

Different CO₂ Capture Methods Based on Metal-Organic Frameworks

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Abstract: The increasing human production activities have led to an increase in carbon dioxide (CO₂) emissions year by year, and the CO₂ concentration in the general atmosphere has continued to increase. The increase in the concentration of CO₂ in the atmospheric environment brings a series of environmental problems, which in turn destroys the earth's ecology. How to remove CO₂ from the atmosphere has become the focus of the current research field. In this research, the advantages and disadvantages of traditional CO₂ capture materials, and the advantages of MOFs itself were introduced, and followed by the introduction of M₂(dobdc) which act as an MOFs type, and the related carbon capacity as well as preparation step, physical and chemical properties of MOF-801/PEBA with its performance and experimental data for carbon capture. The rht-MOF-7 that modified by amine and triazine functional groups shows high affinity for CO₂, and the capture capacity of MOFs when working with amine and fluorine are also mentioned. And the CAU-1 can achieve a modest CO₂ uptake with a high adsorption due to equal heat. The description of pore size adjustment and active site distribution effecting carbon capture is also discussed.

1 INTRODUCTION

Industrial production and anthropogenic emissions have caused a sharp rise in atmospheric carbon dioxide (CO₂) levels. The amount of CO₂ in the atmosphere is expected to continue to grow, and experts are still unable to address large-scale emissions. The continued increase in the concentration of carbon dioxide in the atmosphere has brought about a series of knock-on effects. For example, rising CO₂ concentrations lead to global warming, causing serious damage to the earth's ecological environment. Global warming is directly responsible for different serious problems, such as sea level rise and food security. In order to avoid further damage to the earth's ecological environment, reducing carbon dioxide emissions or removing CO₂ already in the atmosphere has received increasing attention.

During the daily industrial process, a diverse of various functional materials have to capture CO₂ being emitted and then through regeneration (Sumida, 2012). First step needs accurate selectivity and high affinity between materials and the gas to make sure CO₂ is completely removed. And the second step requires abundant energy to break the binds, let material gets rid of CO₂. In addition, the

amine method to capture CO₂ holds several advantages, such as simple operation and high CO₂ removal efficiency. Moreover, they are commercially available and improvements on the method have been made over time. For instance, the absorption performance of the whole method will be further improved if a mixture of various solvents is used as the absorption liquid for CO₂, achieving the best carbon capture performance. However, the existing amine method does have various problems and limitations. Firstly, such capture process is very energy-consuming, specifically in the regeneration of absorbents. Due to the high stability of products formed in the chemisorption process, the backward reaction, which is the desorption process, is not favored, therefore high energy is required for regeneration of the aqueous alkanolamine absorbents. Furthermore, the corrosive nature of amine solutions toward the vessels limits the concentration of alkanolamine species. And it is required to be heated to a regeneration temperature, leading to great regeneration energy and derived costs. The amine method also has limitations like relatively low stability towards heating and decomposition of amine over time, leading to lower performance in absorption over time.

Although these methods are very effective, there

are still some problems. For example, the problem is that the existing methods for removal CO₂ will lead to high cost and concerns about the efficiency and stability of the whole process. In addition, due to the energy-intensive nature of current processes, new technologies are required to reduce energy requirements. Porous materials have been studied, aiming to replace aqueous absorbents, as they have the potential to greatly reduce the energy costs in carbon capture processes as well as increasing the efficiency of such processes (Belmabkhout, 2016). Zeolites are microporous aluminosilicate minerals, which have high chemical and thermal stability. Most importantly, as solids, zeolites have much lower heat capacity as compared to aqueous alkanolamine solutions, thereby resulting in a lower energy penalty for regeneration. Moreover, zeolites have a well-developed structural chemistry, which would lead to optimized zeolites for carbon capture processes. However, zeolites' main limitation is the hydrophilic nature, so water vapor would compete with CO₂ for adsorption sites and the porous materials will get saturated with water vapor eventually, leading to lower adsorption capacity for CO₂ over time. Activated carbons are carbons produced from carbonaceous source materials, possessing pores. Compared to zeolites, activated carbons are hydrophobic, therefore the issues from water vapor are not main concerns. Activated carbons have high surface areas and therefore high adsorption capacity. However, due to the uneven distribution of pores and the various pore sizes in activated carbons, they are more suitable for high-pressure gas separation applications compared to low-pressure carbon capture processes, such as trace CO₂ capture. Although both zeolites and activated carbons can be used to achieve efficient carbon capture, there are some disadvantages. For zeolites, they are outstanding in many aspects but it can be easily saturated by water vapor. For activated carbon, the pores for activated carbon do not have uniform size, even though it has high surface area, but the adsorption capacity in low pressure condition is not satisfactory.

