Synthesis Methods and Influencing Factors of Metal Organic Framework Material MIL-53

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Abstract—Regarded as brand-new porous material, metal organic framework (MOF) has a certain ability to remove pollutants due to its high porosity, high specific surface area, adjustable micropore size and easy functionalization. Compared with other metal organic framework materials, MIL-53 has a relatively higher specific surface area and stronger hydrothermal stability, which leads to excellent performance and application prospects in the removal of pollutants. In this paper, synthesis methods of metal-organic framework material MIL-53 are introduced, and the influencing factors in the synthesis process using hydrothermal method are discussed, including the component ratio, type of organic solvent and pH value. Due to less dependence on residence time and organic solvent, mechanical method can reduce energy consumption and has latent value for future application. Among different influencing factors, reducing the pH of solution when synthesizing MIL-53 using hydrothermal method seems to save time and achieve rapid formation.

1. Introduction
Metal organic frameworks (MOFs) are porous materials with large specific surface area and adjustable pore size, which are formed by coordination of metal ions and multi-electron organic ligands [1,2]. The metal ions currently and mostly used in synthesis process mainly include Mg²⁺, Cu²⁺, Cr³⁺, Al³⁺ and Fe³⁺ [3,4]. Férey et al. [5] carried out studies on the synthesis of MIL-n using trivalent metals, terephthalic acid (H₂BDC) and trimellitic acid (H₃BTC). MIL-53 is one of the typical representatives. Its synthesis process is generally carried out under hydrothermal conditions, forming a MO₄(OH)₂ (M=Cr³⁺, Al³⁺, Fe³⁺) corner-sharing octahedron connected by terephthalate groups. Compared with other MOF materials, MIL-53 has a relatively higher specific surface area (up to 2000 m²/g) and pore volume, while still maintaining good stability at high temperatures, thus showing excellent performance in pollutant removal research. However, the synthesis of MIL-53 usually takes plenty of time, and the yield is too low for industrial use, which affects future applications of the material, not to mention the cost and recycle ability. Therefore, improving the yield of product, and achieve rapid synthesis of MIL-53 are of great importance.

In this paper, synthesis methods of metal-organic framework material MIL-53 are introduced, and the influencing factors to hydrothermal method are discussed, including the component ratio, type of organic solvent, pH value and synthesis temperature.
2. Synthesis methods of MIL-53

2.1. hydrothermal method

The method is to put the ligand, metal salt and organic solvent in a container and react for a period of time under a certain pressure and temperature. The metal ions and organic ligands can complete the self-assembly process, thereby obtaining the required metal organic framework [6]. In specific, the raw materials for preparing MIL-53(Cr) by hydrothermal method are generally chromium nitrate [Cr(NO$_3$)$_3$·9H$_2$O], terephthalic acid(H$_2$BDC) and water. The component ratio of Cr(NO$_3$)$_3$·9H$_2$O, H$_2$BDC and water is usually 1:1:280 or 1:1.5:280, and a small amount of hydrofluoric acid is added. After being stirred evenly, the mixture is transferred to the polytetrafluoroethylene reactor, which is put into an electric heating oven under airtight conditions. The reaction is carried out in the container under a constant temperature which is usually 220℃, and the reaction time is up to 72 hours. After that, the reactor is cooled, the product is washed with deionized water, and the initially synthesized MIL-53 powder can be obtained. When it comes to MIL-53(Al), the metal salt is substituted for AlCl$_3$·6H$_2$O.

The initial product of MIL-53 has crystalline terephthalic acid attached to the inner surface of the pores, so the product needs to be purified to dissolve and remove the excess terephthalic acid to achieve higher specific surface area. Due to the low solubility of terephthalic acid in water, solvents with greater solubility with terephthalic acid are necessary, such as ethanol, dimethylformamide (DMF), and ammonium fluoride.

The hydrothermal synthesis method is simple and safe, and has been widely used in the synthesis of metal organic frameworks. Nowadays most of the article reports still use this method to prepare MIL-53. However, since the time spent for heating in the reactor often reaches several days, the relatively longer synthesis time is an obvious disadvantage of the hydrothermal synthesis method.

