Carbon Dioxide Capture in Metal-Organic Frameworks

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Abstract: Excessive carbon dioxide emissions have caused several environmental problems. This has an unpromising impact on the Earth's ecosystem. Metal-organic frameworks (MOFs) attracted more and more attention because of their extraordinary specific surface area, adjustable framework and excellent stability in the effective capture and conversion of carbon dioxide. This article introduced the main synthesis methods of MOF materials, including ionothermal synthesis, mechanochemical synthesis, sonochemical synthesis and ultrasound synthesis method. Each synthesis method of MOFs has its advantages such as shorter reaction times or faster screening rates, which contribute to the development of the synthesis of MOFs. The key evaluation metrics for carbon dioxide capture using MOFs including adsorption isotherm, adsorption ability, enthalpy and high selectivity also were discussed, which have a direct impact on the capture of carbon dioxide. Additionally, the main carbon capture by MOFs in power plants, such as post-combustion capture, capture before combustion and oxy-fuel combustion were also highlighted.

Keywords: Carbon dioxide; metal-organic frameworks; synthesis

1. Introduction

Industrial development in recent years has led to a global society that is largely dependent on the burning of fossil fuels. The burning of fossil fuels produces a gas called carbon dioxide. Carbon dioxide is by far one of the most significant greenhouse gases. Excessive emissions of carbon dioxide contribute to global warming as well as to bad. Shifting energy sources from fossil fuels to clean energy is feasible, but such a change would require considerable changes to the current industry and many technologies are not yet developed. The development of technologies that can effectively capture and store carbon dioxide before retrofitting existing energy facilities is therefore crucial to protecting the environment. The most serious problem facing CO_2 capture today is the huge energy loss that occurs during the capture process. Based on current technology, the cost of capturing CO_2 from power plant emissions is seven-tenths of the consumption of the CCS [1]. The cost of capturing CO_2 must therefore be reduced if large-scale capture is to be achieved.

Achieving CO_2 capture requires materials with high selectivity for CO_2. At the same time, the material needs to be stable during capture. The high density of the material ensures that the adsorbed material is as small as possible. One of the current commonly used capture material is alkanolamine aqueous solution. The other one is porous materials. Alkanolamine aqueous solution has some drawbacks when it is used to adsorb CO_2. Alkanolamine aqueous solution is relatively unstable when heated. The decomposition of the amine causes the adsorption performance to decrease over time. Also, amine solutions are corrosive to the vessel. The low specific heat capacity of solid porous adsorbent materials makes them excellent materials for capturing carbon dioxide. One of these is zeolite, which has excellent chemical and thermal stability when capturing carbon dioxide. It is a porous aluminosilicate material.

Metal-organic frameworks (MOFs) are rapidly developing in several fields such as gas storage, multiphase catalysis, molecular catalysis and drug delivery. This has attracted a lot of attention. MOFs have an excellent surface area. Meanwhile, the properties of MOFs can be tuned. MOFs are synthesized in many different ways, usually by combining a metal ion with an organic ligand to form

a crystal. Many factors affect the properties of the material. The extraordinary surface area of the MOFs greatly makes the ability to absorb carbon dioxide stronger. For example, the MOF-177 has a storage density of up to 320 cm^3(STP)/cm^3 at a pressure of 35 bar [1]. By far the most studied MOF is $ZnO_4(BDC)_3$. It is also called MOF-5 (Fig. 1). It is composed of tetrahedral clusters connected by $[Zn_4O]^{6+}$ligands. This makes it cubic and the lattice is three-dimensional. Furthermore functionalized derivatives of this type can be prepared using other linear dicarboxylic acid linkages. The length of the linker and the functional groups on the aromatic backbone of this structure can be easily modified while maintaining the overall framework connectivity. Such materials are known as reticulated metal-organic frameworks. The different pore sizes and pore functions of MOFs determine the various properties that can be achieved by using different linker types to tune the material. Adsorption capacity is an important factor to be considered in the evaluation of MOFs. The weight of carbon dioxide absorbed, is the amount of carbon dioxide that is adsorbed in one unit mass of adsorbent material. It determines the mass of MOFs needed for forming the adsorption bed needed. Volume capacity is the density of carbon dioxide stored in the adsorbent material and this parameter has an important impact on the size of the adsorbent bed. These two are significant in terms of the efficiency of heating of the MOF. They also influence the loss of energy needed for the regeneration and adsorption of the carbon dioxide capture material. Materials with large surface areas tend to possess higher capacities as observed under high pressure. Some materials with a medium surface area also possess excellent adsorption properties due to their high-affinity density of exposed metal cations. The adsorption performance at low pressures depends largely on the chemistry of the material pores. Those materials with highly functionalized surfaces tend to have a higher capacity [1].

