Study on preparation of metal-organic framework membrane and pore size adjustment method

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Abstract: Metal-organic framework materials have the advantages of large specific surface area, high porosity, strong adjustability of framework structure, adjustable chemical and thermal properties, etc., and can be used as ideal membrane materials. In this paper, the preparation methods and conditions of several common metal-organic framework materials, as well as how to adjust the pore size, are reviewed, and the advanced membrane treatment technology is prospected.

1 Foreword

Metal-organic framework material is another important new type of porous material besides zeolite and carbon nanotubes. As a new type of porous material with the most heat and foresight, it has incomparable advantages compared with traditional inorganic materials such as silicate molecular sieve, phosphate molecular sieve and porous materials such as carbon and silicon. Although the pore structure of traditional inorganic porous materials is regularly arranged, the pore size can not be controlled systematically. The pore size of metal-organic framework membrane can be easily adjusted by changing metal source, organic ligand, reaction solvent and temperature. In this paper, several commonly used preparation methods of organic metal skeleton membranes and pore size adjustment methods are introduced.

2 Preparation method of metal-organic framework film

Common preparation methods of metal-organic framework films include in-situ synthesis, secondary growth, mixed matrix membrane, chemical modification of carrier surface and layer-by-layer growth.

2.1. In-situ synthesis method

In-situ synthesis is a method of soaking the carrier without any crystal in the precursor solution, thus growing a large number of crystals. At first, the metal-organic framework material forms crystal nucleus, and then, it grows alternately to produce continuous thin films. Huang Aisheng’s research group [1] used different coupling agents (such as silane, dopamine, etc.) as connecting carriers, and prepared different ZIF series metal-organic framework films by in-situ synthesis. Wang prepared PA/ZIF-8 nanocomposite films by in situ growth and interfacial polymerization. first, the ZIF-8 particles were grown in situ on the supported polysulfone porous film as an interlayer, and then the polyamide was encapsulated on the ZIF-8 interlayer by interfacial polymerization, and finally the film with interlayer was formed. the content of the ZIF-8 and the number of layers of the membrane can also be controlled by repeatedly growing in the precursor solution.

2.2. Secondary growth method

Secondary growth method, also called crystal coating method, refers to coating the seed crystal first in the process of preparing the film, then placing the seed crystal in the solution phase, and growing again to form the film. Although the operation of the secondary growth method is more complicated than that of the in-situ growth method, the control advantages of the secondary growth method in pore structure, crystal orientation and film thickness are obvious. See table 1 for the specific method and operation process. Zhao Zhenxia et al.[2] successfully prepared MOF-5 crystal films on Al2O3 glass slides by secondary growth method.

Table 1. Specific method and operation process of secondary growth method

| Way                      | Operation and conclusion                                                                 |
|--------------------------|-------------------------------------------------------------------------------------------|
| Manual crystal coating   | Firstly, the surface of α-Al2O3 carrier was modified by polyethyleneimine, and then the MOF synthesized by Cu (NO3) 2 ·3H2O and 4,4- hexahydroisopropylidene benzoic acid was connected with the modified α-Al2O3 to prepare a continuous and dense MOF film. |

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2.3. Mixed matrix membrane method

Mixed matrix membrane (MMM) is a kind of composite material composed of polymer matrix, in which a large number of particles are embedded. MMM not only inherits the properties of polymer, but also is influenced by filling materials. It has the mechanical elasticity and high porosity of polymer materials. In the mixed matrix membrane method, firstly, alumina particles with porous structure formed by the traditional porous alumina preparation method are dispersed and mixed in a polymer solution, and then a mixture which is easy to coat and diffuse is formed; then, the film is scraped by a scraper or prepared by a spin coating method; and finally, the solvent is volatilized by curing or drying, so that the metal-organic framework materials added to the membranes formed in the polydimethylsiloxane polymer matrix increased, but the selective permeation weakened. SEM images show that there are voids around the porous ceramic particles, indicating that the adhesion between the porous ceramic particles and the polymer is weak, so the membrane has no selective permeation channels. Because the polymer is nonpolar and has weak surface interaction with the polymer, the adhesion between the polymer and the polymer is very weak.

2.4. Chemical modification of carrier surface

Continuous membrane with high concentration and no defects can improve the flux of membrane, and then enhance the selective permeability of membrane. In the preparation process of mixed matrix membrane, when pure metal-organic framework materials are combined with polymer materials, membrane defects or cracks easily occur, which directly affect the chemical properties of the membrane. This problem can be improved by modifying the surface of metal-organic framework, the chemical modification of carrier surface is a common method to modify metal-organic framework materials. The polymer in the mixed matrix film was modified by silanization modification, which realized the versatility of the film, and the interaction between materials was also improved. However, in C₃H₆/C₃H₈ gas separation, the thicker the
A film has poor selectivity and gas permeability, which may be due to the relatively poor internal microstructure of the prepared ZIF-8 crystal layer. Because the synthesis conditions of this method are mild, it is suitable for assembling organometallic skeleton membrane on polymer substrate. While many organometallic framework films can be prepared by this method, these SURMOF films are more suitable for scientific research, because the growth and preparation process of MOF films prepared by this method is very time-consuming and complex. More problems will be encountered in mass production.

