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2D Metal-Organic Frameworks

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Abstract

The metal organic framework (MOF) is a crystalline porous material formed of an inorganic metal ion or cluster and an organic ligand. The invention has the characteristics of large pore volume, high specific surface area, variable structures, and multiple functions. It was widely applied in the fields of gas storage, separation, catalysis, sensing, and biomedicine. The emergence of this kind of material, to a large extent, has provided opportunities for the common development of other disciplines. In this chapter, the recent research and development of MOFs materials, including the synthesis methods (sol-gel method, hydrothermal solvothermal method, and microwave synthesis, etc.), the development status, the applications, i.e., hydrogen storage, energy storage, gas adsorption, catalytic reaction, sensors, biomedical applications, and so on, and the research hotspots of MOFs will be addressed.

Keywords: MOF, biomedicine, gas storage, sensors, catalysis

1.1 Introduction

Amidst the highly porous materials, metal organic frameworks (MOFs) exhibited incomparable tunable and structural diversity. Furthermore, MOFs

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synchronously demonstrate porosity and excellent electrical conductivity, which are a burgeoning group of materials and provide a wide range of applications, for instance, energy storages, electrocatalytic oxidation, gas adsorption, biomedical [1–6]. The atomic-level control over molecular and supramolecular structure provided by MOFs gives the chance for exploiting some new materials for a variety of applications [7].

As a new type of porous inorganic-organic hybrid crystal material, MOFs materials have attracted extensive attention in chemistry, material, physics, and other fields. It combines the characteristics of inorganic and organic materials. It has a wide range of potential values in gas storage and separation, luminous, sensing, catalysis, magnetism, and other fields. When MOF_S was made into membrane, the application of MOFs material in gas phase field was expanded. The gas separation application of MOFs extends from adsorption separation to membrane separation. By using the adjustable or modified characteristics of pore size, shape, and surface chemical properties of MOFs, MOFs material is endowed with better membrane separation performance for some light gas molecules. In addition, MOFs film extends the detection range of MOFs to gas, which can realize humidity detection and fluorescence detection of other gases or vapors. In these cases, the MOFs will play an important role in the generation, transmission, adsorption, and storage.

The objective of this chapter is to summary recent literature describing the progress of MOFs. We first review the technology about how to grow MOFs thin films, including sol-gel method, hydrothermal solvothermal method, and microwave synthesis, etc. Whereafter, we summarized the structural feature and physicochemical properties description of MOFs. Subsequent sections discuss the MOF films in various applications, including hydrogen storage, energy storage, gas adsorption, catalytic reaction, sensors, biomedical applications, and the like. Finally, we discuss some limitations of MOFs in practical application.

1.2 Synthesis Approaches

The synthesis of two-dimensional (2D) MOFs compounds materials is generally carried out by cultivating single crystals. X-ray single crystal structure analysis is the most important method to determine the structure of metallic organic skeleton materials [8]. The accurate molecular structure of organometallic skeleton materials can be obtained by analysis. At present, the methods of synthesizing organometallic skeleton materials reported in the literature mainly include solution volatilization method, diffusion

method, and hydrothermal/solvothermal synthesis route. These methods complement each other and sometimes use different synthesis methods or the same method and different conditions to obtain materials with different structures and functions [9]. With the development of collocation chemistry and material chemistry, ultrasonic synthesis, ion-liquid method, solid phase reaction method, sublimation method, microwave synthesis, method and two-phase synthesis method have also been applied to the synthesis of MOFs materials. Various synthesis ways have their own advantages and disadvantages. Therefore, the choice of synthesis methods is very important for the synthesis of MOFs, and even affects its structure and properties.

1.2.1 Selection of Synthetic Raw Materials

When the synthesis of MOFs is started, it is important to maintain the integrity of skeleton looseness in addition to geometric factors. Therefore, it is necessary to find sufficient mild conditions to maintain the function and structure of the organic ligand, while having sufficient reactivity to establish the coordination bond between the metal and the organic [10].