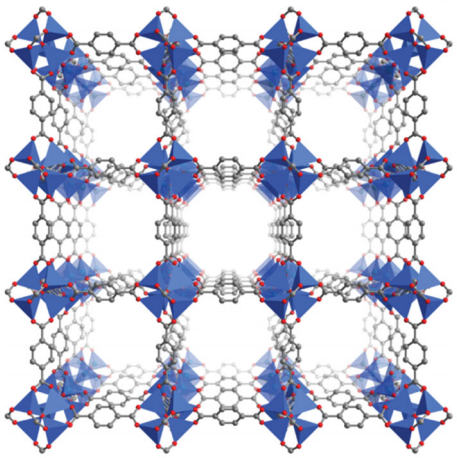


Fig. 1 The structure of MOF-5 [1].

2. Synthesis of MOFs

MOFs have a low frame density, a great surface area and a tunable surface structure. This allows MOFs to have good CO_2 storage capacity. The way of synthesis MOFs is usually using modular synthesis. In this way, metal ions and organic ligands combine to form crystals in a multivacancy network. In recent years, an increasing number of methods used to synthesize MOFs have emerged, each requiring different conditions. The adjustment of factors like temperature, time of reaction and solvent during the synthesis steps can all have an impact on the properties of the material. In most methods, the regent used in the process takes up the voids in the pores of the MOF. Using a vacuum or heat these solvents occupying the internal pores can be eliminated nevertheless to obtain an extraordinary surface area. When applied to CO_2 capture, these surfaces can be well used for gas separation and can be adjusted to obtain good selectivity. This section briefly describes several synthetic methods (ionothermal synthesis, mechanochemical synthesis, sonochemical synthesis and ultrasound) used to synthesize MOFs, each of which has its advantages such as no need for solvents, shorter reaction times, or faster screening rates.

2.1. Ionothermal Method

Using ionic liquids as solvents and agent is the method called ionothermal synthesis. Ionic thermal synthesis is used to prepare MOFs. The most important feature of the ionothermal method is that it uses ionic liquid as a solvent. Many kinds of ionic liquids with cations like pyridinium-based ionic liquid possess chemical properties similar to those of chemicals known to act as excellent templates. An important characteristic of ionic liquids is that they have no detectable vapor pressure. This feature is a good way of avoiding the difficulties associated with high hydrothermal pressures. Recent works report the ionothermal synthesis of EMImCd(BTC) with the ionic liquids EMImBr [2].

2.2. Mechanochemical Synthesis

The synthesis of MOFs mostly requires large amounts of time and organic solutions, which have an inevitable impact on the environment. One of the advantages of mechanochemical synthesis is that it reduces the use of organic solutions very well. There are three different methods of mechanochemical synthesis [3]. The first is neat grinding. Neat grinding enables reactions to be conducted without the need for a solvent. The second is liquid-assisted grinding. It uses the amount of liquid as catalysts to increase the fluidity of the reagents, resulting in a faster reaction time. The third is ion-and-liquid assisted grinding. It uses catalytic liquids containing salt additives to obtain faster reaction rates. In 2006, it was reported that using a neat grinding method to prepare microporous MOFs HKUST-1 (Fig.2). It was achieved by combining copper acetate monohydrate ligand with isonicotinic acid, with by-products eliminated by heating [4].