To sum up, the preparation methods, advantages and disadvantages of common metal-organic framework films are shown in Table 2.

Table 2. Preparation methods, advantages and disadvantages of common organometallic skeleton membranes

| Preparation method               | Advantage                                                                 | Disadvantage                                                                 |
|---------------------------------|---------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| In situ growth method           | Crystal or films with nanometer scale can be prepare                      | The membrane that can be prepared is relatively simple                        |
| Secondary growth method         | Controllable seed crystal grows evenly, and the produced film is continuous, with few defects and compactness | Operation is more complicated than in-situ growth                             |
| Mixed matrix membrane method    | Various types of organometallic skeleton films can be prepared             | Compared with pure organometallic skeleton films, the permeability is poor     |
| Chemical modification of carrier surface | The MOF membrane synthesized by post-modification method forms a covalent composite structure, which is far better than the traditional mixed matrix membrane, and its selectivity is also improved | The film forming conditions are difficult to achieve and the operation is complicated |

### 3 Method for adjusting pore size of metal organic framework materials

The pore size of organometallic framework material can be adjusted by changing the organic ligand and length, or changing the metal source, reaction solvent and temperature.

#### 3.1 The regulation of organic ligands and length on the pore size of metal-organic framework materials

One of the important components of metal-organic framework includes organic ligands, so by adjusting the length of organic ligands, the pore size of metal-organic framework can be controlled. Yaghi research group and others\[5\] used phthalic acid (1,4-BDC), 2,6-naphthalene malonic acid (2,6-NDC), 4,4’-biphenyl malonic acid (4,4-BPDC) and 4,4’-terphenyl malonic acid (4,4-TPDC) as organic ligands. By changing the length of the ligand, the pore size can be adjusted from 0.38nm to 2.88nm, Wang Keke et al.,[6] designed and synthesized three kinds of porous materials with different pore sizes (Hf-FUM, Hf-BDC and Hf-BPDC).

#### 3.2 Metal sources control the pore size of metal-organic framework materials

In the process of adjusting the metal-organic framework, the selection of metal source can have a certain influence on the adjustment of material pore size. A majority of metal sources are subpopulations of transition metal ions, such as Fe\(^{3+}\), Zn\(^{2+}\), Cu\(^{2+}\), because the subterranean orbitals of these metal ions are not filled with electrons and can be coordinated by lone pairs of electrons of organic ligands. Rose et al.,[7] prepared Cu-FDA, Fe-FDA and Al-FDA with 2,5-furandicarboxylic acid (FDA) as organic ligand and Cu\(^{2+}\), Fe\(^{3+}\) and Al\(^{3+}\) as metal sources under the same experimental conditions. The aperture of Cu-FDA is smaller than that of Al-FDA, and its average aperture is 0.66nm. In Fe-FDA materials, the pore size distribution ranges from 0.6 nm to 10 nm. Therefore, under the same organic ligands and experimental conditions, coordination with different metal ions such as Fe\(^{3+}\), Zn\(^{2+}\), Cu\(^{2+}\) and Al\(^{3+}\) as metal sources can be effectively controlled.
3.3 Regulation of the pore size of metal-organic framework materials by reaction solvent and reaction temperature

Different solvents have great differences in polarity. During the formation of metal-organic framework materials, weak interaction may occur between solvent molecules and framework, which can stabilize metal-organic framework materials and control the pore size of framework materials. Sahiner et al. [8] prepared metal-organic framework materials with trimellitic acid (C₉H₆O₆) as organic ligand, CuSO₄ as metal source and ethanol and deionized water as solvents. When ethanol is used as the reaction solvent, the synthesized material does not produce mesoporous structure. When deionized water was used as the reaction solvent, the results were different from those of ethanol, and mesoporous structure appeared in the synthesized materials, with a pore size of 15.56nm. Gérard Férey’s research group [9] found that due to the different dielectric constants of water at different temperatures and the different coordination capacities and modes of carboxylic acid ligands, the structures and pore sizes of the generated organometallic skeleton materials are different.

4 Conclusion and prospect

The preparation method of hybrid membrane based on metal-organic framework material has important academic value and industrial application prospect. With regard to the preparation of organometallic skeleton films, many research groups have explored the preparation methods of different series of organometallic skeleton films with excellent film properties through experiments, but the preparation technology still has some shortcomings, the control of intergranular defects is still the main problem, and the high raw material cost is also worthy of attention.

Similarly, suitable pore size plays a key role in the application of metal-organic framework materials. Compared with traditional inorganic or organic porous materials, metal-organic framework materials can easily control organic ligands, metal sources, solvents and reaction temperatures to construct suitable pore sizes.

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