First of all, the metal components are mainly transition metal ions, and most of the valence states used by Zn^{2+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Ru, and Co^{2+}. Secondly, organic ligands should contain at least one multi-dentate functional group, such as CO_2H, CS_2H, NO_2, SO_3H, and PO_3H. CO_2H was more commonly used in multi-dentate functional groups, such as erephthalic acid (BDC), tribenzoic acid (BTC), oxalic acid, succinic acid, etc. The selection of suitable organic ligands can not only form MOFs with novel structure, but also produce special physical properties. In addition, solvents can dissolve and protonize ligands in the process of synthesis. Metal salt and most ligands are solid as solvent is needed to dissolve it. Before metal ions and ligands are coordinated, ligands (such as carboxylic acids) need to be deprotonized, so alkaline solvents are often used. At present, many deprotonated alkaloids are used as organic amines, such as triethylamine (TEA), N, N2 dimethyl formamide (DMF), N, N2 diethylamide (DEF), N2 methyl pyrrolidone. At the same time, they are good solvents. In recent years, there are gradually examples of deprotonation with strong bases such as sodium hydroxide. Sometimes, solvents can also coordinate with metal ions as ligands or form weak interactions with other ligands, such as hydrogen bonds, which can be excluded by heating and vacuum. Finally, in order to make the synthesized organometallic skeleton have ideal pores, it is necessary to select the appropriate template reagent. Template reagents are sometimes separate substances, sometimes the solvents used.

1.2.2 Solvent Volatility Method

Solvent volatility method is suitable for the metal salt and ligands with good solubility and the obtained products that have a poor solubility in the used solvent. If the solubility of the ligands is poor, the dissolution of the ligands can be promoted by proper heating, and the coordination reaction can also be accelerated. The crystallization of the obtained coordination products is precipitated in the process of cooling [10, 11].

Solvent volatilization method is the most traditional method to synthesize MOFs materials and the principle of this method is that the crystal precipitates from saturated solution by solvent volatilization or decreasing temperature, and slowing down the volatilization rate or cooling is beneficial to the cultivation of perfect crystal form [12].

Specifically, by dissolving the selected organic ligands and metal salts in the appropriate solvent and placing them at rest, waiting for their slow self-assembly to form complex crystals.

1.2.3 Diffusion Method

Diffusion method means that the metal salt organic ligands and solvents are mixed into solution in a certain proportion, put into a small glass bottle that is placed in a large bottle with deproteinized solvent, seal the bottle mouth of the large bottle, and then the crystal can be formed after a period of static setting. Diffusion methods can be divided into gas phase diffusion, liquid layer diffusion, and gel diffusion.

1.2.3.1 Gas Phase Diffusion

The gas phase diffusion method is to dissolve the selected organic ligands and metal salt in the appropriate solvent, and then cause the lazy volatile solvent or volatile alkaline substance (for the carboxylic acid ligand containing hydrogen protons) to diffuse into the solution to reduce the solubility of the obtained complex product or speed up the coordination reaction, so that the complex precipitates in the form of crystallization. The volatilization rate of volatile solvents or alkaline substances in gas phase diffusion method will affect the nucleation speed of the complexes, and then affect the quality of precipitated crystals.

1.2.3.2 Liquid Phase Diffusion

The liquid phase diffusion method is to dissolve the selected organic ligands and metal salt in different solvents, and then put the seed solution

on top of the other solution, or add another solvent to the interface of the two layers of solution that can slow down the diffusion rate. The reactant diffuses slowly and reacts in the solvent, and the reaction product precipitates in the form of crystal. The diffusion rate of reactants in liquid phase diffusion method will affect the morphology of the precipitated crystals.

In general, the diffusion method is mild and it is easy to obtain high-quality single crystal, but it is time-consuming and the solubility of reactants is required to be better and can be dissolved at room temperature.

1.2.4 Sol-Gel Method

The sol-gel method is to use the compounds containing high chemical active components as precursors, which are uniformly mixed in liquid phase, hydrolyzed and condensed, and form a steady transparent sol system in the solution. In this process, the sol was slowly polymerized between aging colloidal particles to form a three-dimensional (3D) network structure gel before the network was filled with illiquid solvents to form a gel. After drying, sintering, and curing, the gel prepared molecular and even nano-substructure materials [13].