To this end, the development of new high-efficiency carbon capture materials has become a current research focus. Moreover, different types of carbon capture functional materials have also been gradually developed, such as metal-organic frameworks (MOFs). MOFs are a kind of compounds with one, two- or three-dimensional structures formed by the coordination of metal ions or clusters with organic ligands. People use MOFs for gas storage because of the pores in it. MOFs may help increase

the energy density of the gas stored in the tank, thereby increasing travel distance or reducing the space required for the tank, rather than increasing the pressure in the tank, which results in high tank weight and compression costs. Compared with the two porous materials introduced above (zeolites and activated carbons), the use of MOFs shows great advantages in carbon capture because they are tunable in both porosity and chemical functionality. For example, in the carbon capture process, there are synergistic effect that can result in rapid and strong adsorption of CO₂ in the pores, excluding larger and smaller molecules, make the material has high selectivity for CO₂ when compared with Reactive amine-containing materials or complete molecular sieves. As a result, MOFs are expected to replace zeolite and activated carbon for carbon capture in the future.

In general, this research will mainly introduce the synthesis of several typical MOFs materials and their performance regulation. On this basis, the carbon capture performance of these MOFs materials was further systematically analyzed.

2 MOFS-BASED CO₂ CAPTURE

MOFs materials have been widely used in the selective separation of gases and show attractive application prospects, due to its highly coordinatively unsaturated metal surface sites. One notable example is the use of the prepared Mg₂(dobdc) for gas separation (Sumida, 2012). As the CO₂ molecule features electronegative O atoms and an electropositive C atom, any metal site that could donate or accept electrons would be great adsorption choices, as shown in Fig. 1. However, many current materials with such features perform rather average (Liu, 2019), such as Cu-BTC which had only modest carbon capture capabilities, due to low isosteric heat of CO₂. Even the best adsorption capacity reported, Mg-MOF-74, was comparable to other sorbents like zeolites (Liu, 2019). However, strongly basic metals with unsaturated coordination sites like Mg and Cu have great potential as building blocks for the preparation of new MOFs-based functional materials to capture CO₂. Increasing the number of open metal sites allows greater opportunities for gas-MOF interactions, with metals with multiple oxidation states yielding some of the best CO₂ adsorption values (Aniruddha, 2020).

For instance, MOF-801 resembles UiO-66 in terms of its backbone architecture and exhibits a high affinity for CO₂ as a result of the coordination of

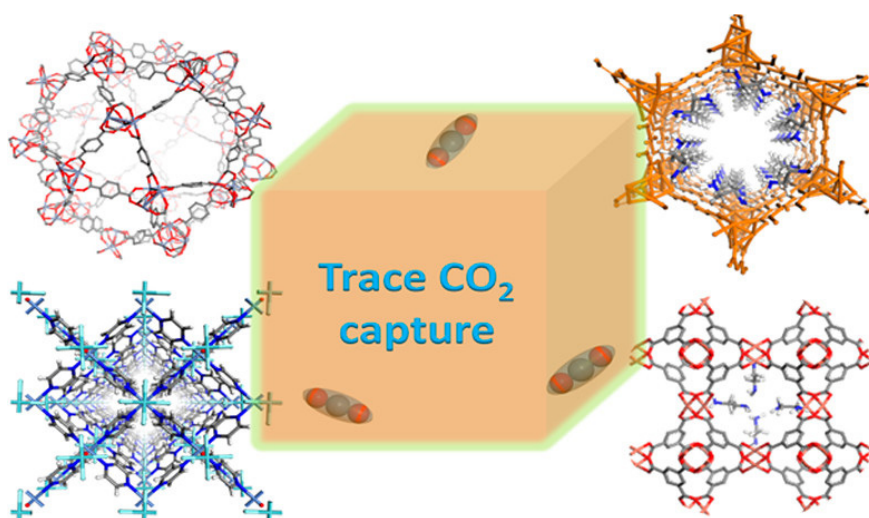


Figure 1: Application of MOFs materials for CO₂ capture (Liu, 2019).

