Preparation Methods of Metal Organic Frameworks and Their Capture of CO2

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Abstract. The increasingly serious greenhouse effect makes people pay more attention to the capture and storage technology of CO2. Metal organic frameworks (MOFs) have the advantages of high specific surface area, porous structure and controllable structure, and become the research focus of CO₂ emission reduction technology in recent years. In this paper, the characteristics, preparation methods and application of MOFs in the field of CO₂ adsorption and separation are discussed, especially the application of flue gas environment in power plants.

1. Introduction
Since the industrial revolution, the global economy has developed by leaps and bounds, the rapid development of economy in human society consumes a large amount of fossil energy, so that the content of atmospheric CO₂, NOx, CH₄ and other gases increased dramatically, which increased CO₂ content led to a severe global greenhouse effect. CO2 capture and storage (CCS) is the primary task of controlling CO₂ emissions and mitigating the greenhouse effect.

The traditional materials for absorption and capture of CO₂ by physical or chemical methods mainly include activated carbon, zeolite molecular sieve, liquid ammonia, amino liquid, metal oxide and solid materials containing lamination functional groups. In view of the existing problems and shortcomings of existing CO₂ capture materials, the appearance of a new material-metal-organic frameworks (MOFs) has improved the current situation of CO₂ capture and storage technology in recent years. MOFs are inorganic metal centers (metal ions or clusters of metal) and bridged organic ligands that are interconnected by self-assembly to form a class of crystalline porous materials with periodic network structures. Most of these metal organic frameworks have high porosity and good chemical stability.

Because of the structure of the hole and the large surface area, MOFs have a wider application prospect, such as gas adsorption separation, catalyst, and optical materials. Most of the MOFs have good selectivity, good adsorption capacity, excellent stability and reproducibility compared with traditional materials [1, 2], and most of their adsorption mechanisms are physical adsorption.

The discovery of MOFs was derived from the study of Prussian blue-Fe coordination polymers [3]. After a variety of coordination polymers, the final MOF-5 ([Zn₄O (BDC )₃](DMF)₈(C₆H₅Cl)(H₂BDC = 1,4-phthalic acid, DMF = N, N-dimethylformamide)) was proposed by Yaghi et al., followed by new CO₂ adsorption properties of different functional groups with different functional groups organic skeleton compounds continue to appear, such as ZIF series, MIL series, so on. As the geometric composition of materials, size and function can be flexible changes, more than 2000 MOFs structures...
have been reported and studied only in the past ten years [4]. Figure 1-1 shows the schematic diagram of the classical MOF-5 porous structure.

![Figure 1. Schematic diagram of the classical MOF-5 porous structure.](image)

2. MOFs material characteristics

2.1. Spatial structure and functional diversity

MOFs flexible metal centers and organic ligands make them exhibit spatial structure and functional diversity. The metal center contains almost all metal elements, among which the most widely used are Zn, Cu, and Fe and so on. For organic ligands, early Nitrogen-containing Heterocyclic Ligands tend to collapse, and now the main choice is stable Carboxylate Ligands. At present, the carboxylic acid ligands with good stability are mainly selected. Because of the wide variety of carboxylic acid ligands to be selected and modified, MOFs materials with different spatial structures can be synthesized.

2.2. Porosity and large specific surface area

Porosity is an important property of materials used in catalysis, gas adsorption and separation. In the preparation of MOFs materials, organic ligands and metal ion clusters are regularly arranged evenly, thus forming regular spatial network structures. The guest molecules are involved in the growth and formation of the crystal, so the porous structure of the MOFs material is formed after the removal of guest molecules.

The specific surface area (BET) of the material is another important index to evaluate its catalytic performance and adsorption capacity. In general, the catalytic and adsorptive properties of the materials increase with the increase of specific surface area of the material in a certain range, therefore, it is necessary to change the organic ligands and connecting arms of MOFs to obtain materials with larger specific surface area. Yaghi and Li prepared MOFs materials with BET value above 4000 m²/g were prepared by selecting suitable ligands, as shown in Table 2-1.

| Material | Ligand | BET value(m²/g) |
|----------|--------|-----------------|
| MOF-177  | 4,4',4''-benzene-1,3,5-triyltribenzoate (BTB) | 4500 |
| MOF-200  | 4,4',4''-(benzene-1,3,5-triyl-tris (benzene-4,1-diyl)) tribenzoate (BBC) | 4530 |
| MOF-205  | 2,6-naphthalenedicarboxylate (NDC), BTB | 4460 |
| MOF-210  | biphenyl-4,4'-dicarboxylate (BPDC), BTE | 6240 |

2.3. Unsaturated metal sites

If there are coordination unsaturated metal sites in the structure, they are usually coordinated with DEF, water, ethanol and other volatile small solvent molecules, these solvent molecules can be removed by appropriate activation methods to expose the unsaturated metal sites. These exposed unsaturated metal
sites can be coordinated with NH$_3$, H$_2$S, CO$_2$ and other gases, so as to achieve the role of gas adsorption and separation.

3. Preparation of MOFs

Due to the important application of MOFs in many fields, many researchers have been looking for a simple synthesis method with low process efficiency, low energy consumption and low raw material in recent years. Since the discovery of MOFs, its preparation method has been improved. Figure 3-1 shows the development of MOFs synthesis technology for nearly 20 years [5]. Next, we will introduce several representative methods of preparation.

