

Carbon Dioxide Capture in Metal-Organic Framework

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Abstract. The greatly risen level of atmospheric carbon dioxide after the industrial revolution leads to serious problems and concerns, including health issues and global warming. Therefore, the significance of carbon dioxide capture can not be overemphasized. Metal-organic framework (MOF), a brand-new and potential kind of material, can be utilized in several processes of CO₂ capture because of its high capacity as well as high selectivity. In this review, the key parameters for evaluation of the MOF used for CO₂ capture, which is directed related to the performance of materials, are addressed and discussed. Several important and practical evaluation indicators are also mentioned, for economic cost and stability, and tolerance to impurity. Additionally, factors that affect the performance of CO₂ adsorption in both structural and external degrees of MOF are shown and reviewed. This article provides a different perspective of parameters for MOF materials and indicates critical features for the organic linkers and metal ions that are used to build the whole framework.

Keywords: CO₂ capture, metal-organic frameworks, adsorption.

1. Introduction

The increased concentration of CO₂ has the potential to generate several issues, one of which is the concern of climate change. The global temperature raises 1.5 °C can require some ways of carbon capture technology [1]. The main source of CO₂ emissions is coal-fired power stations, and chemical industries, where CO₂ is among the exhaust gases. The process of catching CO₂ before it reaches the atmosphere, transporting, and storing it for hundreds or millennia is known as CO₂ capture (carbon sequestration) [2]. Pre-combustion capture, post-combustion capture, direct air capture and oxyfuel combustion capture are four major ways to collect carbon dioxide. Since other than oxy-fuel capture, all processes of capture are with impurities regarding CO₂, which requests the selectivity and capacity of the materials used in CO₂ ought to be as high as possible. Metal-organic frameworks (MOFs) are greatly potential adsorbents for increasing the selectivity as well as the capacity of carbon dioxide with its changeable structures. Metal cations and organic ligands are two major constituents of MOFs. The materials are always quoted as a mixture of organic and inorganic materials, the mono-, di-, tri- and tetra-valent ligands are the most common organic units [3]. These materials can collect enormous amounts of CO₂, and where these CO₂ molecules are bonded within porous frameworks is critical for creating materials that are much more effective [2].

There are various types of MOF for CO₂ capture. SIFSIX-1-Cu has outstandingly high working capacity while Cu-Sp₅-EtOH has high selectivity of CO₂ versus nitrogen [4]. With a high Q_{st} value, Mn₂L₂(H₂O)₂(DMF) performs well in both selectivity and working capacity in CO₂ capture [5]. In addition, some different metal ions (Co, Zn, Ni, Mg, etc.) MOFs leads to different CO₂ adsorption capacity [6]. In the CO₂ capture process, working capacity and selectivity are the most crucial parameters for MOFs which directly determine the number of adsorbents used in the process. The enthalpy of adsorption, Q_{st}, is another key value in the aspect of evaluating the materials since the change of enthalpy of adsorption values would lead to the changes in selectivity, energy cost, and adsorption kinetics [7].

This review mainly introduces some major parameters for the evaluation of MOFs in CO₂ capture including working capacity, selectivity, the enthalpy of adsorption, and economic cost. This paper also highlights the stability and tolerance to impurities, such as water molecules and hydrogen sulfide.

Additionally, this review discussed some factors that would affect the performance of the adsorption of CO₂.

2. Evaluation of MOFs for CO₂ capture

To ensure that the MOF created is suitable for CO₂ capture, it is essential to introduce some important parameters, which are set to evaluate the performance of one certain material.

2.1. Working capacity

Working capacity (Δq_{CO_2}), one crucial parameter of the evaluation for MOFs in the CO₂ capture, directly determines the amount of adsorbent that is needed in the process of CO₂ adsorption. Gravimetric and volumetric measures are usually conducted with the experimental procedures to find the maximum uptake of CO₂ with one material. The gravimetric uptake is the amount of CO₂ (measured in mass or volume) absorbed per gram (unit mass) by the adsorbent at a stated temperature while the volumetric uptake is the amount of CO₂ absorbed per cubic centimeter (unit volume) of the adsorbent. These two uptake values are the factor that needs to be considered initially in the assessment of MOFs.