hydroxyl groups to Zr clusters (Sun, 2019). The MOF-801/PEBA composite membrane had much better CO₂ permeability and selectivity. MOF-801 particles are created via a multi-step process. In an autoclave, fumaric acid and ZrOCl₂ was dissolved in a mixture of N, N-dimethylformamide (DMF) and formic acid (20:7 by volume). The hydrothermal synthesis was placed in an autoclave at 130 °C for 6 hours, after which the white particles were precipitated and washed at least three times with DMF and methanol. The cleaned particles underwent solvent exchange with methanol and three DMF rinses per day for three days in a row. To create the activated MOF-801, the solvent exchange particles were vacuum dried at 150 °C for 12 hours. An ethanol/water solvent was used to disperse MOF-801 nanoparticles, and the mixture was agitated and sonicated for two hours. The PEBA was then combined with the MOF-801 dispersion at 80 °C while being stirred and refluxed for two hours. A mixed matrix composite membrane made of MOF-801/PEBA was created. In order to create a pure PEBA composite membrane as a control, the PEBA solution was spin-coated on the PAN support under the same circumstances. The PTFE petri dish also develops a thick layer. The films were dried for two to three days at ambient temperature, the solvent was then removed and vacuum dried. The weight of MOF divided by the sum of the weights of MOF and PEBA was used to calculate the loading of MOF-801 in the film.

The capacity of mixes is assessed through measurements of gas permeation. A constant volume system was used to measure the permeability of pure gas at 20 °C. Before measuring each gas, the

membrane and permeation system accumulated overnight. Under a specific pressure, gas is pumped into the gas reservoir, and the sensor records the permeability's change as a function of pressure. The prepared MOFs were characterized by using SEM, XRD, FT-IR and TGA, as shown in Fig. 2. The synthetic MOF-801 octahedral structure had a homogeneous particle size distribution according to the SEM images. These tiny nanoparticles make it easier to create mixed-matrix composite films that are uniformly thin. XRD was further used to examine the crystal structure of the produced materials, and the thermogravimetric analysis (TGA) was used to examine the thermal stability of the produced materials. The outcomes demonstrate that at 500 °C, the synthesized MOF-801 goes through three steps of mass loss. The first minimal weight loss of the activated sample occurred prior to 100 °C and was brought on by the elimination of moisture. The second weight loss occurred at about 250 °C and was caused by the evaporation of visitor molecules from the pores of MOF-801. These molecules included solvents like DMF and methanol. The final breakdown points of MOF-801 shows at about 500 °C after additional heating, proving the substance's high thermal stability. Although MOF-801 has a greatly enhanced affinity and adsorption capacity for CO₂, it has a relatively low adsorption capacity for N₂. The adsorption capacity of CO₂ grew significantly as the adsorption operating pressure increased, whereas the adsorption capacity of N₂ barely changed. This behaviour suggests that particular CO₂ gas adsorption sites exist, proving that CO₂ has a greater affinity than N₂. The outcomes demonstrate the potential of MOF-801 as a N₂-selective CO₂ adsorbent.

