Advanced Metal–Organic Frameworks for Gas Separation

Xiao Guo *

Beijing Royal School, Beijing, 102200, China

* Corresponding author: guoxiao@st.brs.edu.cn

Abstract. In the chemical process, the effective separation of small gaseous molecules with similar physical and chemical properties is of great significance. In addition, clean energy sources such as hydrogen and methane are regarded as an ideal alternative to conventional fossil fuels. However, at present, the storage technology of this kind of natural gas is not perfect. The entry of harmful substances produced by human activities into the atmosphere has become a global danger that is becoming more and more worrying. It has become an important topic for scholars and industries Development of a multi-stage channel structure with high efficiency and low energy consumption for effective separation, storage or capture of toxic and harmful substances. In order to solve this problem, we intend to study the adsorption and adsorption of MOFs in the environment aboutH2/N2, H2/CO and H2/CH4 and some other gases. Compared with molecular sieve, activated carbon and other conventional inorganic porous materials, MOFs have a broad application prospect in gas adsorption and storage with unique properties. At present, the research of metal-organic frame materials with high stability has made great progress. Through the implementation of this project, it is expected to promote its wide application in air pollution control and other aspects.

Keywords: metal-organic frameworks, gas separation, molecular simulation, applications of MOFs.

1. Introduction

In recent years, membrane technology tends to play an increasingly crucial role in gas separation. MOFs are expected to become a new type of molecular sieve membrane because of its unique structure-activity relationship. The characteristics of MOFs used in composite substrate films were analyzed. Compared with the organic-inorganic composite properties of molecular sieves, MOF nanoparticles have good nesting properties and can be formed by hollow or spiral winding. Because of its low cost, small area, low power consumption, easy to operate and easy to operate, it has become a new technology with great market competitive advantage. In recent years, membrane method has been used to separate of CH_4, air separation and natural gas deodorization. High molecular membrane process has been perfected in industrial production because of its good processing performance, high economic feasibility, low energy consumption and so on. The material is widely used in adsorption separation, catalysis and sensing because of its large porosity, large specific surface area, clear pores, structural diversity and a variety of functions. Compared with other inorganic filling materials, MOF materials are unique in that: (1) There are many kinds of ligands that can be selected, and different ligands can be used to construct different types of MOF materials. (2) MOF materials can be modified by post-synthesis method (PSM) Realize to operate the pore size and MOFs internal structure. (3) Pore volume about MOFs is higher, but its concentration is lower, so at the same amount, MOFs have a strong effect on the composite film [1]. The next of this article will cover adsorption and adsorption of MOFs in the environment about H_2/CH_4, H_2/CO and H_2/N_2 and other gases. Compared with conventional molecular sieves and activated carbon, MOFs materials have excellent physical and chemical properties and show great application prospects in adsorption and storage.

2. MOF Structure

Metal-organic frameworks (MOFs) is a kind of MOFs crystal with specific structure, positive charge, assembled by a series of organic components, certain structure, "connector" as the basic unit, special structure, specific structural characteristics and different structural characteristics. These "nodes" composed of metal elements connect the two arms of the link to each other, thus forming a "cage" with repeated effects. Because of its hollow characteristics, the internal surface of metal-organic frame (MOFs) is active. At present, scholars at home and abroad have successfully prepared metal-organic frame materials with a specific surface area of 7800 square meters / g. Take this as an example. If you can show the area of a spoonful of this material (about 1 g solid), it is enough to cover a football field. Compared with other porous materials, MOFs has special structural diversity: unified pores, atomic-scale spatial distribution, adjustable pores, rich types and so on. And the changes of topological structure, geometric structure, scale and chemical properties of the network. This enables researchers to regulate the skeleton topology, pore structure and function.

2.1. High Specific Surface Area

MOFs is the largest class of solid materials known at present, and its porous structure determines the specific surface area of MOFs. In recent years, people have made a variety of explorations on MOFs materials, and found more MOFs materials. In his research, Mr. Furukawa found a new type of MOF-200 for the first time, whose Langmuir specific surface area can reach 10400 m^2/g [2]. The measured results of the specific surface are very close to the experimental results.

2.2. Unsaturated Sites

The unsaturated metals in MOFs materials can be coordinated with CO_2, hydrogen sulfide and SO_2, as well as with some amines and carboxyl groups, so as to realize the selective absorption of CO_2 and SO_2. In addition, MOFs can also be used as a catalyst in catalytic reaction. On this basis, there is a strong pi coordination between MOFs and unsaturated metal atoms, which can enhance the selectivity of ethylene compounds compared with van der Waals force. Because of their abundant unsaturated sites, MOFs such as MIL-53 show higher adsorption capacity and better CO_2 selectivity at low pressure.