In 2017, Tian *et al*. [14] synthesized a porous monolithic metal-organic framework monoHKUST-1 ($Cu_3(BTC)_2(H2O)_3$, BTC = 1,3,5-benzenetricarboxylate) by a sol-gel process. In the reaction process, the crystal primary MOFs particles were first formed, then the mother liquor was centrifuged, and the dense solid (gel) was washed for removing the unreacted precursors.

In summary, sol-gel method demonstrated following advantages: 1) The reactants may be uniformly mixed at the molecular level when the gel was formed as the primary materials utilized in the sol-gel method were first disseminate to the solvent for forming a lower viscosity solution, the uniformity at the molecular level can be obtained in a very short period of time. 2) In the step of solution reaction, add a small amount of elements, what is needed to achieve uniform doping of 2D metal-organic skeleton at the molecular level. 3) The reaction temperature required for sol-gel synthesis is lower, so it is easier to carry out the reaction than the solid state reaction [15]. What's more, the components in the sol-gel system were diffused in the nanometer range, while the components in the solid state reaction were diffused in the micron range, so the reaction of the sol-gel system is easy and the reaction temperature is low. 4) Various new 2D metal-organic frameworks materials can be prepared by selecting suitable conditions. On the other hand, sol-gel method's disadvantages are described as follows: 1) the used raw materials are more expensive, some organic materials are harmful to health; 2) the whole sol-gel process usually takes a long time,

often taking a few days or weeks; 3) there are a number of micropores in the gel, which will escape a lot of gases and organic matter and produce shrinkage in the drying process of 2D metal-organic frameworks [16].

1.2.5 Hydrothermal/Solvothermal Synthesis Method

Hydrothermal/solvothermal synthesis is the most effective way to synthesize MOFs that refers to the fact that ligands, metal salt, and reaction solvent are put into the reaction vessel together. At high temperature and high pressure (generally below 3,000 C) [12], the difference of solubility of each component is minimized and the viscosity of solvent decreases and the diffusion effect is strengthened which makes the complex tend to crystallization and precipitate. Large skeleton organic ligands with low solubility at room temperature and pressure are very suitable for hydrothermal/solvothermal method. In general, the crystals synthesized by this method are easier to generate high-dimensional frame structures than the reactions at room temperature. According to the different reaction vessels used in the synthesis process of hydrothermal/solvothermal method, they can be divided into two common methods: reaction kettle and pipe sealing [17, 18]. Zheng *et al.* [19] synthesized a series of novel POMMOFs from $\{Ni_6PW_9\}$ cluster with 2D structure under a hydrothermal route.

Li *et al.* [20] synthesized flake MOF-2, with zinc ion and terephthalic acid in different solvents. This kind of flake material with 1.5–6 nm thickness, and they found that, if different solvents were used, the thickness of the prepared nanoparticles was different. After comparing methanol, ethanol, acetone, and DMF as solvents, it was found that the nanoparticles were the thinnest when acetone was used as solvent, and the monodisperse nanoparticles prepared would not regroup.

This method has a short reaction time and solves the problem that the reactants cannot be dissolved at room temperature. The solvents used in the synthesis, especially the organic solvents, have different functional groups. Different polarity, different dielectric constant, different boiling point and viscosity can greatly increase the diversity of synthesis route and product structure. Solvothermal growth technology has perfect crystal growth. Equipment simply saves energy and other advantages, so it has become a hot spot in recent years.

1.2.6 Stripping Method

Peeling 3D layered organometallic skeleton (MOFs) from top to bottom is one of the effective ways to control the preparation of ultra-thin

organometallic nanoparticles on a large scale, because the interlaminar interaction force is weak van der Waals force or hydrogen bond, and peeling can be realized by simple mechanical grinding or ultrasonic method.

