

Metal-Organic Frameworks Synthetic Approaches and Applications in Energy Industry

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Abstract. The search for innovative solutions to environmental and social challenges is undoubtedly crucial in materials science, especially in the field of metal-organic frameworks (MOFs). This review describes the history of MOFs, as well as seven methods of MOF synthesis and their advantages and disadvantages, such as hydrothermal method, microwave-assisted method, and so on. Humans have made significant progress in synthesizing various MOF materials for gas storage, transportation, and other applications, but there is still much to be explored and understood about these complex substances. As researchers strive to discover new materials and their potential uses, a huge untapped area of potential awaits further exploration. Ultimately, the key to meeting environmental and societal challenges lies in the advancement and creative design of MOFs.

1 Introduction

In modern society, the energy demand is crucial for daily life and productive activities. However, the heavy reliance on fossil fuels, which account for approximately 86% of the energy sources, poses significant environmental threats such as greenhouse gas emissions and climate change [1]. This has led to a growing awareness of the need to transition to alternative, sustainable energy sources. Various options like ocean, solar, wind, geothermal, hydrogen, and nuclear energy have emerged as promising alternatives to fossil fuels. These alternative energy sources have been the focus of extensive research and development efforts, and are increasingly being adopted on a global scale [2]. For instance, natural gas now contributes to around 29% of the United States' total primary energy consumption. As people continue to explore and invest in these new energy fields, the shift towards sustainable energy solutions is steadily gaining momentum [3].

The growing use of natural gas as a gaseous fuel is attributed to its high methane content, which boasts a higher hydrogen-to-carbon ratio compared to traditional energy sources like coal and petroleum. This results in lower carbon dioxide emissions for the same energy output. Nonetheless, challenges persist in the storage of natural gas due to issues such as energy density, operational costs, storage convenience, and safety concerns [4]. Traditional methods of storing natural gas through compression (CNG) or liquefaction (LNG) are cumbersome and require complex equipment. To address these challenges, researchers have developed Metal-Organic Frameworks (MOFs) capable of adsorbing significant amounts of natural gas, known as Adsorbed Natural Gas (ANG) [4]. These porous adsorbents offer a promising alternative for gas storage in hydrogen and methane applications. ANG

technology offers several advantages over conventional storage methods, as its high porosity increases the energy density of natural gas and allows for the customization of pore surfaces for gas separation. This capability opens up possibilities for purifying the gases needed for various applications.

Before the advent of MOF materials, many materials were also searched for to adsorb, store or separate gases as well as target molecules. The first discoveries made by mankind in the field of adsorbent materials were zeolites and activated carbon [5]. There is one thing that these materials have in common, which is that they are all porous materials. The large number of pores in the material can significantly increase the surface area of the adsorbent material, which facilitates the adsorption function of the material. However, zeolite has fewer pores, which indicates that the adsorption surface area of zeolite is relatively small and the adsorption efficiency is low [6]. Activated carbon has a very large number of pores, which means it has a considerable adsorption surface area. Therefore, for a long time, people have used activated carbon as an adsorbent in daily life, production or experiments. However, with the development of the times and the progress of science and technology, the adsorption efficiency of activated carbon can no longer meet the needs of human production. Therefore, people began to look for adsorbents with higher adsorption efficiency, which are MOFs. MOFs have a very high adsorption surface area, which makes it has a much higher adsorption efficiency than those of zeolite and activated carbon. MOFs have a porosity of more than 7000m²/g [7], and MOFs have a pore size that can be adjusted so that the functionality of the MOFs can be altered by adjusting the size of the pore. There are several functional sites on the surface of MOFs, and the functionalities of MOFs can be changed by adjusting

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the pore size. There are many functional sites on the surface of MOF, and by changing the structure, pore size and functional groups of MOFs, the performance of MOF can be changed so that it can meet the needs of people's actual production. The research on MOF is still ongoing: to explore the stability of its structure, how to adjust its structure to meet the needs of different fields, what factors affect the performance of MOF in storing and separating gases, etc. These are all to be continued in the future. All these need to be further investigated in the future. In this paper, people will summarize some MOF synthesis methods, as well as their advantages and disadvantages, to help people understand how to choose the corresponding method to produce the MOF structure they want.

2 Structure of MOFs

2.1 Designing of MOFs

MOFs and their ligand skeletons are novel composite structures constructed by skillfully combining different types of metal ions with ligands. This type of backbone material is made of multiple microporous organic molecules or ligands linked to them by metal ions, metal oxides, etc. In the preparation of MOF materials, a variety of different ligands can be used, which have different functions. These include polytopic organic acids such as oxalic acid, 4,5-imidazole dicarboxylic acid, and 6,6'-dichloro-4,4'-di(pyridine-4-yl)-1,1'-binaphthyl-2,2'-diol [8].

MOFs can be endowed with specific functionalities through the deliberate selection of linkers and metal nodes [9]. Various synthetic strategies have been employed to customize the chemistry, stability, particle size, and flexibility of these frameworks [10]. Through "post-synthetic modification," MOFs can undergo further adjustments to fine-tune their properties by swapping, altering, or completely removing linker or node components within the structure. Furthermore, the control of crystallographic phases, crystallite size, and morphology allows for the modification of the surface chemistry of MOFs [11]. This capacity to tailor such characteristics is a key advantage of these unique porous materials, enabling precise control over host-guest chemistry for applications in energy storage [9].

