Stability Improvement Methods and Application Progress of Metal-Organic Frameworks

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Abstract: Metal–organic frameworks (MOFs) are a kind of product produced with a combination of an inorganic metal center and a bridged organic ligand. Because of its porosity and high specific surface area, it has attracted much attention. However, due to the metal center and coordination bond is affected readily by other environmental factors, MOFs materials have relatively poor stability, which severely hampers its application in various fields. In this research, two ways of improving stability are summarized, one is via de novo synthesis, and the other is through post-synthetic modification to improve the stability of MOFs. Moreover, MOFs and its application fields, including gas separation and storage, catalysis, medicine, sensing, rechargeable batteries and capacitors production, are prospected.

1. Introduction

Metal-organic frameworks (MOFs) are porous materials with periodic network structure. They are composed of organic ligands and metal ions or metal clusters (inorganic metal centers)[1]. The common synthesis methods include hydrothermal method, liquid-phase diffusion method, microwave synthesis method and so on. MOFs are widely used in gas separation and storage[2], catalysis[3], medicine[4], sensing[5], rechargeable batteries and capacitors[6], etc. Compared with other porous materials, it has the characteristics of adjustable structure[7], high specific surface area[8], and large porosity[9]. The excellent properties of MOFs make them have attractive development prospects and potential. In the development of MOFs, its poor hydrothermal stability and mechanical stability are important factors restricting the application of MOFs.[10]

In the past 20 years, researchers have found that when MOFs come into contact with water molecules in the environment, H⁺ and OH⁻ ionized from water molecules will coordinate with organic ligands and metal centers respectively, resulting in significant changes in structural properties, which has seriously limited the development of materials[11]. For example, MOF-5, a porous material formed by Zn40 and dimethyl terephthalate, has good catalytic performance[12][13]. However, when the MOF-5 sample is exposed to air for 10 minutes, a new peak appears at 9 ° in the XRD image (Fig. 1), indicating that the structure has changed[14]. This characteristic greatly hinders the application of this kind of composite materials in the actual production activities. Similar to MOF-5, other MOFs like HKUST-1[15], STU-1[16], SDU-1[17], PCN-426-Mg[18] all have broad application prospects, but their stability is extremely poor. Therefore, it is urgent to improve the stability of MOFs.
Nowadays, many researches have put forward effective strategies to improve the stability of MOFs. The ideas of modification methods can be summarized into two types. One is to redesign and synthesize stable MOFs, while the other is to improve the stability of existing MOFs. The former can be further divided into the ideas of enhancing the strength of coordination bond, mixing metal ions and inserting stable pillars. The latter can also be roughly divided into post synthesis group modification and composite material synthesis\(^{[10]}\). MOFs with high chemical stability can be used in the application fields with special operating conditions, such as gas separation and storage\(^{[19]}\) and catalyst manufacturing\(^{[20]}\).

This paper aims to review two ways to improve the stability of MOFs materials, of which one is to redesign and synthesize stable MOFs materials, and the other is to improve the stability of existing MOFs materials. The application prospects of MOFs with high stability in the fields of gas separation and storage, catalysis, medicine, sensing, rechargeable battery and capacitor manufacturing are also analyzed.

2. Redesigning and Synthesizing Stable MOFs

Redesign and synthesis is a common idea, of which the principle is that the unstable metal ligand bond broke\(^{[21]}\), and then a more stable coordination bond is formed to obtain stable products\(^{[22]}\). The solubility of polydentate organic ligands and metal salts, solvent polarity, ionic strength of medium, temperature and pressure all play key roles in this method\(^{[23]}\).

2.1. Enhancing the Strength of Coordination Bond

According to the theory of palmitic-stearic acid, metal ions with higher positive charge number have higher coordination and binding strength with carboxylic acid ligands, while metal ions with lower positive charge number have higher coordination and binding strength with nitrogen-containing ligands\(^{[24]}\). Therefore, strong coordination bonds can be used to construct stable MOFs materials\(^{[25]}\). Cheng-Yong Su et al. \(^{[26]}\) formed a stable three-dimensional metal organic framework (LIFM-38) by using the strong coordination bond between Zn\(^{2+}\) and fluorinated dicarboxylic acid ligands. Moreover, they observed that LIFM-38 could still maintain its high crystallinity after exposure to air for one month, and the subsequent collapse could be repaired. The stability of MOFs in acid-base environment determines whether they can be used in the field of catalysts. Shu-Qi Deng et al. \(^{[27]}\) constructed a MOFs material named SCNU-Z2. An imidazole group in the ligand is replaced by a tetrazole group, and the charge of the framework changes from cation to anion. SCNU-Z2 was soaked in water with pH range of 3-11 for 30 h, and then the material was characterized by PXRD shown below (Fig. 2b).\(^{[27]}\)
The results show that the structure of the material is almost stable, which confirms the acid-base stability of the material. Moreover, SCNU-Z2 can catalyze the degradation of methylene blue and other dyes at low temperature, dark and room temperature, and the degradation rate can reach 97% (Fig. 2a).\cite{27} In conclusion, MOFs with strong chemical stability can be prepared by enhancing the strength of coordination bond, which has a good application prospect.