Junggeburth *et al.* [21] use CTAB as surfactants, 1-hexyl alcohol and water as mixed phase microemulsion method. ZnBIM 2D organic complexes with lamellar accumulation were prepared from zinc acetate and benzimidazole. The single layer of the coordination polymer is only 2.6 nm, and the monolayer polymer plus surfactants layer is only 5.2 nm.

For the intercalation/chemical stripping method, the organometallic nanoparticles obtained by mechanical peeling are usually small in size, larger in thickness, and less efficient (<15%). Therefore, the experimental method has been improved on this basis. Recently, Ding *et al.* [17] inserted the ligands containing disulfide bonds into layered MOFs by coordination insertion and then realized the efficient peeling of layered MOFs through the fracture of disulfide bonds, and to a certain extent, it can regulate the fracture process of disulfide bonds to achieve controllable preparation of organometallic nanoparticles (Figure 1.1). They cleverly use bipyridine ligands containing disulfide bonds to obtain MOFs, with increased interlayer spacing through the intercalation of pyridine ligands, and then regulate the interlaminar interaction of layered structures through the chemical reduction and fracture process of disulfide bonds, thus realizing the efficient chemical stripping of layered MOFs to obtain ultra-thin organometallic nanoparticles.

In addition, the above methods of synthesizing 2D metal-organic frame are bottom-up synthesis. Zn (bim) (OAc) MOFs ultra-thin nanoparticles were synthesized from the bottom up with a thickness of 5 nm. The yield of this technique can reach 65% by an intercalation/chemical stripping

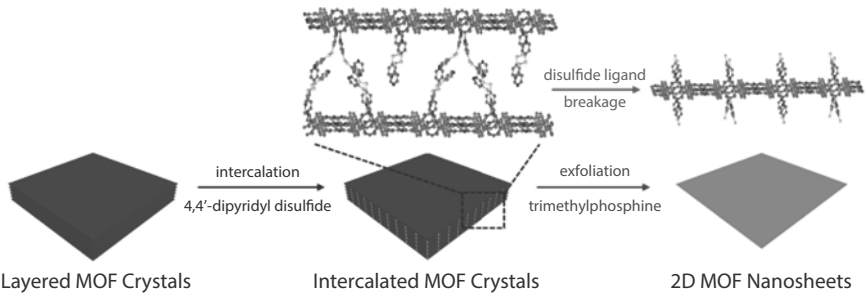

Figure 1.1 Schematic illustration of the overall process developed to produce 2D MOF nanosheets via an intercalation and chemical exfoliation approach [reprinted with permission from ref. 17. Copyright 2017 American Chemical Society].

method [22], the metal organic nanoparticles with 1-nm thickness can be prepared efficiently (~57%) by stirring at room temperature. At the same time, different thickness organometallic nanoparticles can be further obtained by controlling the reduction process of disulfide bonds in disulfide ligands. Considering the large number of organic ligands and metal ions/clusters available in MOFs synthesis materials, the method reported in this paper was used to prepare 2D metal organic nanoparticles with different structure and properties. This thickness controllable intercalation/chemical stripping method has a broad prospect in the preparation of ultra-thin metal organic nanoparticles, and this preparation method provides another different method for the controllable preparation of 2D nanomaterials.

1.2.7 Microwave Synthesis Method

Microwave is the electromagnetic wave, whose frequency is 300 Hz~300 GHz and the wavelength is between 1 mm to l m. It has longer wavelength and better penetration than infrared, far infrared, and other electromagnetic waves used for radiation heating because microwave can transfer energy through molecular dipole rotation and ion conduction to heat the material. Therefore, in the process of microwave heating, the molecules will vibrate violently and rub with each other and raise the temperature [23]. The internal and external heating of the material is almost at the same time, which makes microwave heating have the advantages of fast heating rate, high energy utilization rate, and no pollution to the environment compared with the traditional heating method. It has attracted extensive attention in the field of material synthesis.