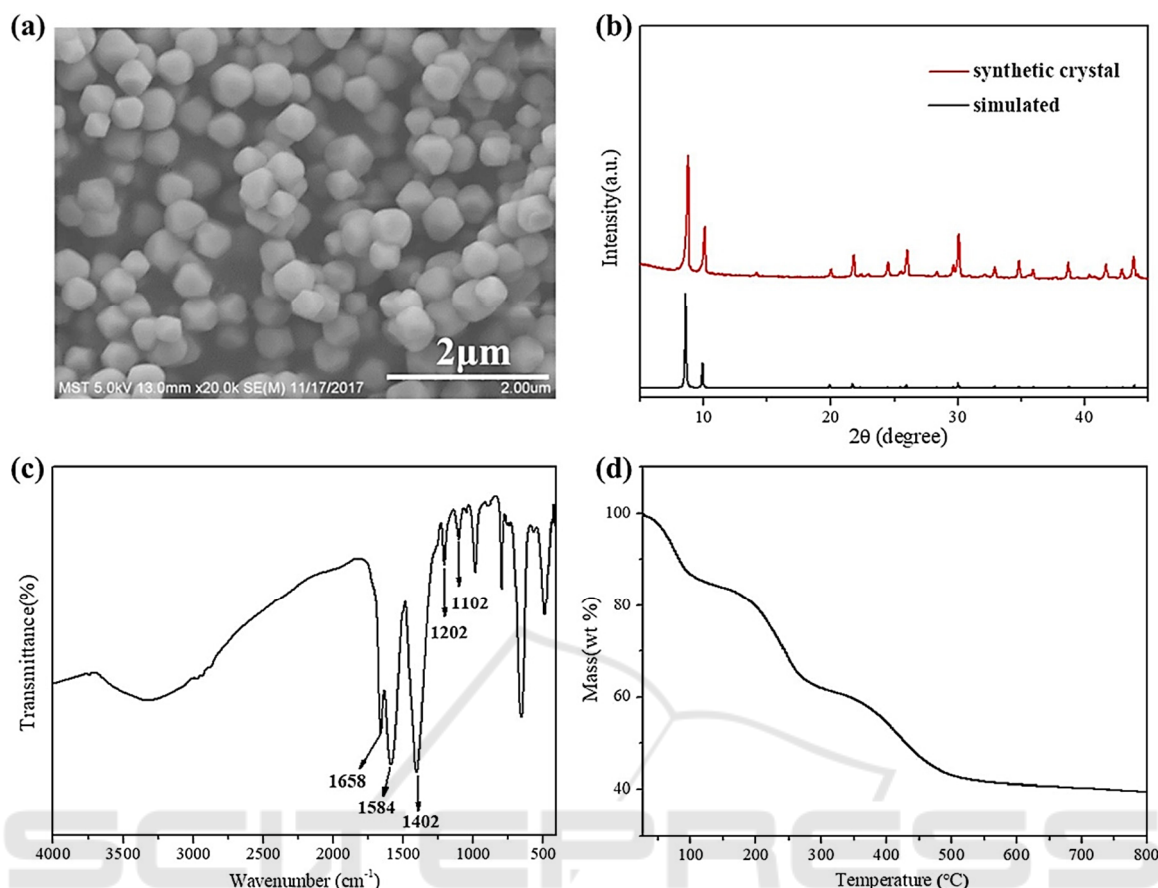


Figure 2: SEM, XRD, FT-IR and TGA characterization of the prepared MOFs materials (Sun, 2019).

If some active functional groups are introduced in the preparation of MOFs materials, the prepared MOFs materials can exhibit better carbon capture effect. For example, the prepared rht-MOF-7 displayed high affinity for CO₂ (Sun, 2019), where the added functional groups including amine and triazine functional groups enhanced attraction towards CO₂. Enhancement of CO₂ capture can be achieved with functional groups, where the introduced different functional groups can donate electrons. The outer orbital of the N atom in the amine group has a pair of electrons that can be used for contribution. Two approaches to tethering amine units to MOFs to enhance CO₂ capture are achievable, but amine corrosion is not something that most MOFs can experience, so the stability of MOFs is particularly important. For example, it is to attach amine groups to organic ligands. In the pores of Cu-BTtri, the N atom in the amine is bound to the C atom of CO₂ through the strong Coulomb force, and the O atom of CO₂ is bound to the copper atom of the unsaturated site (Sumida, 2012). Apparently, the

amine-grafted Cu-BTC could not over-absorb a satisfactory amount of CO₂. At higher CO₂ partial pressure, the amine units blocked the small pores and reduced the absorption capacity compared with bare materials. Therefore, some mesoporous MOFs were used for the modification of amines. A family of fcu-MOFs that were based on ligands that were rare earth metals, fluorinated and non-fluorinated and either included or excluded hetero-functionality was analyzed. This enabled fine-tuning of the MOFs such as the fact that earth metals were electron rich and possessed high charge density that was localized. An MOF that contains open metal sites but no tetrazolate and fluoro groups, Y-pek-MOF-1 showed one of the highest CO₂ volume adsorption till today. Zn₄O(BDC)₃ has functionalized ligand analogues by differing the substitution of linear dicarboxylate linkers, and are also referred to as IRMOFs, which are distinguished by different pore sizes and functionalities (Sumida, 2012).