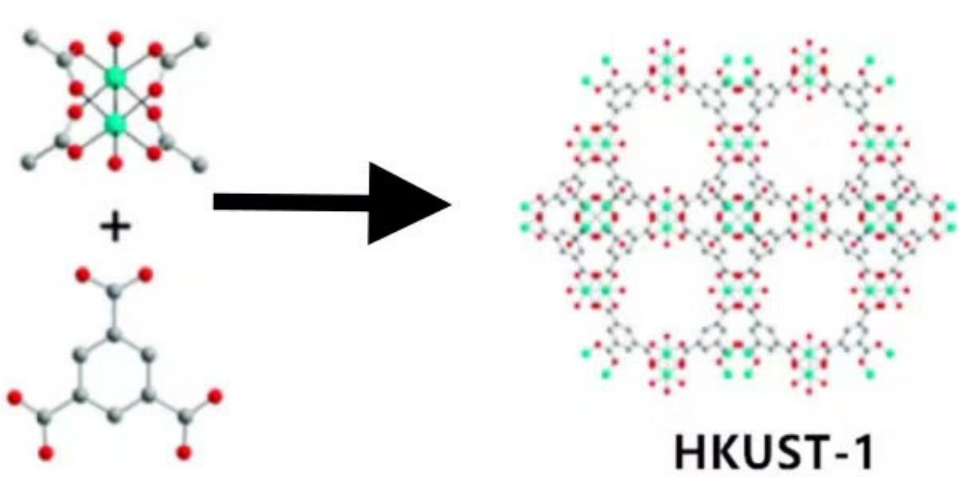


Fig. 2 HKUST-1 from combining copper salt with trimesic acid [4].

2.3. Sonochemical Synthesis

Sonochemical Synthesis methods allow for uniform nucleation and can reduce crystallization times by a significant amount [5]. The main features of biochemistry are the creation, growth and collapse of bubbles. This generates extremely high local temperatures and pressures which can produce excellent heating and cooling rates. The reactivity of the metal as a reactant is enhanced by this high-intensity acoustic wave. In 2008, MOF-5 was synthesized using sonochemical methods for the first time. The time taken to synthesize was greatly reduced and the crystals were found to be significantly smaller [5].

2.4. Ultrasound Synthesis

Ultrasound is a very fast, simple method. It is friendly to the environment. It has been used extensively in the synthesis of organic aspects. Recently it has been used for the synthesis of MOFs. It is reported that When ultrasound is used to synthesize copper-based MOF (STAM-1), a completely

different product is obtained, which is named STAM-2. The STAM-1 is dispersed in water and then irradiated with pulsed ultrasound for several hours. At this point, significant cloudiness can be observed in the suspension, together with a slight blue color.

3. Evaluation of MOFs Materials for Carbon Capture

3.1. Adsorption Isotherm

When evaluating carbon capture materials, Scientists use single-component gas adsorption isotherm data. A proven and popular technique for determining the surface area of a material is using it to adsorb nitrogen at low temperatures. It can also determine the size of the pore. The nitrogen-relative pressure (P/P_0) determines the surface adsorption capacity of nitrogen on a solid surface. The adsorption and relative pressure P/P_0 fit the BET equations. When P/P_0 is between 0.05 and 0.35. This serves as the foundation for the nitrogen adsorption method of measuring specific surface area. Capillary condensation causes nitrogen to start condensing in the micropores when P/P_0 is 0.4 or larger than 0.4, nitrogen will condense in micropores, because of capillary condensation. Then scientists can test the volume and sizes of the pores using theoretical analysis and experiments. The Pureness of the CO_2 is captured is something vital. This can be determined by estimating the selectivity of adsorption for CO_2 over other gases using these data. Understanding the binding environment of CO_2 in the framework's pores in great detail can reveal important details about the structural and chemical characteristics influencing the reported material performance.

3.2. Adsorption Ability

When assessing MOFs for CO_2 capture, their adsorptive ability is an important factor to take into account. The amount of CO_2 absorption determines the mass of the MOFs need for constructing the adsorbent bed. Great surface areas of MOFs strengthen the ability to adsorb large amounts of CO_2 For instance, at 35 bar, the amount of CO_2 that MOF-177 can adsorb in unit volume is 320 $cm^3(STP)/cm^{3.}$ This is roughly 9 times greater than the amount adsorbed at the same pressure in a container without the MOFs.

3.3. Enthalpy

The enthalpy of adsorption of CO_2 has a big impact on the performance of any material for CO_2 capture applications. Researchers can determine the adsorptive selectivity by measuring the number of the enthalpy of adsorption, which reveals the affinity of the pore surface for carbon dioxide. It also determines the energy needed to release the carbon dioxide molecules during the process of regeneration. Scientists wish to have control of the binding strength of the carbon dioxide molecules because a binding that is too strong can lead to a high regeneration cost. However, if the binding is too weak, although the cost will be lowered and carbon dioxide will be regenerated easier, the purity of the captured carbon dioxide would be lowered too, due to the decreased adsorption selectivity. The enthalpy of carbon dioxide during the process of adsorption is typically represented as Q_{st} which means isosteric heat of adsorption. It is a function of the amount of carbon dioxide adsorbed because there are numerous distinct binding environments inside the ores of MOFs. The Q_{st} value, which is often computed using at least two adsorption isotherms at similar temperatures, is a value that informs us of the average enthalpy of adsorption when a gas molecule is adsorbed at specific surface coverings. The Clausius-Clapeyron equation is typically used to fit the isotherms into a high-order polynomial equation to create an expression for P (pressure).[6].