Gordon *et al.* [24] synthesized MIL-53 (Fe) crystal used $FeCl_2.6H_2O$ and H_2BDC as raw materials by traditional heating method and microwave method. Scanning electron microscope analysis showed that the particle size of MIL-53 (Fe) crystal synthesized by microwave method is 1~5 μm, and the particle size distribution of MIL-53 (Fe) crystal synthesized by traditional heating method is 5-25 μm. The particle size distribution of MIL-53 (Fe) crystal synthesized by traditional heating method is 5-25 μm.

Microwave heating can realize rapid and uniform heating, so that the reactants can be mixed and uniform in a short period of time, so that the nucleus can crystallization rapidly, and the smaller particles and crystals with uniform size can be obtained by rapid crystallization.

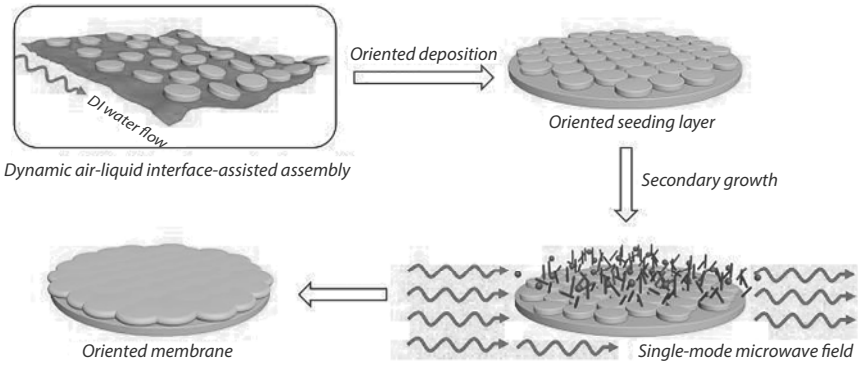

Figure 1.2 Schematic illustration of the preparation procedure of highly *c*-oriented NH_2-MIL-125 (Ti) membrane by combining oriented seeding and controlled inplane secondary growth (Red sphere: Ti^{+4} ion, black rod: NH_2-BDC) [reprinted with permission from ref. 25. Copyright 2018 Wiley].

1.2.8 Self-Assembly

Sun *et al.* [25] introduced a highly *c*-oriented NH_2-MIL-125(Ti) Membranes by In-Plane Epitaxial Growth route, as shown as Figure 1.2. By using the method of dynamic gas-liquid interface self-assembly, the highly oriented monolayer of seeds can be obtained by orientation deposition of seeds. The controlled epitaxial growth process was realized by using single mode microwave reactor and transition metal sulfide TiS_2 as titanium source in the secondary growth process. C-axis oriented NH_2-MIL-125 (Ti) thin films were prepared by combining seed orientation deposition and controllable epitaxial secondary growth. The film has excellent gas separation performance. The ideal separation coefficient of H_2/CO_2 is 24.8 at 30°C and 1 bar, which is much higher than that of Nusen diffusion coefficient.

1.2.9 Special Interface Synthesis Method

Special interface synthesis method was used to assist the growth of 2D MOFs nanoparticles at some special interfaces (gas-liquid interface or liquid-liquid interface). For example, Kambe *et al.* [26] demonstrated a single-layer or multi-layer nickel dithiopentyl ring nanoparticles named nano-1. They use nickel acetate and phenylhexathiol as ions and ligands to facilitate the reaction of liquid-gas contact surface to form 2D MOF

materials. The thin layer containing benzene hexamercaptan was spread on the surface of aqueous solution containing $Ni(OAc)_2$ and NaBr. After evaporation of ethyl acetate, the nano-1 nanoparticles will be formed at the liquid-gas interface and then they will be transferred to pyrolysis graphite with high crystallization orientation. Rodenas *et al.* [27] exhibited a three-layer synthesis strategy to synthesize CuBDC nanoparticles. The mixture of DMF and acetonitrile was arranged vertically into three layers to prepare other reaction systems. At the top of layer was the acetonitrile solution that dissolves copper nitrate, and the bottom layer was the DMF solution that dissolves terephthalic acid. The two layers use a mixture of the same amount of DMF and acetonitrile as the transition layer. When the ions in the upper layer and the ligands in the lower layer slowly spread to the intermediate layer, ultra-thin CuBDC nanoparticles appeared. Importantly, this three-layer synthesis method is commonly used and can be extended to synthesize 2D MOFs nanoparticles coordinated by other metal nodes and ligands.