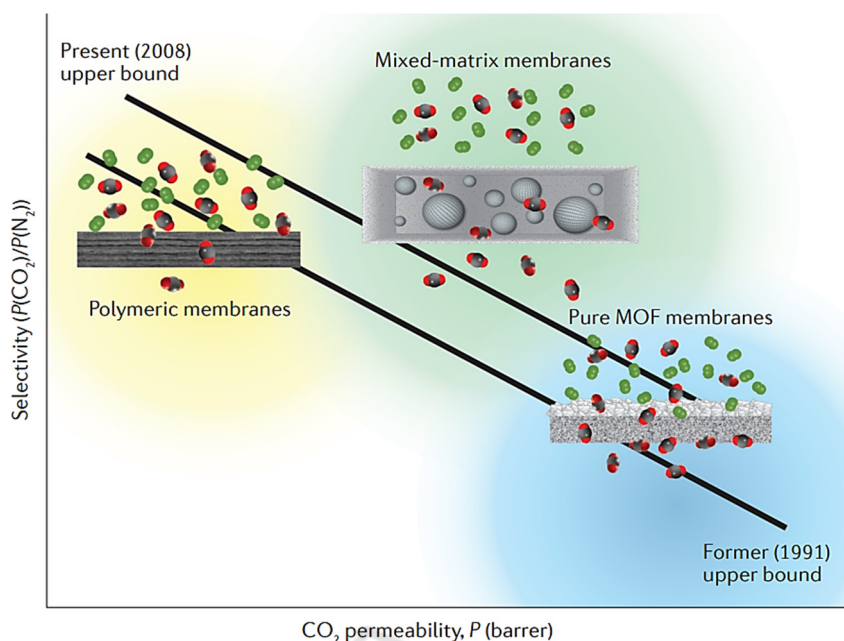


Figure 3: The selectivity and permeability of CO₂ with the prepared MOFs materials (Trickett, 2017).

The inclusion of heteroatoms, atoms which are not carbon, usually those which are nucleophilic, serve as strong interactors with CO₂. Amines are of great interest, and one such MOF, CAU-1 achieved a modest CO₂ uptake with a high isosteric heat of adsorption (Trickett, 2017). As shown in Fig. 3, the as-prepared MOFs material exhibits excellent performance in carbon dioxide selectivity and permeability. In addition, according to the relevant research, the CAU-1 was synthesized by solvothermal method (Zhong, 2021). The samples were heated to 125 °C in an autoclave for 5 h, cooled to room temperature, and rinsed three times with CH₃OH. The impurities in the channels were then completely removed by three purifications (5-6 h with magnetic stirring) with deionized water.

SiFSiX features ultra-micropores, whose size can be precisely fine-tuned by trying different combinations of organic ligands and metal cations in the overall structure. For example, SiFSiX-3-M was made from MSiF6 and features a uniform distribution of adsorptive sites due to its one-dimension channel which is tailored for CO₂ capture. Isostructural analogues of these MOFs also show phenomenal CO₂ capture capabilities. CALF-20 provides nanosized pores which form weak but preferential binding to CO₂ over water. It prevents the issue of contaminants ruining the entire process by inhibiting the formation of hydrogen bonds to water, preventing water from adsorbing onto the material and blocking CO₂ adsorption. The key highlights of CALF-20 is that it

features a massive surface area, displays selective CO₂ physisorption at high capacities and has low energy requirement (Ozin, 2022). Due to its tailored one-dimensional channels and uniformly distributed adsorption sites, SiFSiX-3-Cu exhibits a CO₂ capture capacity of 1.24 mmol/g. When using NbOF clusters, the obtained NbOFFIVE-1-Ni is more attractive to CO₂ than SiFSiX-3-Cu because the attraction of negatively charged fluoride anions and positively charged carbon atoms can form a one-dimensional chain to attract CO₂. In addition, the results show that the small pores in it allow the MOFs to possess a strong CO₂ capture capability. Therefore, when CO₂ passes through the small hole, special deformation occurs, which slows down the gas propagation. The uniform distribution of fluoride anions also helps SiFSiX-3-Cu and NiOFFive-1-Ni achieve strong ability when capture. The high affinity of Fluorine ions attracts C cations in CO₂, increasing the mutual adsorption and reaction rates (Bhatt, 2016). As shown in Fig. 4, compared with other porous materials, the prepared MOF materials also showed excellent performance in CO₂ adsorption. Of course, in order to improve the CO₂ adsorption capacity of the MOFs material, the open metal sites of the MOFs material can also be regulated (Montoro, 2012).