However, it is more important and practical to consider the CO₂ uptake at on-load conditions and off-load conditions at work in practice, rather than absolute capacity. That emphasizes the importance of Δq_{CO_2} , the uptake of carbon dioxide in the adsorption (on-load) state minus the uptake of CO₂ in the desorption (off-load) state of certain pressure and temperature in the capture process. This is the most relevant and important measure in the field of the performance of MOFs.

$$\Delta q_{CO_2} = q_{ad} - q_{de} \quad (1)$$

Although measuring the CO₂ capacity at the standard total pressure of 1 bar is relatively easy, the reality is far more complex than this, for example, CO₂ is always mixed with other gases. Therefore, it is more appropriate to consider the partial pressure of CO₂ in the case, which can be presented by adsorption isotherms in Fig. 1. Moreover, the figure also shows different types of isotherms. The majority of MOF exhibit type I isotherm, which is also known as the Langmuir isotherm (Fig. 1). However, the performance of some flexible adsorbents is presented by the type F-IV, which is fairly desirable in the pressure swing adsorption (PSA) procedure, for the Δq_{CO_2} can be nearly 100% of the uptake value [6]. That indicates the fact that the materials in the F-IV type have great potential to be used in the CO₂ capture, compared to other types of the isotherm.

Generally, for MOFs used in CO₂ capture, if the working capacity under the condition of 0.15 bar and 1 bar is greater than 2 mmol g⁻¹, then this material is outstanding for CO₂ capture, especially for direct air capture (DAC). The working capacity SIFSIX-1-Cu is found to be 4.89 mmol g⁻¹ (0.15 bar and 1 bar) [8], which is fairly distinguished, thanks to its SIFSIX ligand. With this special character, compared to other MOFs with relatively low working capacity, it needs much fewer materials to absorb the same amount of CO₂, especially in the large-scale process, which can significantly reduce the cost of manufacturing and regeneration.

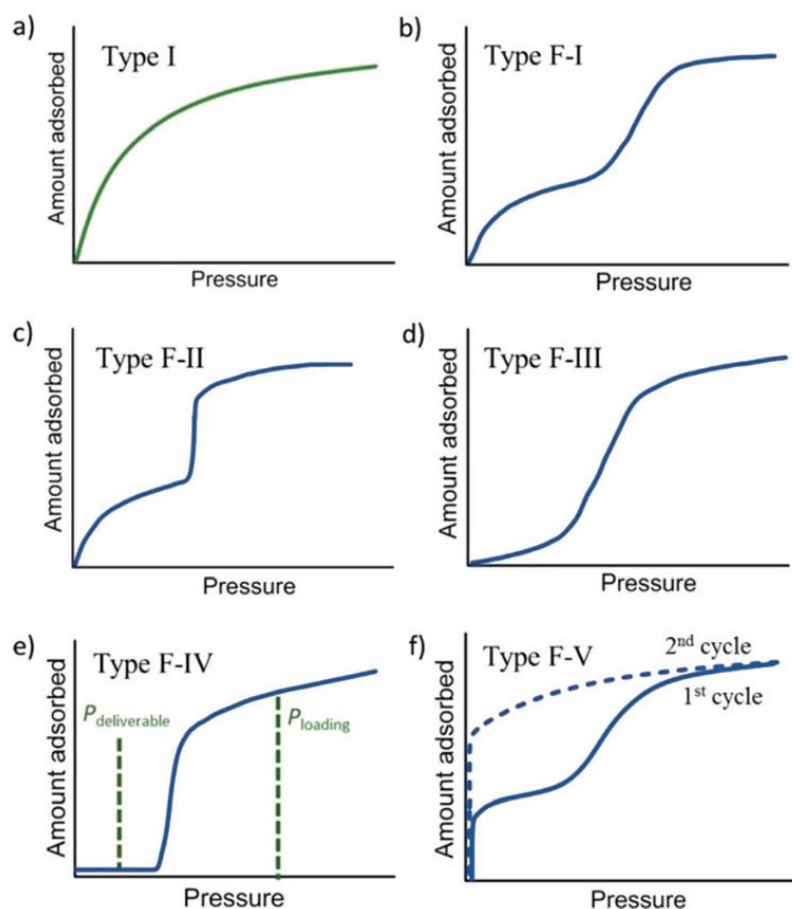


Figure 1. Different types of isotherms of MOFs [9].