3. Molecular Simulations

3.1. Applications of Molecular Simulation

The molecular simulation method is used to calculate the physical properties of the system, which mainly includes two stages: (A) calculate the interaction potential energy categories molecules either ion in to system, plus (B) work out in equation about motion in to the system. (A) about intermolecular force required on stage (A), there is no relevant experimental data, so we can only use quantum calculation based on the first principle, it can also be a method of combining theory with experiment. The second section gives a brief overview of the current methods for studying intermolecular interactions. (B) the step can be solved by perturbation theory and other approximation methods, or by high-speed computer. The latter technology is called molecular simulation [3].

4. Practical Applications of MOFs in Gas Separation

4.1. MOF Nanosheets

The introduction of two-dimensional nanostructures into composite materials in a polymer matrix is expected to become a new type of functional assembly for gas separation and other fields. Through the research on MOFs, it is expected to further expand its application fields. However, the preparation of single-layer MOFs is currently facing great challenges. This project intends to use the "bottom-up" method to prepare a series of 1,4-phthalic acid copper-based MOFs with micron-scale and nano-scale structures. Based on this, the application of MOFs in polymer can not only obtain excellent separation effect of CO_2/CH_4 mixed gas, At the same time, since separation about CO_2/CH_4 mixture are still greatly improved. From the scanning electron microscope of sectional focused ion beam, it can be seen that unlike isotropic crystals, MOF nanosheets occupy a large proportion in to cross sectional area of the films, as a result, it enhances of molecular resolution efficiency, and eliminate the non-selective permeation path.

Pore size and internal surface properties of metal-organic skeleton materials [4]. It encounters some difficulties, which restrict its scope of application, such as complex production and treatment often accompanied by unsatisfactory mechanical stability. From the relationship between the main chain selection of MOFs and polymer mechanics and chemical stability and the controllable preparation process, this project intends to composite MOFs with polymer and apply it to the field of gas adsorption [5,6]. However, existing MOFs preparation methods can only obtain a granular material, or a granular material. This not only increases the difficulty of the combination about two portions at polymer matrix, but also restricts the combination about two portions in it composites. Therefore, advantages of adding MOF to polymer materials are still very few. If the concentration of MOF is too high, its mechanical properties will be destroyed [7]. Study on submicron metal-organic frame (MOFs) as filler for filler, and some research results have achieved gratifying results in recent years [8,9]. The high aspect ratio and ideal micro-MOFs nanostructure proposed in this project provides a new idea for improving the integrated performance of the two materials. Two-dimensional MOF structures were prepared using layer by layer or epitaxial growth processes on solid substrates [10,11]. Anyway, how to fully integrate it with polymer materials to prepare metal-organic framework (MOFs) nanosheets with a uniform three-dimensional structure is a hot and difficult point in current research. This project intends to use the "bottom-up" method to prepare MOFs with high crystallinity and complete structure, and combine them with polymer matrix to prepare high-performance MOFs composite films.

4.1.1. Copper 1,4-Benzenedicarboxylate MOF Lamellae

However, conventional amine adsorption not only consumes energy, However, there is also a great demand for dangerous chemicals, Therefore, the development of CO_2 selective separation membrane materials is an effective way to solve this problem [12,13]. As can be seen from figure 3, when bulk CuBDC crystallization is added to the polyimide substrate, the separation selectivity is slightly lower than that of the pure polyimide reference film. This result suggests that composite films previously crystallized with bulky, isotropic fillers have poor separation properties [14].