1.2.10 Surfactant-Assisted Synthesis Method

Surfactant assisted method is also an effective method to generate 2D MOFs materials. The addition of surfactants not only limits the growth of MOFs along the vertical direction but also helps to disperse the synthesized MOFs nanoparticles. For example, Zhao *et al.* [12] found that the Zn-TCPP MOF coordinated by zinc ions and TCPP (4-(4-Carboxylphenyl) porphyrin) can obtain a 2D lamellar chopped bulk MOFs. It is formed by the connection of one $Zn_2(COO)_4$ water wheel metal node with four TCPP ligands. PVP can selectively stick to the outer sphere of MOFs, stabilize the existence of Zn-TCPP nanoparticles and limit its growth along the vertical direction, and promote the formation of ultra-thin Zn-TCPP nanoparticles. Ultra-thin Zn-TCPP nanoparticles can be obtained when a certain amount of polyvinylpyrrolidone (PVP) was added.

1.2.11 Ultrasonic Synthesis

Ultrasonic synthesis is a new comprehensive subject which intersects chemistry and acoustics that belongs to the frontier subject in chemical synthesis [28]. As a special way of inputting energy the high efficiency of ultrasonic wave plays a difficult role in material synthesis by other methods such as light, electricity, heat, and so on. Ultrasonic chemistry can improve

the yield of the reaction to control the chemical reaction then change the reaction process and initiate a new chemical reaction. In recent years, ultrasonic chemistry has developed more rapidly and has been widely used in synthetic chemistry, material science, chemical industry, and biology. Ultrasonic method can be effectively used in the synthesis of MOFs and can effectively control the size and morphology of MOFs by controlling ultrasonic time and ultrasonic output power. It has very important application value in material synthesis.

For the synthetic method of MOFs, in addition to the above-used methods, there is a sublimation synthesis method. In the process of development of MOFs, new synthesis methods have been reported in the process of development of MOFs according to the actual needs in the development of MOFs materials.

1.3 Structures, Properties, and Applications

1.3.1 Structure and Properties of MOFs

The metal-organic frame structure was formed by the reasonable self-assembly reaction of central metal ions or metal clusters and bridged organic ligands [29]. Because of the different choices of metal and organic ligands, a variety of crystal materials with vacancy and channel structure can be obtained because of their various arrangement and combination forms [30]. The transition elements have strong bonding ability, deformation, and polarization ability, and can be combined with organic elements. In recent years, alkali metal ions, alkaline earth metal ions, and some ions with special properties have joined the metal ions that construct MOF_S. The metal cluster is the key to develop MOFs materials. The various coordination modes of metal ions or metal clusters and the size of the configuration, the rigid flexibility and their own spatial effects have an important connection with the construction of multi-functional coordination polymer configurations [31].

In addition to the above-mentioned structural and pore size tunability, 2D MOFs materials have their other structural properties, such as porousness and high surface area. The porosity is the property of the material containing a certain number of holes. MOFs contain size-adjustable pores, pore channels, or pore cages. The aperture range is between the no-hole to the mesopore. Most of the pore channels of the 2D metal-organic framework materials are microporous, which is unfavorable to the rapid

diffusion of small molecules and material transport. Specific surface area is another important index to evaluate the catalytic performance and adsorption capacity of porous materials. One of the main purposes of constantly changing the metal centers and ligands of a 2D metal-organic framework is to give the material a high nose beam area [32].