2.2. CO₂ selectivity

The definition of CO₂ selectivity of a certain adsorbent is the ratio of CO₂ uptake value over the uptake value of another gas in given conditions including temperature and pressure. And to be specific, for a certain binary mixture, the selectivity of CO₂ adsorption can be presented as follows ($q_{i,j}$ indicates the working capacities of CO₂ and another gas, and $p_{i,j}$ denotes the partial pressure of these gases).

$$S_{ad} = \frac{q_i/q_j}{p_i/p_j} \quad (2)$$

Since pure gas cannot be obtained in reality, this parameter is significant in the evaluation of MOF material, especially in the direct air capture (DAC) and pre-combustion capture, where the amount of other gases is usually high [10]. Selectivity of carbon dioxide versus nitrogen (S_{CN}) is greatly relevant in the process of post-combustion of MOF in CO₂ capture. Cu-Sp5-EtOH is a highly porous material, whose S_{CN} is high and therefore very suitable for CO₂ capture in post-combustion [4]. As one study shows [11], if S_{CN} can be improved to 500 from 100, the economic cost of C-capture can be significantly decreased (>45 to ~30 Euro per tonne of CO₂). Therefore, the selectivity of the adsorbent not only affects the purity of the gas adsorbed but also affects the economics of the process. It is highly desired to create a MOF material whose selectivity is high to reduce the cost and efficiency of adsorption.

The CO₂ selectivity is affected by the type of adsorption, i.e., physisorption and chemisorption in MOFs. Generally, the selectivity of chemisorption will be higher than physisorption, due to the different forms of interaction. Ni-MOF-74, a typical material of chemisorption, is one of the MOFs with the highest selectivity of CO₂ over N₂, 307 (IAST, 15:85) [12,13].

2.3. Regeneration of MOFs

Minimizing the energetical cost occupies an important position in the field of CO₂ capture. The energy cost in the processes of adsorption and desorption can be reduced greatly by fine-tuning the thermo-dynamics of the interaction between adsorbates and adsorbents, which is fairly essential for improving the efficiency of the utilization of energy for CO₂ capture [13]. The regeneration of MOFs is a very important way of the reduction of energy costs. The MOF materials can be regenerated through several procedures: temperature swing adsorption, pressure swing adsorption, vacuum swing adsorption and hybrid methods. In all these processes, the energy cost of adsorption and desorption is an essential aspect to be considered. Therefore, the enthalpy of adsorption (Q_{st}) must be taken into consideration.

The Q_{st} of the CO₂ molecule is one of the fundamental physical characteristics, which indicates the energy released when one mole of CO₂ binding to adsorbents. The magnitude of Q_{st} directly dictates the affinity towards carbon dioxide of the pore surface, which is a determinant of the selectivity of CO₂ and the energy needed to release carbon dioxide in regeneration [14]. Q_{st} values can be computed by Clausius-Clapeyron equation [15].

$$(\ln P)_N = -\frac{Q_{st}}{R} \times \frac{1}{T} + C \quad (3)$$

R denotes the ideal gas constant, T refers to temperature, and C is addressed as one certain constant. Therefore, Q_{st} value can be obtained from the slope of this graph.

Compared with other gases which are more massive in the atmosphere, such as nitrogen and oxygen, since CO₂ has high polarizability and quadrupole moment, it is more suitable for MOF to have an ion with high electrostatic charge or open metal sites. By that, a selective and strong interaction will be established between MOF and CO₂ [16]. Because if the Q_{st} is too high, the regeneration cost would be much higher to break the interactions between molecules; and if the Q_{st} is too low, although less energy would be required, the selectivity of carbon dioxide over other components would decrease, leading to the increase of adsorbent used.

As Zhao et al. indicate [5], the Q_{st} value of CO₂ adsorption of a 3D MOF, named Mn₂L₂(H₂O)₂(DMF), is 39.1 kJ mol⁻¹, a value greater than most distinguished MOFs, such as MOF-5 [17], due to its uncoordinated N-heteroatom, with which the binding strength between the nitrogen atom and CO₂ molecule can be enhanced. The energy used in the desorption stage is greater, leading to a higher regeneration cost. But the CO₂ uptake (32.4 cm³/g at 273 K) is also higher than many famous porous materials without uncoordinated N-sites.