2.2. Doping Metals

Many studies have found that the framework stability of MOFs materials is improved by doping new metal ions\cite{28}\cite{29}. The water stability of many other MOFs materials can be improved by selecting more inert metals\cite{30}. Cheng-Yong Su et al.\cite{31} obtained metal porphyrins (Rh-PMOF-1 and Ir-PMOF-1) by introducing two kinds of metal ions doped with rhodium or iridium respectively. The cycle stability of Rh-PMOF-1 was evaluated by measuring the conversion rate after 10 times of repeated cycloaddition reaction of CO$_2$ and epoxides (Fig. 3).\cite{31}

![Figure 3. The recycling experiments for Rh-PMOF-1.](image)

It was found that there was almost no loss of catalytic activity of Rh-PMOF-1, which proved that the cycle stability of Rh-PMOF-1 was improved after doping metal. Moreover, it was obtained in 83% and 73% yields respectively.

In the aspect of medical sensing, most enzymes or drugs are used in the internal environment, such as intestines and stomach, and the optimal catalytic pH of enzymes is about 3-4, which requires the acid and alkali resistance of MOFs materials. Zn-MOFs\cite{32} and Zr-MOFs\cite{33} have attracted much attention due to their good cycle stability. Therein, Zn-MOFs doped with Zr can obtain MOFs with
better stability. Nan Zhou et al. [34] synthesized two new bimetallic Zn/Zr based MOFs by MOFs ion exchange method.

Moreover, they used these MOFs as the scaffold substrate of aptamer sensor to detect cancer marker of protein tyrosine kinase-7 (PTK7). Zr-MOF is beneficial to the immobilization of aptamer chain, while Zn-MOF can stabilize aptamer chain and G-quadruplex formed by PTK7. In electrochemical impedance spectroscopy measurements, the Zn-MO- Zr-MO-based aptamer sensor was stored in a refrigerator at 4 °C for 15 days, and electrochemical impedance spectroscopy was performed in 0.1 M PBS containing 0.001 ng/mL and 1 ng/mL PTK7 per day. The ultra-low detection limits of 0.84 pg/ml and 0.66 pg/ml were obtained, and the extremely low relative standard deviations (RSDs) of 3.38% and 1.24% were obtained, which proved that the Zn/Zr MOFs material had good stability and reproducibility. Metal doping can significantly improve the stability and performance of MOFs, but it is difficult to add metal ions to the target quantitatively and orientationally, which challenges the operation method.

2.3. Inserting Stability Pillar

In some cases, frames with large pore sizes and/or large surface areas are quite unstable. Therefore, it is necessary to insert some stability pillars to maintain the stability of MOFs [10]. Shim Sung Lee et al. [35] synthesized four three-dimensional metals using tert butyl thiophene tetra acetic acid aromatics (H₄TCTA) and Co (II) and Cd(II) nitrates, and then inserted three different types of neutral bridging ligands to obtain samples. Thermal gravimetric analysis showed that the three MOFs with pillar did not decompose until heated to 300°C after the insertion of bridging ligands. Krista S. Walton et al. [36] synthesized MOF-508([Zn(BDC)(BPY)₀.₅] using the join-binding pillar strategy, and carried out material exposure experiments at 0-100% relative humidity (RH). The water vapor adsorption curves of MOF-508 and Zn-TMBDC-BPY (MOF-508-TM) were compared, and it was found that the adsorption water content of MOF-508-TM did not exceed 0.2 mmol H₂O/g at 0-100% relative humidity. However, MOF-508 is close to 5 mmol H₂O/g at 40% relative humidity, which significantly proves that MOF-508 obtains better hydrophobicity by connecting the joint pillar. Hong-Cai Zhou et al. [37] substituted 4, 4-bipyridine (BPY) pillars in two cadmium-base MOF pillars with alkylpyridine derivatives based on the substitution of stronger ligand capping ligands for weaker coordination pillar ligands.
Scheme 2. Schematic Showing the Process of Producing 2D Monolayer MOF Nanosheets from 3D Layer-Pillared MOFs through the Ligand Replacement Approach\textsuperscript{a}

\textsuperscript{a}The rods in gray and yellow represent the replacing and pillar ligands, respectively.