$$(\text{In } P)_N = -(Q_{st}/R)(1/T) + C \qquad (1)$$

At the lowest carbon dioxide pressures, scientists use zero-coverage isometric heat of adsorption to evaluate the strengths of carbon dioxide binding. For example, $Cu_3(TATB)_2$, known as CuTATB-30 with a $-Q_{st}$ (kJ/mol) of 48. It tells us where the strongest bindings are inside the material and can sometimes tell us the exposed carbon cation sites and Amine functionalities. Researchers fit the temperature-dependent isotherm data to the following equation [7]:

$$\ln P = \ln N + 1/T$$
$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \quad (2)$$

a_i, b_i means viral coefficients m, n means the number of viral coefficients needed for the adequate fitting of the isotherms.

Another such method is using single- or dual-site Langmuir-type expressions [8] to see the adsorption isotherms at various temperatures. This method is especially useful when it comes to a material with both weak and strong no dings present at the same time. the total quantity of carbon dioxide adsorbed at a specific pressure is given by the following expression:

$$N = qsat,_A b_A P/ 1 + b_A P + qsat,_B b_B P/ 1 + b_B P \quad (3)$$

For example, $Cr_3O(H_2O)_3F(BTC)_2$, commonly called MIL-100(Cr). It has a BET surface area of 1900, has a CO_2 capacity of 44.2[d] at 50 bar.

3.4. High selectivity

High selectivity in the selection of CO_2 from a variety of gas combinations is a need in CO_2 capture applications. Two basic processes cause this selectivity. A metal-organic backbone with tiny pore diameters allows molecules to diffuse into the pores exclusively within a certain kinetic diameter range in selectivity based on size. The separation of carbon dioxide /nitrogen and carbon dioxide/hydrogen requires a very small pore material with a size selection regime. Certain MOFs contain pores in the size range, but almost all materials with large surface areas and high carbon dioxide adsorption capacity have pores much larger than the molecule. Therefore, most studies of organometallic frameworks use molecular separations based on adsorption phenomena. [8].

Motivated by the exceptional qualities of MOFs made from simple, accessible linkers. The MUF-16 type of materials has piqued scientists' curiosity. The frameworks are made by mixing nickel (II), manganese(II) or cobalt(II) salts in methanol with H_2aip. The MUF-16 are accessible to a variety of entering gases, as indicated by the pore apparent in SCXRD structures of them. BET surface areas of their different materials were obtained from nitrogen adsorption isotherms measured at 77 K (Fig. 3). For all three frameworks, the sum of pore volumes of 0.11 cm^3/g had been determined [9].