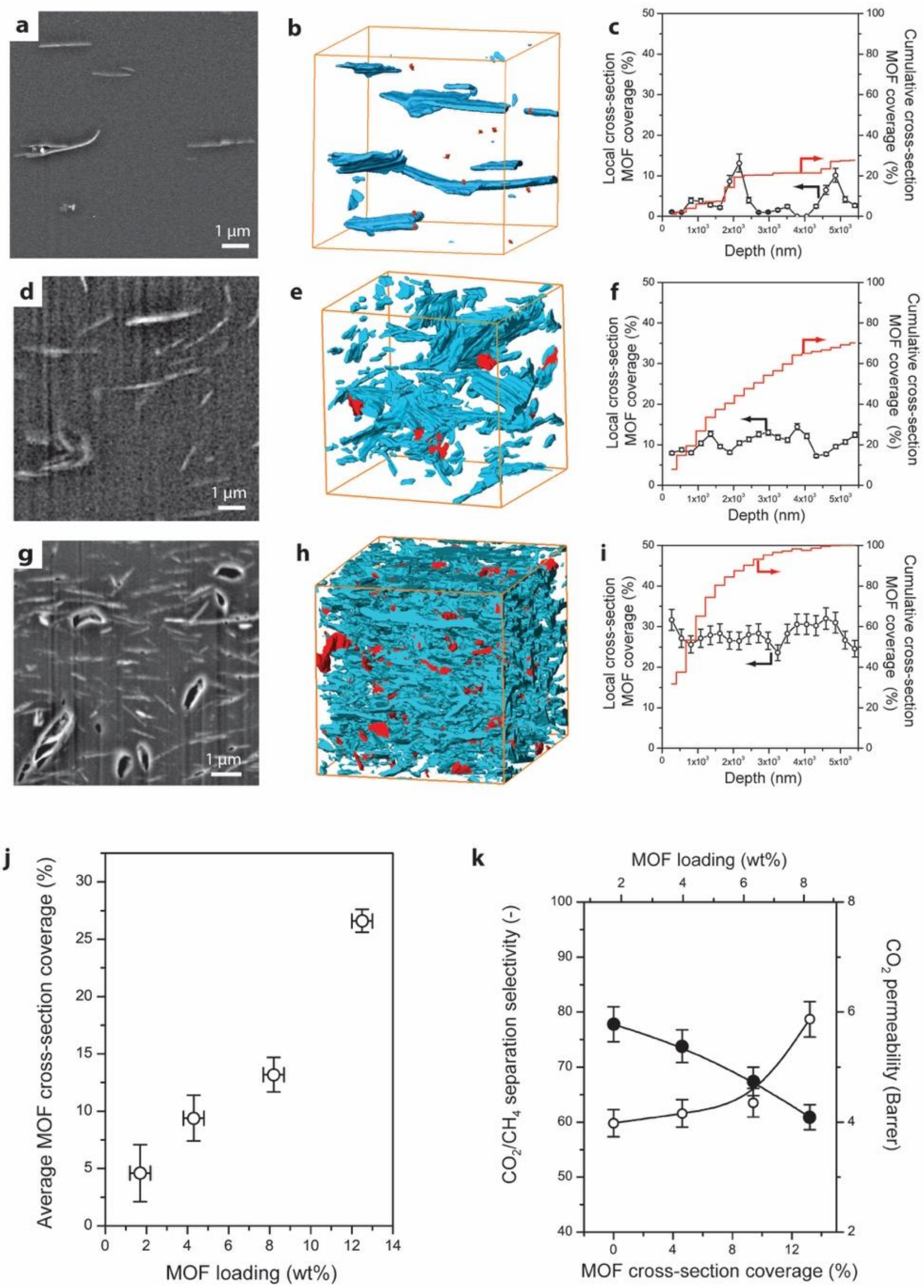

Figure 1. Internal microstructure analysis and separation performance of MOF-polymer composites with varying CuBDC MOF nanosheet loadings [15].

Due to the wide distribution range of the nano-flaky fillers, they are more evenly distributed at different depths, thereby promoting the separation effect to a certain extent. First, although the gas permeability is low, this causes repeated gas differential phenomena, which help improve the selectivity of the separation. For the ns-CuBDC (x) @PI film, this is confirmed by the relationship The correlation between the profile coverage of the fillers and the increased selectivity and reduced CO_2 permeability (as shown in Figure 1). Secondly, and most strikingly, this substance is very good at eliminating unnecessary plasticization, Through the penetration channel independent of MOFs, high selectivity, high selectivity, high selectivity, high throughput and efficient separation of polymer matrix can be achieved. In addition, the quasi-optimal arrangement of ultrafine particles can reduce the number of MOFs used, reduce the film thickness, and increase the CO_2 transmission rate without significantly affecting the selectivity of the separation. Our previous research found that another way to improve gas permeability is to use MOFs nanosheets with larger pores (see Figure 2). The smooth implementation of this project can lay a foundation for the application of MOFs laminated composites in practical engineering. And the establishment of a metal-organic frame assembly with high aspect ratio.

