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Synthesis of Metal Organic Framework Material MIL-101

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Abstract. MIL-101 is a typical metal-organic framework. Mil-101, like the other metal-organic frameworks (MOFs) is a material with high porosity, large surface area, adjustable micro-pore size, and easy functional structure. Contrary to the most MOFs, Mil-101 has a high hydrothermal stability. All of the characteristics collectively make MIL-101 a good candidate for a catalyst support. In this paper, the synthesis methods of MIL-101 materials have been reviewed. It is pointed out that the hydrothermal synthesis method has many problems such as complicated process, many organic waste liquid and low yield. The room temperature fast synthesis method has the potential to provide industrialized production of MIL-101 with its unique advantages.

1. Introduction

The metal organic skeleton is a novel porous compound formed by a multidentate organic ligand containing nitrogen, oxygen or the like and a metal ion bonded by a coordination bond. Compared with traditional silica-alumina molecular sieves, MOFs have high porosity and specific surface area, adjustable pore size and structure, and unique coordination structure. They have good properties in gas storage, separation, catalysis, biochemistry and pharmaceuticals. Application prospects [1-3]. Since the beginning of the study of MOFs materials, a variety of different MOFs have been synthesized. However, due to the poor hydrothermal stability of MOFs, the variety and complexity of the materials, it is difficult to systematically study them by experimental methods and lead to its development is limited[4-5].

According to the development of time, MOFs materials have experienced three different eras: the skeleton structure of the first generation of MOFs materials mainly contains solvents, or neutral and ion guest molecules, and the removal of guest molecules leads to the irreversible collapse of the skeleton, and The thermal stability and chemical stability of the material are poor; the second generation of MOFs have a rigid microporous framework, such as the MOF-5 reported by Yaghi [6] in Science, which is capable of maintaining the framework in the absence of guest molecules. Complete, with long-lasting pores, such materials are still one of the hot research areas in the world; the third generation of MOFs materials has flexible and dynamically controllable skeletons that can stimulate external sources such as light, electric fields and different objects. Molecules and the like react to reversibly change tunnels or pores, and have potential applications in gas separation, sensors and actuators.

In 2005, French FÉREY professor group [7] first reported the synthesis of MIL-101, its structure is shown in Figure 1. First, the metal chromium trimer $[\text{Cr}_3\text{O}(\text{CO}_2)_6]$ and terephthalic acid (H_2BDC) are connected to form a diameter of The 0.86 nm microporous supertetrahedron forms a super tetrahedron and is further connected by H_2BDC to form a three-dimensional skeleton with an MTN topology. The



framework material is a quasi-spherical cage with two pore sizes (2.9 nm and 3.4 nm) (the window thereof) At 1.2 to 1.6 nm), the specific surface area is 4,000 m²/g or more. However, most of the reported MIL-101 has a specific surface area of 2800 to 3400 m²/g [8].

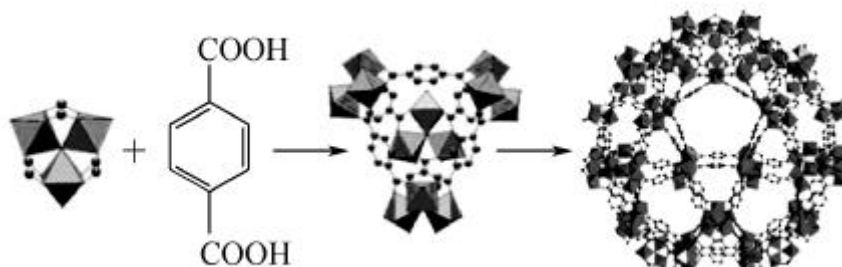


Figure 1. Schematic diagram of the synthesis and structure of MIL-101

When the metal ion centers of MIL-101 materials change, their structural rigidity is easily affected, and the adsorption amount of small molecular gases is reduced. Even when impurities are present during the adsorption process, the structure of MIL-101 material collapses. However, compared with most MOFs materials, MIL-101 has a larger specific surface area and pore volume, and has excellent stability in water, air and common organic solvents, and its skeleton structure does not change at 300 °C, overcoming the problem. Many other MOFs have the disadvantage of poor hydrothermal stability. In recent years, MIL-101 has shown unique advantages in adsorbing CO₂, which has attracted the attention of researchers. This article describes the main synthesis methods of MIL-101.

2. MIL-101 synthesis method

With the expansion of MIL-101 application research, how to improve its crystal structure, improve product yield and simplify the synthesis process has attracted wide attention of researchers. In recent years, people have been researching and improving MIL-101 synthetic raw materials, synthesis conditions and synthesis methods for a series of problems such as low yield and complicated synthesis.

2.1. Diffusion method

The diffusion method [9] is suitable for the cultivation of high-quality single crystals and is used for the analysis of crystal microstructures. This method is mainly used for scientific research because of long synthesis cycle, low yield, and difficult mass production.