2.4. Economic costs: Based upon substrates

The non-negligible factor of the evaluation of MOF material is the economic cost of substrates since it directly determines whether it can be used in scale-up situations, which is an obstacle to the development of an adsorbent [18]. The practicality of using MOF as adsorbents does not only rely on the physical and chemical properties of MOF itself but also its economic cost of production and substrates. According to one study [19], metal salts are usually not expensive, so the main factor of the economic cost would be the linker ligands. For example, a large number of MOFs are based upon poly(carboxylate) ligands, which need several complex reactions to be prepared. Therefore, how to reduce the cost of ingredients, or how to build a framework that requires less expensive precursors but has excellent performance, is a promising way to explore. Also, the ability of manufacturing in large amounts is essential for practical use.

As one study shows [6], developing aqueous-based synthesis at ambient pressure is one of the most hopeful schemes to reduce the economic cost of manufacturing. For the precursor of linkers, aromatic polycarboxylic acids, such as. Trimesic and terephthalic acids are attractive choices in the large-scale process due to their relatively low cost [20]. Also, reducing the process complexity, for instance, avoiding additional recirculation steps, is an important part of synthesis.

2.5. Stability

Ideal MOFs ought to present good stability under a variety of conditions, such as moist environments and relatively high temperatures during a large number of cycles of adsorption and desorption. Without high stability, the frequency of replacement would be significantly increased. Specifically, the desired material should satisfy strong mechanical, thermal, and hydrolytic stability, especially for those materials which need the step of TSA (temperature swing adsorption).

Since all of the gaseous streams are composed of several gases and may have some gases that are 'toxic' to MOFs (e.g., H₂S, H₂O), the desired MOF material should have a high degree of tolerance to the impurities. Otherwise, whenever impurities are adsorbed, additional purification steps are required [21]. The worse situation is that the whole framework will collapse after absorbing some of the impurities. For example, the MOF-74 series are not stable in the condition of water or steam, for the reason that the frameworks with open metal sites will be easily broken with the presence of H₂O molecule. So, it should be noticed that if these materials are used, the concentration of water or steam, the major impurity, ought to be reduced to its lowest.

However, one study shows by computational screening that MOFs with the structure of a ring with a delocalized π bond which satisfies Hückle's Rule (so-called 'aromatic') generally have a low Henry coefficient for water molecules than other structures [22]. Based on this, Al-PMOF and Al-PyrMOF are proved that they are fairly stable in humid conditions [23]. It is shown that there is no crystallinity loss after immersion in water for 7 days. Therefore, it is an excellent choice to use these MOFs in an environment of extremely high humidity.

3. Factors affecting CO₂ capture using MOFs

The adsorption process of carbon dioxide is mainly affected by the physical and chemical properties of MOFs. High surface areas offer markedly increased uptake capacities than some other materials. Organic ligands containing some basic functional groups are one of the most significant techniques for improving CO₂ collection and separation. Besides that, designing MOFs with characteristics such as open metal sites, different pressure, or surface-area results in the improved acknowledgment of their adsorption amount those performances. MOFs, of course, can use multiple interactions within a single structure to accomplish those remarkable CO₂ adsorptions [24].

3.1. Metal ion

MOFs contain one essential part which is metal ions. Those isostructural MOFs that contain open metal sites need to use a method called partial metal replacement. [25]. There is a series of MOFs that link with Cu(II) and Pd(II) in CO₂ capture. To talk about SIFSIX-1-Cu-type MOF, except the framework can be retained, octahedral geometry Cu²⁺ ions need to be extensively substituted in various ratios with Pd²⁺ ions with square planar geometry which is shown in Fig. 2 [25]. This shape of MOF which is SIFSIX-1-Cu-type MOF can have a high CO₂ adsorption capacity since it contains open metal sites which means it is based on its structure variation. The frameworks' zero-coverage isosteric temperatures of CO₂ adsorption provide essential information on their affinity for CO₂. When this approach is applied to the isoreticular series which is the MOF-74 links with metal, it is observed that Mg-MOF has the greatest carbon dioxide affinity (47 kJ mol⁻¹), and the followings are 26 kJ mol⁻¹ which is Zn-MOF-74, and Ni-MOF-74 is 37 kJ mol⁻¹, then is Co-MOF-74 with initial affinities 41 kJ mol⁻¹. As a result, the high affinity of carbon dioxide confers better charge quadrupole interactions between the magnesium open metal sites and CO₂ in the Mg-MOF-74 due to the ionic nature of the MG-O bond [6]. Besides, when there are similar loading pressures, Mg-MOF-74 has an approximately two to four times higher CO₂ adsorption than the other isoreticular these types of MOF compounds, those Ni²⁺, Co²⁺, Zn²⁺ are among the M elements. Based on previous work, Caskey, et al. found out the change of metal ion can affect the capacity when the temperature and pressure are controlled. Here are some examples, the change of metal ion-X (Mg, Zn, Ni, Co), in 1 bar pressure, Mg-MOF-74 would be the most capable one which is 8.0 mmol g⁻¹, followed by Co-MOF-74 has the