3 CONCLUSION

This research introduces the synthesis methods of

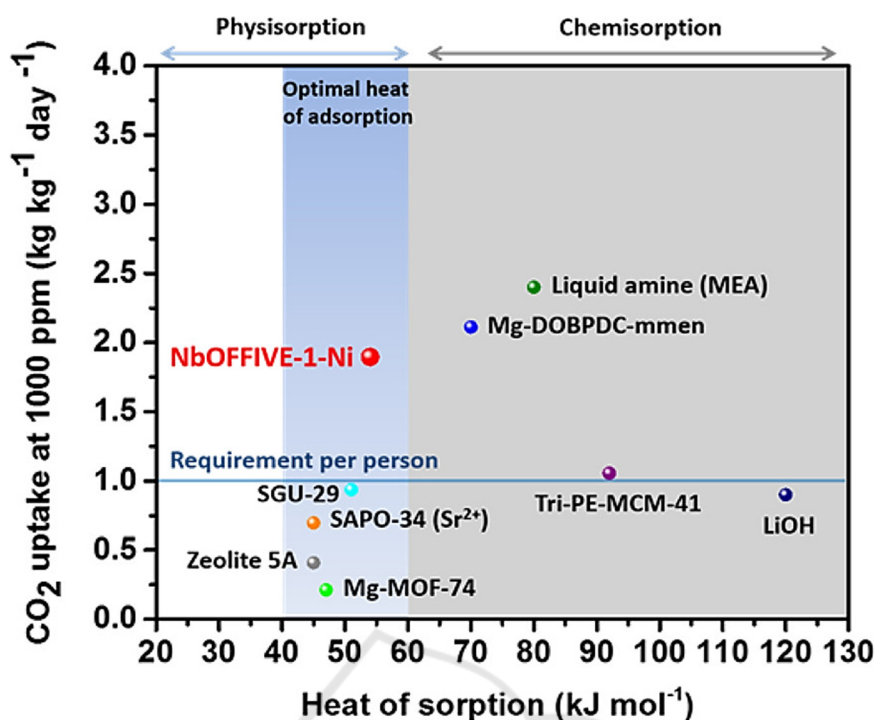


Figure 4: Performance of the heat of adsorption- CO_2 uptake with different porous materials (Bhatt, 2016)

different MOFs materials and their performance in carbon capture. To further improve the carbon capture efficiency of MOFs materials, different preparation strategies were used, such as surface modification. In the future, as more and more solid sorbents, especially porous materials, are researched and produced, key parameters need to be evaluated to discover the optimal solid sorbent carbon capture process. First, the adsorption capacity of the solid adsorbent needs to be high. Second, the adsorption kinetics should favor the separation of CO_2 from other gaseous components such as nitrogen, oxygen, and carbon monoxide. The adsorption rate should also be relatively high, resulting in higher industrial efficiency. In addition, the adsorption should have high selectivity to CO_2 , which not only can capture a higher proportion of CO_2 , but also ensure the high purity of the captured CO_2 . From the perspective of energy demand and cost, the regeneration conditions should be mild, so the temperature and energy required for the regeneration of solid sorbents are relatively low, which is advantageous compared to traditional aqueous sorbents. However, there is a trade-off between the working capacity and the regeneration requirement, as the higher the adsorption enthalpy, the more favorable the adsorption of CO_2 , but also the higher heat required for the desorption process. In addition, the solid adsorbent should have high stability, especially against steam and other

impurities such as NO_x and H_2S . Therefore, if the material is to be used in real industrial applications, life cycle and performance analysis should not be performed under N_2/CO_2 mixed conditions, but more engineering evaluation should be performed in a dynamic environment. Finally, when it comes to industrial applications, it is always important to scale up the yield of various porous materials, as well as the cost per process.

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