospects in the field of carbon dioxide capture. Additionally, by employing different techniques to modify various MOFs (including the addition of different functional groups), improved

adsorption efficiency and selectivity can be achieved, which is crucial for practical applications. This article introduces several major adsorption mechanisms, and concepts such as adsorption enthalpy and adsorption capacity, and demonstrates the different carbon dioxide adsorption capabilities of various MOFs by discussing the performance of several MOFs. Finally, a summary is provided.

Looking ahead, the use of MOFs for carbon dioxide capture holds great promise, and there are numerous MOFs awaiting development, research, and application. Because of their strong affinity for acidic gases and excellent features including crystallinity, stability, enormous surface area, and flexible pore size, metal-organic framework engineering for adsorption purposes is still in the pre-commercialization stage at the moment. In addition to these factors, there are several challenges that need to be addressed regarding the applicability of MOFs in technology, including large-scale synthesis, cost-effectiveness, sufficient purity, and chemical stability. From a structural perspective, modifying the metal centers within the framework is a feasible avenue for carbon dioxide capture. Furthermore, future directions include the development of more MOFs that meet all basic adsorption criteria, requiring continued efforts from scientists in synthesis schemes, property improvement, thermodynamic studies, and reactor design.

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