capacity 7.0 mmol g^{-1} , following are Ni or Zn-MOF-74, and their capacity are 5.8 and 5.5 mmol g^{-1} respectively [6].

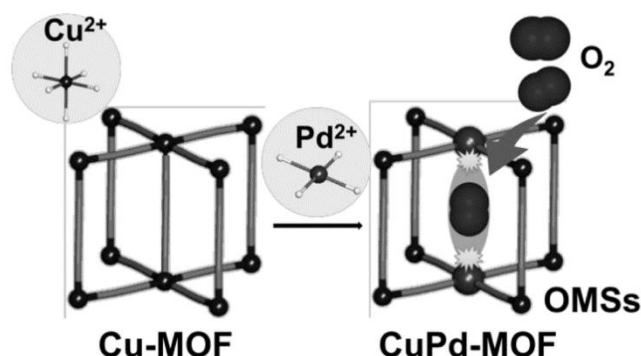


Figure 2. CuPd-MOF's systematic synthesis *method* by partial metal replacement [25].

Additionally, another strategy to boost the CO_2 adsorption capacity is to put MOFs' multimetallic secondary building units on open metal sites [24]. Broadly speaking, open metal sites are produced by conducting a MOF with some coordinated ligands, for example, CH_3OH , H_2O , and HKUST-1 on the secondary building units, with the vacuum and the heat to eliminate these linkages while maintaining the entire structure as a whole. This regularly leads to increased porosity in the activated material [25]. The CO_2 capacity of HKUST-1 with open metal sites under 1 bar and 298 K is 4.1 mmol g^{-1} [26].

3.2. Organic ligands

The organic ligand in MOFs is an organic molecule called a linker. With ligand exchanging or partial ligand exchanging, post-synthetic modification procedures can be employed to replace an existing organic linkage group in a prefabricated MOF with a new linker or ligand. The pores in some situations are the whole framework of MOFs that can be customized for special applications thanks to the interchange. Post-synthetic modification techniques can be used to change the organic ligands [27]. This method often changes the pore size of MOFs. Moreover, the interactions between MOFs and CO_2 will be influenced. Precast MOF crystals are rinsed with the appropriate solvent and then submerged in a fresh linker solution to undergo ligand exchange in this process. The exchange frequently requires the use of heat and occurs over a period. Post-synthetic ligand exchanges allow the incorporation of functional groups into MOFs, however, they cannot survive synthesis because of some factors, for instance, temperature, pH, other reaction conditions, or would build the barriers to synthesis due to competition with donor groups on the ligand [28].

3.2.1. Amine functionalized MOFs.

The stronger CO_2 capture MOFs contain primary alkyl amine-functionalized pores which are shown as R-NHR . Due to their selectivity, they can react with CO_2 and generate covalent C-N bonds [29]. Adding an $-\text{NH}_2$ group (a strong base) into the post-synthetically functionalize MOFs primary group is feasible. As well as to directly synthesize MOFs with NH_2 -based linkages, as shown in Fig. 3 [30]. CH_2NH_2 can functionalize the IRMOF-74-III's pores, and it is covalently bonded with each ligand, then it can collect CO_2 at low pressure [31]. In the ETB-type structure, the functionality of amine can be found. Following this it can be generated by magnesium oxide rods allowing the species IRMOF-74-III to ingather CO_2 even when H_2O is present. Carbon dioxide adsorption occurs at the alky-amine level, with H_2O unwilling to reach the open magnesium site, allowing IRMOF-74-III- CH_2NH_2 to maintain its framework of it, and the measured value of approximate humidity is 65% [32]. At room temperature, which is 298 K, and at 0 to 12.3 bar pressure in this range, IRMOF-3 has a greater CO_2 adsorption capacity from 0 to 14.7 mmol g^{-1} .