3.1. Solvothermal Synthetic

In 1995, Nalco chemical company and Professor Yaghi proposed the synthesis of MOFs by Solvothermal Synthetic. The mixed solution of inorganic salt and organic connecting arms are put into a sealed reaction vessel to heat the mixed solution to form an insoluble framework, and insoluble substances precipitate and form crystals. The temperature of the reactant can reach its boiling point, so the solvent can be partially or completely dissolved.

3.2. Electrochemistry Synthetic

In 2005, BASF first synthesized MOFs material HKUST-1 by electrochemical synthesis [6]. In this method, the copper plate as the source of captions can effectively prevent the production of corrosive ions and other by-products, and the proton solvent can ensure the transformation of hydrogen ions and prevent the dissolution of cathode. Figure 3-2 a) and b) show the schematic diagram of the method. In 2011, Dinca found that anodic dissolution had limitations. In order to solve these problems, Dinca et al proposed an electrochemical method for cathode precipitation [7]. Different from anodic dissolution, this method directly dissolves the metal salt as the metal precursor into the electrolyte solution directly with the organic connecting arm. Figure 3-2 c) and d) show the cathode deposition device and the schematic diagram of the reaction.

![Figure 3. Anodic dissolution cell (a) and anode forming HKUST-1 (b), Cathode settling chamber (c) and precipitate on cathode to form MOFs (d).](image-url)
3.3. Microwave Synthetic
Jhung suggested that MIL-100 can be prepared by microwave synthesis with chromium benzoate three as the raw material in the presence of hydrofluoric acid in aqueous medium [8]. The reaction mixture is placed in the microwave oven 1-2h, the temperature is kept at 220 degrees, or placed in the sealed polytetrafluoroethylene autoclave 4h. The results showed that chromium appeared in the mixture after 2h reaction, and the crystal yield reached 44% after 4h, which was equivalent to the yield of 4 days by the traditional synthesis method.

3.4. Spray-drying Synthetic
The method can be used to guide the chemical reaction by local heating of the droplet. First, the solution containing precursor is atomized, and the process can inject one or more solutions at a certain speed (feed rate), then the air or nitrogen is compressed at another constant speed (discharging rate). Then, each atomized droplet is heated to a certain temperature by the high temperature gas and begins to evaporate, MOFs micro particles begin to form inside the droplet, after that, the particles formed are compact together until all the droplets are evaporated to form larger particles of MOFs. As show in Fig.3-3.

![Figure 4. Spray-drying method for the production of MOFs.](image)

3.5. Flow Chemistry
In 2011, Ameloot et al. demonstrated for the first time that microfluidics can be used to synthesize organic metal materials [9]. Two years later, Faustini et al. proposed the synthesis and modification of MOFs by using micro oil droplets as reaction vessel and Solvothermal and Hydrothermal method [10], as shown in Fig. 3-4. The reaction phase is injected into the immiscible carrier fluid (oil), The micro droplets are generated spontaneously, and then the droplets flow through the flow channel to form a certain structure of MOFs.
4. Adsorption and separation of CO$_2$ by MOFs

4.1. Single component CO$_2$ adsorption
The adsorption of CO$_2$ on MOFs belongs to physical adsorption. The adsorption sites of guest molecules CO$_2$ and MOFs materials form stable structures by the action of Van Edward force and electrostatic force to achieve the effect of adsorption of CO$_2$. The adsorption of CO$_2$ on MOFs is mainly affected by specific surface area and functional groups, although the specific surface area of some MOFs has reached a larger value, but for a long time, the absorption value of CO$_2$ for most MOFs materials under 298K and 1atm is 1mmol/g, compared with activated carbon and other materials, there is not much promotion.

4.2. Multi component CO$_2$ adsorption
In multi component gases, the adsorption of CO$_2$ on MOFs mainly depends on the pore shape, pore size, dynamic diameter of gas, temperature and pressure. The ability of different materials to adsorb and separate CO$_2$ from different gas components is different, and the adsorption and separation ability of CO$_2$ can be improved by changing different organic ligands and adding unsaturated metal sites.

4.3. Adsorption under high CO$_2$ pressure
Under high pressure, the CO$_2$ adsorption property of MOFs material is mainly related to the specific surface area and void volume of the material, the materials with larger specific surface area and void volume generally exhibit higher CO$_2$ saturation adsorption capacity. The BET values of MOF-210 is 6240m$^2$/g. Under the conditions of 298K and 5MPa, its saturated adsorption capacity of CO$_2$ reaches 54.5mol/kg, which is the maximum value of all MOFs materials under the same condition.

4.4. Adsorption of CO$_2$ at low pressure
The adsorption of MOFs on CO$_2$ under low pressure is based on the CO$_2$ partial pressure of flue gas in the flue of power plant generally in the range of 0.01MPa-0.02MPa. Under low pressure conditions, the material with large surface area has a poor trapping effect on CO$_2$, which is mainly affected by the adsorption heat of the material. Yazaydin et al. found that MOF-74 (Mg) is one of the most saturated adsorption capacity of the material in 298K, under the condition of 0.01MPa, its value is 5.95mmol/g.

5. Conclusion
Metal organic frameworks have great potential in the field of CO$_2$ adsorption and separation because of their spatial structure and functional diversity, porosity, large specific surface area, and unsaturated metal sites. In recent years, the synthesis technology of MOFs materials has been developed.
continuously. Solvothermal Synthesis is still the most widely used method. The adsorption effect of MOFs on CO₂ is related to the material structure, pore diameter, guest molecular aerodynamic diameter, temperature, pressure and other factors. The adsorption characteristics of single component gas, multi component gas, high pressure and low pressure are also different.

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