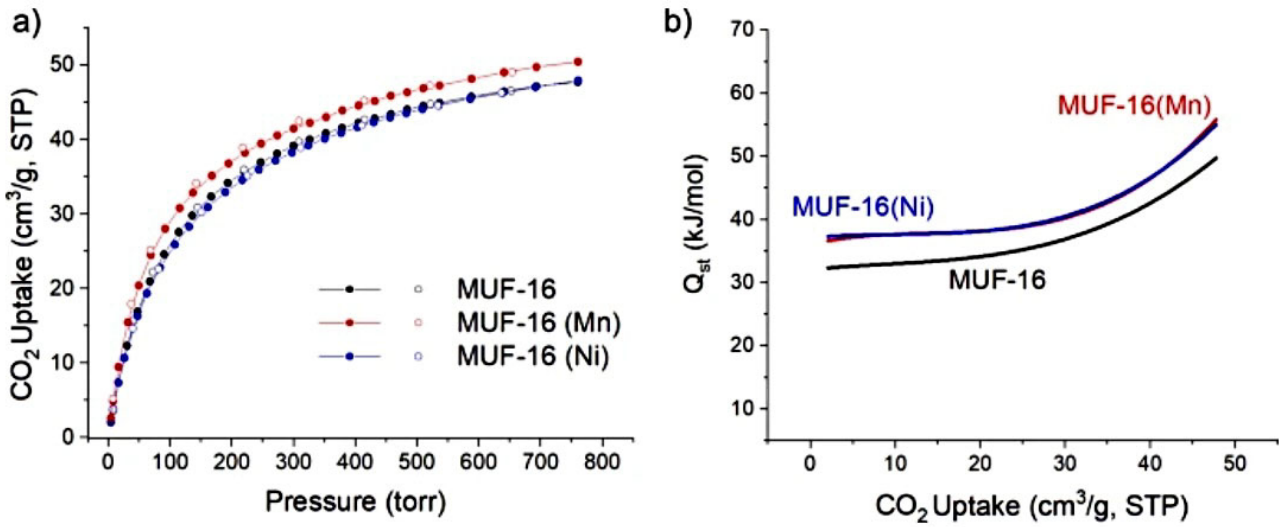


Fig. 3 a. CO_2 volume adsorption and desorption isotherms at 293K for three types of MUF-16. b. As a function of CO_2 uptake, the computed heats of adsorption (Q_{st}) for CO_2 binding to MUF-16s are shown. Adsorbents with a high affinity for CO_2 and a moderate heat of adsorption have the potential to absorb large amounts of gas while being simple to recycle [9].

Even though certain MOFs do include holes in this size range, nearly the materials with greater specific surface area and CO_2 adsorption capability have pores that are far bigger than molecules.

Therefore, molecule separation based on adsorption phenomena is used in the majority of investigations of metal-organic skeletons [8].

4. Main Scenarios of Carbon Capture by MOFs in Power Plants

4.1 Post-combustion Capture

Most effluent is made up of nitrogen and others like water, oxygen, carbon monoxide, NO_x, and SO_x, the majority of the flue gas produced by the burning of coal in the air has a low CO_2 content at about 15-16%. When it is at a total pressure of around 1 bar, the gas stream is let loose. The emissions would be anticipated to reach the carbon dioxide scrubber at between 40 and 60 °C since SO_x removal would take place before CO_2 collection [8].

4.2 Capture before Combustion

Decarbonating before combustion is part of the CO_2 capture process, which leaves no carbon dioxide produced during combustion. Here, coal is gasified to create synthesis gas, sometimes known as "syngas," which is a combination mostly composed of hydrogen, carbon dioxide, and water [10]. To create carbon dioxide and hydrogen ("shifted syn gas"), this gas combination is put through the process of the water-gas shift at high pressure and somewhat raised temperature. Then, pure hydrogen can be produced via CO_2 capture before combustion. It means separating carbon dioxide from H_2O. Pure hydrogen is then burned in a power plant to produce energy[8].

Pre-combustion CO_2 capture has many advantages over combustion of oxy-fuel methods and CO_2 capture before combustion may help with its quick industrial adoption. These gases are produced under high pressure. The partial pressure of carbon dioxide during the combination of these gases is higher than the pressure of the gas after combustion. This may be a relevant factor. So the loaded material can be regenerated by reducing the pressure of the material, which is more advantageous practical and energetically than a process dependent on vacuum or temperature swings [11].

4.3 Oxy-fuel Combustion

In comparison to the pre-combustion and post-combustion collection, oxy-fuel combustion is a relatively novel method for reducing carbon dioxide emissions. Both the fact that most power stations can be easily adapted with a system that uses oxy-fuel combustion. The emission is almost exclusively carbon dioxide making this approach very advantageous.

In a typical setup, a cryogenic separation unit that uses a distillation technique to separate oxygen from the other dry air constituents supplies the plant with O_2 that is >95% pure. When coal is burned when it is rich in oxygen, the oxygen entry is diluted to a partially low pressure by the carbon dioxide from the flue stream. This reduces the emission of nitrogen oxide pollution. The approaches may then be applied directly to sequester the industrial waste gas, which is just carbon dioxide. Water vapor is easily condensed. So it can be removed easily from the gas stream. This approach has enabled CO_2 collection rates greater than 95%, which is not yet feasible with post-combustion and pre-combustion separations [9].

5. Summary

With large surface area, adjustable pore structure and excellent stability, metal-organic frameworks (MOFs) have been widely applied in the capture of carbon dioxide. In this article, synthesis methods, applications and evaluation indicators of MOFs for capturing CO_2 at ambient temperature and pressure were discussed. The mechanochemical synthesis shows shorter reaction times and the sonochemical synthesis can reduce crystallization times to obtain uniform crystals. The high adsorption ability and high selectivity of MOFs can contribute to the capture of carbon dioxide. By changing the ligands the chemical properties of the metal-organic frameworks can be modified to create better materials. Additionally, compared to the pre-combustion and post-combustion collection, oxy-fuel combustion is a relatively novel method for reducing carbon dioxide emissions, which emissions are almost exclusively carbon dioxide.

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