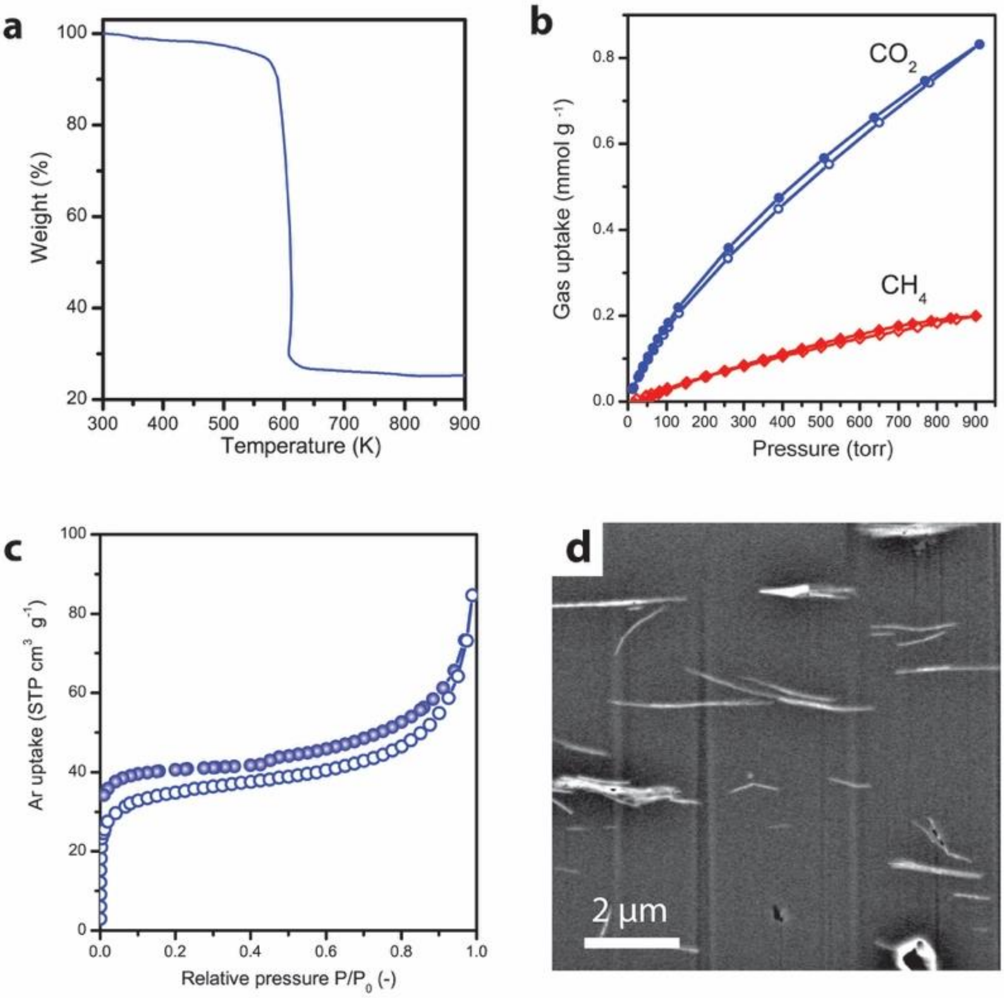

Figure 2. Synthesis of copper 2,6-naphtalenedicarboxylate MOF nanosheets and the polyimide-based MOF- polymer composite thereof [15].

4.2. PEI Modified MOF

PEI is a kind of polymer containing a large number of amino acids, can react with CO_2 to produce polyurethane. Chen et al. MIL-101 (Cr) is a new metal-organic skeleton material. Carbon dioxide adsorption capacity abput PEI-MIL-101-125 is over than 4 times greater than MIL-101 under the condition of 323 K, 0.15 pm and 1bar (0.20 and 1.00 mm mol g^{-1}). The selectivity of PEI-MIL-101-125 for $15/75CO_2/N_2$ gases mix in 298 K, 323 K and 770 K and 1200, respectively [16]. PEI-impregnated UiO-66(PEI@UIO-66) The synergistic action of polyvinyl alcohol (UIO-66) and CO_2/CH_4 might significantly Significant improvement about CO_2 adsorptive capacity inCH_4/CO_2 selectivity. capacity about CO_2 and CH_4/CO_2 selectivity about PEI@UIO-66 were 2.41 mm, respectively, and compared to separation about CO_2/CH_4. 338 K, the relative humidity (relative H) is 54%. Its working ability and CO_2/CH_4 selectivity were studied CO_2 are expressed as 251 respectively, the yield increased by 48.8% and 126% compared with the dry state. In density functional theory (DFT), plus water vapor might accelerate the adsorption rate about CO_2, thus reducing the absorption rate of CO_2 [17]. MOFs and mesoporous silica modified by PEI show good CO_2 trapping ability, but they are easy to be dissolved by organic amines in the process of charge and discharge, which greatly restricts their practical process [18].

5. Conclusion

Membrane separation technology has the advantages of simple operation, small footprint and energy saving, so it is a new technology with the most development prospect at present. Because of their controllable pore size, shape and surface properties, MOFs have become a very popular new type of separation materials. The organic combination of MOFs and flexible polymer is expected to break through the contradiction Study on the correlation between permeability and selectivity in conventional separation process, so as to achieve the purpose of industrialization.

However, in order to obtain a metal-organic framework-polymer film with excellent performance, there are still many problems to be solved. At present, there are some problems in MOFs, such as uniform particle distribution, good interface bonding with polymer materials, defect-free films and high-flux films. As mentioned above, many strategies have been suggested to overcome this difficulty. Second, through the copolymerization of MOFs and conventional polymers/composition, the chemical bonding between MOFs and polymers is used to improve the interface between materials and polymer bodies.

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