2.2. microwave method

Microwave synthesis is a synthesis method that uses the function of microwave radiation heating to speed up the reaction process and achieve rapid crystallization. The energy transmission method of microwave synthesis is different from the that of the solvent method. The rapid crystallization is achieved by the direct interaction of electromagnetic waves and reactants. Microwave synthesis mainly depends on the contact of electromagnetic waves and movable charges to conduct energy. Solvent molecules and reactant ions are polarized under the electromagnetic field, and an electric current is formed in the solution. The electric resistance of the solution generates a lot of heat and accelerates the movement of reactant molecules.

Due to the direct interaction between radiation and the reactants, a better heating method is provided under microwave assistance, which can achieve a high heating rate and uniform heating effect for the entire sample, and crystals of smaller size can be synthesized. Gordon et al. [7] synthesized highly crystalline MIL-53(Fe) in 10 minutes from microwave irradiation and in 7 minutes from ultrasound irradiation. Therefore, this method has the advantages of shorter reaction time and uniform product distribution.

2.3. mechanical method

Mechanical synthesis is a method of converting mechanical energy into chemical energy to synthesize materials. Compared with hydrothermal method and microwave method, this method can obtain the target product through mechanical movement in a ball mill. Mao [8] mixed the chromium salt and H$_2$BDC uniformly. After the mixture was grinded for 30 minutes, the reactant was added to a polytetrafluoroethylene reactor. Under non-solvent conditions, MIL-100(Cr) and MIL-53(Cr) can be obtained under 220℃ for 24h to 48h. The study found that when chromium chloride hexahydrate (CrCl$_3$·6H$_2$O) was used as a chromium source for synthesis, the surface area (1310m$^2$/g) and pore volume (0.84cm$^3$/g) of MIL-53(Cr) prepared by this method were similar to those of the solvothermal method, and it had more excellent catalytic performance.
Since it requires less heating or organic solvents, mechanical synthesis can definitely reduce energy consumption and also help reduce environmental pollution during the synthesis process. To be more important, this method is suitable for the synthesis of large quantities of metal-organic framework materials, which provide latent value for future industrial use.

3. Influencing factors in synthesis of MIL-53 by hydrothermal method

3.1 the component ratio
When synthesizing MIL-53 by hydrothermal method, the ratio of metal salt, terephthalic acid and water is generally 1:1:280, and some ratios are 1:1.5:280. Different ratio leads to products with different status. Zhou et al. [9] tried to synthesize MIL-53(Cr) at a ratio of 1:1.5:280 and 1:2:280. By comparing the XRD results of the product, it was found that increasing the content of terephthalic acid in the solvent can make the product align better with the standard spectrum, which may lead to better crystallinity. The specific surface area measured after the purification treatment by the reflux method was 1355.9 m²/g, which was close to many reported values. Combined with the SEM image, it can also be seen that several times of washing using DMF can remove the excess terephthalic acid inside and outside the pores.

The change of component ratio not only leads to different specific surface area, but also influences photocatalytic performance afterwards, since the ratio of metal and organic ligand affect the crystallization process to some extent. Liu et al. [15] prepared MIL-53(Fe) under different component ratio, and Rhodamine B(Rhb) was used as model pollutant to test the photocatalytic activity of the products. After 180 min of visible light irradiation, the pseudo-first order reaction kinetics of RhB degradation over the MIL-53(Fe) at ratio of 1:2 was 0.0286, which was the highest among different component ratios including 1:1 and 1:1.5.

3.2 type of organic solvent
For hydrothermal method, pure water is sometimes selected as the solvent, and dimethylformamide (DMF) are often used as the solvent. These two methods have their own advantages and disadvantages. When pure DMF is used as the solvent, the yield of the sample can reach more than 80%, but with poor crystallinity. When pure water is used as the solvent, the low solubility of terephthalic acid ligand in water results in low yield (20%-30%), but the obtained sample has higher crystallinity. Although the solvent in the former method contains DMF, both methods still require purification steps to remove unreacted impurities. Cheng et al. [10] used a mixed solvent, which was a mixed solution of water and DMF to synthesize NH2-MIL-55(AI), trying to achieve high yield and high crystallinity at the same time. By comparing the morphology of the product with different proportions of water in the solvent, it was found that the crystal morphology, size and measured specific surface area of the product vary under different solvent ratios. Among them, the smallest grain size was 76nm, and the largest specific surface area was 1882 m²/g, which was a big improvement compared with the value reported in the general articles.