1.3.2 Application in Biomedicine

Organometallic skeleton materials can selectively adsorb and separate different gases molecular. By measuring the adsorption properties of different gases, it can be found that, under certain conditions, the adsorption capacity of the material for carbon dioxide, nitrogen dioxide, carbon monoxide, and other gases is particularly large, but the adsorption capacity for nitrogen, oxygen, and methane is very small. Because of the great difference of adsorption capacity, the material has the potential to separate and purify the gas. Scientists have studied the sustained release of ibuprofen, an anti-inflammatory and analgesic drug, using 2D MOFs as a drug carrier. In order to study its pharmacokinetics, the structure of the material was simplified to cylindrical. Compared with other materials with similar size, the drug content of the material was higher and the drug release time was longer. This makes it possible for mesoporous MOFs to be used in the sustained release of larger drug molecules and also opens up the application prospect of 2D organometallic frame materials in the field of biomedicine [33, 34].

1.3.3 Application in Gas Storage

In the study of micropore function of MOFs, the stability of structure is a very important factor. The pores of MOFs are stable, and the skeleton structure will not change when the guest molecule is removed. Under the condition of heating, the structure can also be kept unchanged above 300°C. Because most of the 2D metal-organic frame materials have pore structure and special structure, they have potential applications in gas storage. For 2D MOFs materials storage applications, mainly focused on methane and hydrogen and other fuel gas. The methane adsorption properties of 16 kinds of MOFs with MOF skeleton structure were studied by scientists. The pores of these skeletons are uniformly and periodically arranged. The porosity is 91%. Through the comparison of hydrogen adsorption capacity of several skeletons, it is shown that 2D MOF materials have great potential for hydrogen storage, and the surface area is not the only determinant

of adsorption capacity, and the existence of functional groups also plays a very important role [35–37].

1.3.4 Application in Sensors

Anion recognition of super component subassemblies of gold and ligands has recently been widely studied. Because anions play a key role in most biochemical reactions, selective recognition of sensitive anions is of great importance to environmental and biomedical applications. MOFs/CPs (coordination polymers) are a unique representative of anions due to their diverse structural units (ligands and metal ions) and various adjustable frameworks. The anions are different in size and shape, they can experience interactions with the frames of MOFs and CP in different intensity and then cause obvious changes in photophysical properties, giving rise to sensing applications [38, 39].

The interaction between anion and main frame is one of the most effective ways to fabricate MOFs anion sensor. The most of anion exchange processes are controlled by thermodynamic parameters, which may bring about selective anion exchange, and the allowable range is designed according to the size, shape, and charge of specific anions. Ion MOF (IVMOF) is the best substrate for anion exchange, which depends on the total charge of the bone rack and the pore ratio involved in it [39]. The framework of photoluminescence quality distribution can monitor anion exchange phenomenon through appropriate optical output.

1.3.5 Application in Chemical Separation

The separation process of benzene and cyclohexane is regarded to be one of the most complex and difficult processes in the chemical industry [40, 41]. Cyclohexane is the main by-product in the process of benzene hydrogenation, it is necessary to remove it from the mixture to obtain the target intermediate product for the use of the later step. However, the similarity of kinetic diameter and boiling point of benzene and cyclohexane limits the use of conventional methods (such as fractionation) in separation process. After skillfully selecting the construction unit for reasonable cavity functionalization, MOF effectively realized the separation of benzene and cyclohexane by adsorption process with low energy demand [42]. Among them, a frame material DAT-MOF-1 is constructed by adding the core of diamino triazine (diamino triazine, DAT) to the bridged group of monocarboxylic acid. The structure analysis shows that the 3D skeleton of the MOF bonded by supramolecular hydrogen bond has a pore size of 0.671 nm ×

0.708 nm. DAT-MOF-1 shows excellent separation performance of benzene/cyclohexane, at 298 K, the adsorption amount of benzene is 1.5 mol kg^{-1}, while that of cyclohexane is only 0.2 mol kg^{-1}. The reason can be attributed to the different strength interaction between benzene and cyclohexane and DAT-MOF-1 framework. The result of the separation process was assessed by the ideal adsorption solution theory (IAST): the adsorption selectivity of isomolar benzene/cyclohexane mixture was more than 200.