Two-sided hydrophobic 2D MOF nanosheets with single thickness were prepared. The water contact angles on both sides were detected to be 129° and 139° respectively. These observations confirm that the surface of 1 or 2 nanosheets has indeed been modified with hydrophobic alkylpyridine functional groups to obtain better hydrophobic stability. The insertion of the stability pillar can divide the space into smaller Spaces to increase the adsorption capacity of small molecules\textsuperscript{[10]}, which has a bright prospect for the adsorption of small molecules.

3. Modification of MOFs After Synthesis

In addition to the idea of redesigning synthesis, the most commonly used method is post-synthesis modification. In this section, modification of post-synthesis groups and preparation of composites will be discussed as main ideas.

3.1. Modifying Groups

According to the principle of similar phase solubility, the degree of mutual solubility between non-polar or weakly polar organic groups and polar water molecules is not high. According to this principle, the organic groups of the ligands in MOFs can be modified to form a hydrophobic organic framework. Therefore, the water molecules are repelled by the hydrophobic organic framework and cannot enter the metal center of the framework material, so that the structural stability and adsorption performance of the material will not be affected. For example, in 2010, Joseph G. Guyen et al.\textsuperscript{[38]} modified IRMOF-3( netlike metal and organic framework material) with different amounts of amide-substituted amines. The modified IRMOF showed contact angles (all greater than 100°) consistent with hydrophobic materials (i.e., 90-150°). Percent Conversion and Contact Angle Measurements for some IRMOF and MIL Materials are shown in Table 1.\textsuperscript{[38]}

| Number | Compound          | % Conversion | Contact Angle (deg) |
|--------|-------------------|--------------|---------------------|
| 1      | IRMOF-1           | N/A          | ~0                  |
| 2      | IRMOF-3           | N/A          | ~0                  |
| 3      | IRMOF-3-AM3       | ~99          | ~0                  |
| 4      | IRMOF-3-AM4       | 98 ± 3       | 116 ± 6             |
| 5      | IRMOF-3-AM5       | 96 ± 3       | 119 ± 10            |
| 6      | MIL-53(Al)        | N/A          | ~0                  |
| 7      | MIL-53(Al)-AM1    | 91           | ~0                  |
| 8      | MIL-53(Al)-AM4    | 44 ± 8       | >150b               |
Even though the material was exposed to ambient air for several weeks, the contact angle of the sample remained constant. The same treatment for a series of MIL-53 (Levasil framework material) also yielded hydrophobic angles of more than 150°, demonstrating that hydrophobic modification of the group can improve its chemical stability. Based on the same principle, MOFs with good hydrophobicity can be obtained theoretically by using plasma-enhanced chemical vapor deposition (PECVD) to manufacture thin sheets to give high water contact Angle region (hydrophobicity)\(^{[39]}\). Jared B. DeCoste et al.\(^{[40]}\) used this method to treat Cu-BTC with perfluoroalkanes, and measured that the contact angles of Cu-BTC particles treated by Cu-BTC and C\(_2\)F\(_6\) plasma were 59° and 123°, respectively. It is concluded that the hydrophobicity of the material is enhanced by the perfluoroalkane groups on the surface of the pores. In order to further demonstrate the chemical stability of the obtained structures, the samples were treated with X-ray photoelectron spectroscopy (XPS). The sample mainly contains \(\delta \approx -87\) ppm CF\(_2\) group and \(\delta \approx -152\) ppm CF group. The large size and large number of rotating siderbands of the CF\(_2\) and CF species indicate that these CFX groups are tightly bound to the Cu-BTC structure and relatively immobile, thus indicating the stability of the structure. Group modification can create many new properties and high capabilities for materials, so the possibilities of group modification are infinite. The molecular dynamics instability of metal-ligand coordination bonds makes it possible to exchange metal ions with intermolecular organic ligands\(^{[41]}\).

### 3.2. Preparation of MOFs Composites

Adding other materials to fabricate composites is not only beneficial to improve the biocompatibility and high selectivity of MOFs, but, more importantly, also helpful to improve their stability under specific environment.