3.3 pH
The reactants required to synthesize MIL-101 are the same as MIL-53, the main difference is the reaction time. The synthesis time of MIL-101 is generally 8-12h, while the residence time of MIL-53 is usually 72 hours, and there is a transition from MIL-101 to MIL-53 during the reaction. Zhao et al. [11] proposed that lowering the pH of the reaction solution was not helpful to the dissolution of H₂BDC and the formation of chromium trimers, while Khan et al. [12] proposed that the formation of chromium trimers during the synthesis process of MIL-101 is more important than the dissolution of H₂BDC, and appropriately lowering the pH of the solution may be helpful to the formation of chromium trimers.

Accordingly, Zhang et al. [13] used acetic acid instead of hydrofluoric acid as a mineralizer to synthesize MIL-101. It was found that after adding more than a certain amount of acetic acid, the
product at a reaction time of 20h is no longer MIL-101, but MIL-53 instead. In addition, the pores of MIL-101 synthesized by adopting acetic acid as a mineralizer are cleaner, and the specific surface area was also increased, which showed that lowering the pH of the solution can accelerate the synthesis to a certain extent.

![Diagram](image-url)

Fig.1 Different crystallization route for different content of HF added in the hydrothermal synthesis of MIL-53(Cr) [14]

There are also researches hoping to reduce the pH value by increasing the proportion of mineralizers. Li et al. [14] increased the proportion of mineralizer in the synthesis to 1.0Cr: 1.0BDC: 2.4HF: 284H2O, and observed the direct formation of MIL-53 during the 8h reaction, as is shown in Fig.1.

3.4 synthesis temperature

Another important factor in the synthesis of MIL-53 using hydrothermal method is the synthesis temperature. Different synthesis temperature may lead to different specific area value and photocatalytic activity. Liu et al. [15] prepared MIL-53(Fe) under different synthesis temperature and component ratio. It was found that the specific areas increased with the synthesis temperature rising from 130°C to 150°C. However, if the synthesis temperature was over 190°C and below 130°C, the crystal structure may be destroyed. Therefore, a suitable synthesis temperature may lead to better crystallization and more uniform morphology, which can be related to better photocatalytic performance.

![Diagram](image-url)

Fig.2 Stability of large-pore form of MIL-53(Al) after the removal of DMF and cooling to room temperature [16]

In addition, transition between large-pore and narrow-pore can be observed under typical synthesis temperature. William et al. [16] prepared MIL-53(Al) using DMF under different temperatures. It was found that the MIL-53(Al) synthesized in DMF at 120°C remained in the large-pore form under all conditions, as is shown in Fig.2, while the material synthesized at 220°C exhibited a gradual breathing transition to the large-pore form, allowing for increased CO2 adsorption in the 1-20 bar region.

4. Conclusions

The metal organic framework material MIL-53 is widely used in the removal of environmental pollutants, such as antibiotics, organic dyes, aromatic compounds and heavy metals. However, the above results are still in the experimental research stage, while mass production and large-scale
pollutant treatment are yet to be accomplished. There are still problems about the costs, actual adsorption and photocatalytic performance, long synthesis time, complex steps, low yield, and recycling performance. It is still difficult to carry out large-scale industrial applications. Reducing the pH of solution when synthesizing MIL-53 using hydrothermal method seems to save time and can achieve direct formation. Also, mechanical method can get rid of organic solvent, and save reaction time to some extent with less pollution derived from synthesis process. With deeper research on the high yield and rapid formation, MIL-53 as adsorbent and also catalytic material will definitely show great prospects in future applications.

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