1.3.6 Application in Catalysis

H_2 is a green renewable energy and the most ideal fuel to meet the future energy demand. Because of the abundance of water resources on the earth, the preparation of H_2 by pyrolysis water provides a potential possibility for achieving the goal of human energy, and solar photocatalysis is the best method to produce hydrogen from pyrolysis water, which is attractive and competitive enough. As a photocatalyst, MOFs has many advantages, such as flexible design, adjustable pores, large specific surface area, functionalization, and diversiform structure. The metal center separated by organically connected groups in MOFs is considered to be super dispersed metal quantum dots, which can realize the short distance diffusion of charge carrier in photocatalytic reaction [43]. By adjusting the organic ligands and/or metal central ions, the specific surface product and band gap of MOFs can be adjusted to control its photocatalytic activity to optimize its performance. The combination of carbon and nitrogen compounds, metal nanoparticles, metal oxides, metal complexes, or polyoxometalates (poly ≤ oxometallate, POM) can be directly used in photocatalytic reactions by combining multiple components, such as carbon and nitrogen compounds, metal nanoparticles, metal oxides, metal complexes, or polyoxometalates [44].

1.3.7 Application in Gas Adsorption

NPC (nitrogen-doped porous carbon) prepared by MOFs carbonation showed strong adsorption energy for CO_2. In this process, ZIF-8 was used as model plate, furan methyl alcohol and ammonia as foreign carbon and nitrogen sources, respectively. Researches prepared NPC with high CO_2 adsorption capacity and selective nitrogen content. NC-900 showed the largest adsorption capacity to CO_2 due to its high specific surface area and medium nitrogen content, and the adsorption capacity was 5.1 mmol and 3.9 mmol g^{-1} at 273 K and 298 K, respectively. The adsorption capacity of NC-900 was 5.1 mmol g^{-1} and 3.9 mmol g^{-1} at 273 K and 298 K, respectively. Compared

with the best nitrogen-mixed NPC, it is higher than the known ZIF bone frame. NC-600 has the highest nitrogen content (25.9%, wt), but because of its low specific surface area, it shows CO_2 adsorption of 3.3 and 2.4 mmol g^{-1} at 273 K and 298 K, respectively. Therefore, it can be concluded that the specific surface area and nitrogen content play an important role in the adsorption of CO_2. A series of NPC prepared by MOF-5 and MOF-74 also showed high CO_2 adsorption capacity. In a word, the NPC prepared by MOFs carbonation has excellent properties in gas adsorption, and it can be inferred that the NPC prepared by MOFs carbonation can also be used in the adsorption field of anti-biotics or other gases [45].

1.4 Summary and Outlook

Two-dimensional MOFs demonstrated good structural severability and easy functionalization, which are incomparable to other materials. As a new type of functional molecular materials, 2D MOFs materials developed rapidly and become a hot research topic in the field of material chemistry. In the past few years, different types of MOFs materials have been prepared and have important applications in hydrogen storage, gas adsorption and separation, sensors, drug release, catalytic reactions, and so on.

At present, the main challenge is how to synthesize stable organometallic skeleton materials, because the synthesis of organometallic skeleton materials mainly relies on the following kinds of non-covalent bond forces: hydrogen bond, coordination covalent bond, electro static and charge transfer gravity, and aromatic π stacking. The intensity of the noncovalent bonds is far from comparable to that of covalent bond. Another reason for the instability of organometallic skeleton materials is that the guest solvent molecules coordinate directly with the metal. When the guest is desorbed, it is easy to change the coordination structure. Therefore, one of the strategies to obtain stable organometallic porous materials is to prevent the solvent molecules from coordinating directly to the metal center. Therefore, although a good deal of metal-organic framework materials has been reported, most of them remove the guest molecules, and the skeleton structure can change and even collapse. This requires a reasonable selection of secondary building units, organic ligands, and active metal centers to obtain valuable hole materials. In addition, the change of the ligand in the structure of the MOF material can control the flexibility of the pore structure and can obtain different adsorption properties. The research of the industrial synthesis of these materials and its development in industrial applications will be another challenge for scientists.

With the deepening of the research work, the directional synthesis of metal-organic skeleton compounds with specific topological structure or expected functional characteristics will certainly become a reality in the near future. In practical application, metal-organic skeleton compounds will also play a huge potential functional value.

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