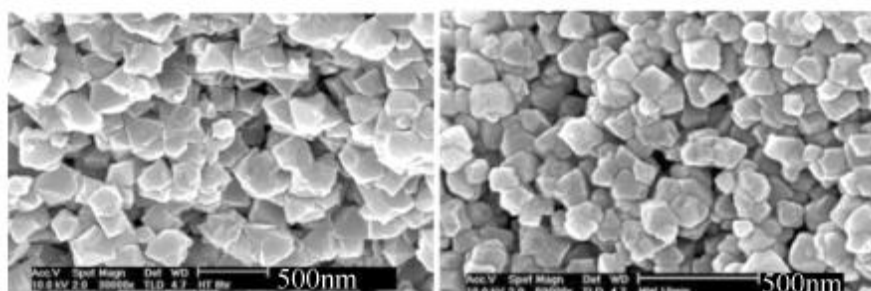
2.2. hydrothermal method

Most of the synthesis of MIL-101 is hydrothermal. First, the chromium nitrate [Cr(NO₃)₃·9H₂O] and terephthalic acid [H₂BDC] are dissolved in deionized water, and a certain amount of hydrofluoric acid is added. After homogenization, it was transferred into a Teflon-lined reactor and statically hydrothermally crystallized at 220 °C and autogenous pressure for 8 h, followed by filtration and purification to remove unreacted organic matter, followed by drying and vacuum activation to obtain a final product. The resulting powder typically has a particle size ranging from microns to microns or even tens of nanometers. Among various preparation methods of nanomaterials, hydrothermal method is considered to be a highly competitive method with less environmental pollution, lower cost, and easy commercialization. Moreover, the conditions of low temperature, isostatic pressure and liquid phase reaction of hydrothermal method not only can easily control the particle size and morphology of the product crystal, but also change the reaction performance of the reactant, and can also reduce the influence on product formation. However, in the synthesis process, the H₂BDC in the raw material liquid is precipitated at the bottom of the tank due to its small solubility in water, resulting in uneven distribution of the raw materials, affecting the crystallization effect, and the yield is low. In order to overcome this shortcoming, Chen Heng et al [10] used dynamic stirring in the crystallization reaction

process. Compared with the static crystallization method under the same conditions, the synthesized MIL-101 has a small grain size and a product yield of more than 20%. Stirring makes the reactants mix more uniformly, promotes the mass transfer and heat transfer process of the system, shortens the crystallization time, and improves the crystallinity of the product.

2.3. microwave method

Conventional hydrothermal synthesis of MIL-101 takes a long time and crystallization time often takes several days. A microwave method for synthesizing MIL-101, which is heated using microwave radiation during crystallization. Due to the strong microwave penetration, the heating is uniform and fast, which not only greatly shortens the reaction time, but also has good reliability and repeatability. So this is a simple, fast and effective synthesis method. In addition, in the synthesis of nanoporous materials and inorganic solid materials, microwave-assisted hydrothermal method provides an effective way to control particle size distribution, phase selectivity and macroscopic morphology. In 2009, HONG et al. [11] prepared MIL-101 by hydrothermal method and microwave radiation synthesis. The results also confirmed that the preparation time of the microwave synthesis method was greatly shortened compared with the hydrothermal method, and the crystal grain size of MIL-101 was uniform and easy to control, as shown in Fig. 2. At the same time, the study also showed that when the synthesis method is the same, the influence of the synthesis conditions is mainly temperature and time, and the solvent concentration and the activation treatment method are supplemented.



(a) Hydrothermal reaction for 8 hours (b) Microwave reaction for 8 hours

Figure 2 SEM image of MIL-101 (Cr) [11]

2.4. room temperature fast synthesis method

The rapid greenhouse synthesis method is a low-energy green preparation method. Yaghi et al. [12] reported the use of triethylamine as a fast deprotonating agent, and successfully achieved room temperature preparation of MOF-5, MOF-74, MOF-177, MOF-199, IRMOF-0, etc., and obtained high specific surface area. The powder crystals have Langmuir values of MOF-5 ($3909 \text{ m}^2/\text{g}$), MOF-74 ($1187 \text{ m}^2/\text{g}$), and MOF-177 ($4944 \text{ m}^2/\text{g}$). However, this method still uses a large amount of DEF or DMF as a solvent, which generates a large amount of waste liquid, which increases the difficulty of post-treatment. Most of the MOFs reported in the literature have crystal yields (based on metal salts or organic ligands) of less than 75%, and there are very few reports on the recycling of residual reactants in solvents and solvents. We believe that developing solvents and recycling of raw materials Technology is a more feasible path for the large-scale preparation of MOFs in the future. It has considerable research and economic value and is in line with the environmental strategy of zero emissions.

3. Conclusion

MIL-101 metal organic framework has a compact structure, large specific surface area, high porosity, adjustable pore size and structure, and unique coordination structure, which has broad application prospects in the field of catalysis. However, its industrial production still faces many challenges. The yield of hydrothermal synthesis of MIL-101 is generally low, the purification process is complicated, a large amount of chemical solvent waste liquid is produced, and the reproducibility is poor. It is

necessary to start from strengthening the crystallization process by changing the solvent. And control the crystallization conditions to improve the synthesis method and simplify the synthesis process. The rapid synthesis method of greenhouse has the advantages of high product yield, simple purification and activation process, and no chemical solvent waste liquid. It is the development direction of MIL-101 synthesis and future industrial production. With the in-depth study of MIL-101 material synthesis at home and abroad, MIL-101 as a new catalytic material will show broad prospects in future practical applications.

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