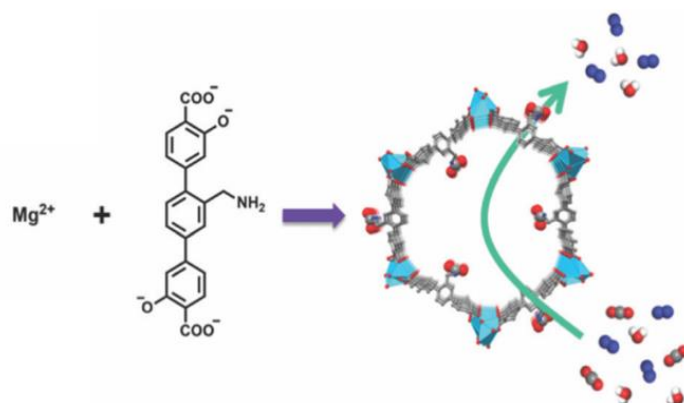


Figure 3. The formation of IRMOF-74-III-CH₂NH₂ with its amine-functionalized linkage and Mg²⁺ ion [30].

3.2.2. Hydroxides.

The C-O single bond can be broken by the hydroxides functional group, which can stabilize the initial M-CO₂ adducts by adding or linking with a substantial hydrogen bonding donor [33]. There are dipolar or quadrupolar interactions between the carbon dioxide and hydroxide functional group, generating increased CO₂ uptake and the same amount of heat of CO₂ adsorption [34]. A variety of MOFs linked with hydroxide can increase the capture, and high temperatures for adsorption, the relevance of OH's involvement has been studied [35]. (OH)-decorated [M₂(OH)₂(BPTC)] adsorption sites. M means metal, which can be In, Ga, and Al. They can demonstrate that the cis-μ₂-OH groups can interact with the CO₂ capture in the end-on fashion via intermediate to weak hydrogen bonding [36]. This leads to a result of the Al (III)-OH...C(=O₂) has the most significant bond between energy and adsorption heat. Therefore, the adsorption capacity of the MOF link with OH can become more extensive. [36] All OH-functionalized materials appear to be potential candidates for practical CO₂, based on these findings.

3.3. Surface area

The increase in the surface area of MOFs contributes the CO₂ adsorption. By using the calculated Langmuir surface of these two MOFs, which are InOF-1 (1065/1093 m² g⁻¹) and GaOF-1(517/570 m² g⁻¹). It shows the highest CO₂ adsorption value of 270.9/131.1 m³g⁻¹ at a temperature of 77 K that equivalent to BET which is the reversible type-I isotherms. Besides, at temperatures 283K and 295K, the thermal outcome of carbon dioxide adsorption of GaOF-1 is 18.31 kJ mol⁻¹, then followed by InOF-1 which is 11.98 kJ mol⁻¹.

3.4. Pressure

When the affinity of MOF changes, the capacity of carbon dioxide adsorption will be changed under several different pressure ranges. The room temperature CO₂ adsorption isotherm in HKUST-1 looks like a typical Type I isotherm. If the majority of the gas is adsorbed at relatively high pressure, it cannot indicate a high affinity of this type of MOF. However, if the gas is adsorbed under a relatively low-pressure condition, then results in a "knee" shape that can indicate a high affinity of that of MOF for CO₂ under given pressure [37]. These settings made CO₂ adsorption intriguing in terms of it from gas since the material has a high CO₂ uptake working capacity [38].

4. Conclusion

In conclusion, MOFs have been proven to be a successful material in CO₂ capture. In this review, the evaluation and factors of MOFs in CO₂ capture were mainly reviewed. For CO₂ capture, the performance of MOFs can be evaluated based on working capacity, CO₂ selectivity, regeneration of MOF and Q_{st}, economic cost, and stability and tolerance to impurity. In addition, metal ions, organic

linkers, and pressure are the main factors in CO₂ capture using MOFs. For metal ions, the changes in metal ions, and changes in open metal sites, can directly affect affinity. The stronger affinity will lead to more adsorption capacity. For organic linkers, the different structures of MOF can be influenced differently, such as amine-functionalized MOFs and those linked with hydroxides(-OH). Different organic linkers will affect the pore size and then change interaction. In addition, the different pressure surroundings can also affect the performance of CO₂ adsorption.

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