#### 3.2.1. Surface Modification

The porosity and structural adjustability of MOFs materials allow them to receive other materials to improve the chemical stability of MOFs materials. New physical and chemical properties and enhanced properties that cannot be obtained by a single component can also be obtained, such as the inclusion of acid-treated polycarbonate wall nanotubes into MOF-5 materials, and the coating of IRMOF-1 with carbon grease, etc.\(^{[42]}\)[\(^{[43]}\)] The composite obtained by hydrophobic surface treatment also has a relatively easy way to improve the water stability. Fengwei Huo et al.\(^{[44]}\) coated the surface of ZIF-67 with reduced graphene oxide (rGO) to investigate whether there is an improvement in stability.

![Scheme 3. Metal-Organic Framework Wears a Protective Cover for Improved Stability](image-url)
soaking in a solution with pH = 1–9, and it was found that the water-skiing angle of SLIP-M material was always less than 3° in the environment with pH = 1–7 (Fig. 4). [45]

Figure 4. Water contact angle of SLIPS-M (a) and SLIPS-C (b). Water sliding angle of SLIPS-M (c) and SLIPS-C (d).

It is confirmed that smooth liquid injection on porous surface can enhance the hydrophobicity and acid stability of MOFs materials.

3.2.2. Internal Incorporation

At present, it has become a popular method to prepare composites by mixing other materials inside. Shuai Luo et al. [46] used the MIL-100/ graphene oxide composite as an efficient adsorbent for the removal of organic dyes from aqueous solutions. Thermogravimetric analysis curves show that GO/MIL-100(Fe) composites contain the most water, about 20% (by weight), compared to MIL-100(Fe) composites. These molecules are readily emptied before 250°C. The TGA curve of MIL-100(Fe) decreases at about 280°C, indicating that the material begins to decompose. However, GO/MIL-100(Fe) composites begin to decompose at 350°C, showing better thermal stability (Fig. 5). [46]

Figure 5. TGA curves of GO/MIL-100(Fe) composites

In the field of gas separation, MOFs materials are limited by their poor stability and non-outstanding performance. Mixed matrix membrane and MOFS materials to improve the way to provide a modification idea. Machiel van Essen et al. [47] adopted the zeolite imidazole salt framework system combined with MOF (MMM) formed in the Matrimid matrix to further improve the hydrothermal stability of the ZIFS series, and the thermal decomposition temperature could reach 500°C. The addition of ZIFs to the matrix resulted in increased CO₂ permeability without selective loss
in all matrices fed with CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4}. In another study in 2021, Jing-Li Luo et al.\cite{48} proposed to redesign and synthesize nitrogen-doped carbon nanotubes by hydrothermal method.

![Scheme 4](image)

Scheme 4. Transformation of Metal-Organic Frameworks into Stable Organic Frameworks with Inherited Skeletons and Catalytic Properties

In the experiment, Co-N/C-900 nanotubes and Pt/C doped nanotubes were used to catalyze the water electrolysis reaction in saturated O\textsubscript{2} electrolyte and a certain current. Co-N/C-900 still maintains 91.8\% of its initial current density after 20000s, which is better than the significant current density loss of Pt/C(68.1\%). The excellent stability of electrochemical cycle was proved. At the same time, more central sites were obtained to enhance the catalytic activity. The method of manufacturing complex with internal incorporation is advantageous to solve the problem of low performance and low stability by starting from the active site and performance site of catalysis.

4. Summary

In this paper, two approaches to improve the stability of metal-organic frameworks are summarized. One is to improve the stability of MOFs materials by redesigning and synthesizing, and the other is to improve the stability of MOFs materials by post-synthesizing modification. Improving the stability of MOFs materials is of great significance in various fields of its application. In the application of gas separation, based on the high absorption capacity and the humidity requirement of the application environment, requirements are put forward for the recyclable gas adsorption capacity and anti-air moisture ability of MOFs materials. In the application of catalysis, because of the pursuit of reaction engineering efficiency and the consideration of the condition of maintaining high activity of catalysts, the acid and alkali resistance and the recyclable catalytic ability of MOFs materials become very important. In pharmaceutical applications, the acid and alkali resistance and mechanical strength of MOFs are significant, as most of them act on the internal environment and sometimes need to carry drugs. In terms of sensing, the sensing MOF material with low water stability will fail and have a short life when monitoring the water environment in most cases. Therefore, it is very important to improve the water stability of MOFs for the application of sensing. In the field of rechargeable batteries and capacitors, since most of the reported MOFs are insulators with insufficient cyclic stability, it is of great significance to obtain MOFs materials with more electrochemical cycling stability and conductive performance by doping metals.

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