2.2 Secondary building units in MOFs

In the realm of MOFs, the fundamental structure is built upon secondary building units (SBUs) comprised of metal ions and oxygen atoms, with organic linkers playing a crucial role in connecting these SBUs within the MOF framework. Predicting the precise structure of an MOF solely based on the combination of organic linkers and metal ions presents a significant challenge. To address this complexity, the concept of SBUs has been introduced. These SBUs are basic geometric units

formed by inorganic clusters linked together by organic components during the reaction under specific conditions. The diagram below showcases the diverse SBUs identified by Yaghi and his colleagues [12]. MOFs have revolutionized the field of materials science in recent years. They break the boundaries of traditional inorganic materials with their unique crystalline structure and rich and diverse properties. This new type of material forms a complex and ordered three-dimensional spatial network by skillfully combining metal ions with organic ligands. Molecular clusters, such as SBU (Di benzothiazole), can connect and assemble to form various configurations, exhibiting excellent physical and chemical properties.

Researchers have utilized specific combinations of these molecular cluster compositions to develop ligand systems with different pore sizes, shapes, and even functionalities. By carefully designing the sequences and combinations of ligands, the framework structures and properties of MOFs can be modulated to meet different application requirements. For example, the porosity of MOFs can be adjusted to optimize gas adsorption or separation efficiency; or the electronic properties of ligands can be changed to tune their electrochemical activities. With a deeper understanding of MOFs and advances in synthesis techniques, scientists are exploring their potential applications in a variety of fields, including energy storage, catalysis, and environmental monitoring.

3 Various synthetic methods for MOFs

The creation of novel Metal-Organic Framework (MOF) materials hinges on the careful consideration of various influencing factors. While maintaining the integrity of the structural building units is paramount, significant emphasis has been placed on developing a series of novel organic ligands. These ligands not only have novel and unique structural features but also have been carefully screened and improved during the synthesis process to ensure that they can exhibit optimal performance under the reaction conditions. Through this series of efforts, we aim to achieve fine-tuning of the synthetic conditions to obtain optimal results in various chemical reactions, opening up new possibilities for chemical research. The nature of the ligands, such as their length and spatial arrangement, the size of the bond angles, and the chiral characteristics, all have an important impact on the structure of the metal-organic frameworks (MOF) materials. The different geometrical configurations of the metal ions likewise play a crucial role in the formation of the materials. At the current stage of research, although the synthesis of MOFs usually still relies on the traditional method of obtaining the desired structure through continuous attempts, this process has been replaced by many systematic and efficient methods. These advanced synthetic strategies have not only improved the synthetic efficiency but also opened up new avenues for the development of novel MOF materials.

To summarise and illustrate several important synthetic pathways that have been widely reported so far, we have performed an in-depth analysis. These pathways cover a wide range of techniques from simple to complex, from laboratory scale to industrial mass production, showing the whole process from raw material selection to final product formation. Detailed operational steps, optimisation conditions, and potential application scenarios are behind each method, enabling researchers to design and construct MOF materials that meet specific needs.

Through these efficient and systematic synthesis methods, researchers can more precisely control the structure and properties of the materials, thus finding more application opportunities in a variety of fields, such as energy storage, catalytic conversion, and drug delivery. In the future, MOFs are expected to become one of the key materials for solving a variety of challenging problems as synthetic technologies continue to advance and innovate.

3.1 Hydrothermal and solvothermal synthesis method

The hydrothermal method is a method of preparing materials in which certain forms of precursors are placed in a kind of sealed pressure vessel, water is used as a solvent, and a hydrothermal reaction is carried out at high temperature and high pressure to dissolve and recrystallize the precursors, and then post-processing such as isolation, washing, and drying are performed to obtain a preliminary purified material [13]. The operation of this method in MOF production is to place the metal feedstock and the organic linker in a mixed water/organic solvent, usually reacting at 80-220°C for 6-72 hours to obtain the MOF material. This method has very wide synthesis windows possible: a wide range of temperatures and pressures are available, and the key step in this method is the activation of the feedstock at high temperatures and pressures. The MOF produced by the hydrothermal method has well-developed grains that are small, uniformly distributed, and lightly agglomerated, allowing for the use of cheaper raw materials and the availability of suitable stoichiometries and crystal shapes [14]. However, hydrothermal synthesis technology is extremely limited in its practical application. Due to the high temperatures and high-pressure conditions involved in the process, these factors make hydrothermal synthesis severely limited in both efficiency and scale. In particular, the traditional hydrothermal synthesis method becomes extremely difficult when the temperature drops below 100°C and the pressure is less than 1 atmosphere. Therefore, scientists are actively exploring new methods and technologies to adapt to lower temperature and pressure conditions to promote the progress and development of hydrothermal synthesis technology. Research in this field is gradually shifting to low-temperature operations and low-pressure environments, to provide more efficient and safer synthetic pathways for materials science, biochemistry, and a variety of other scientific

fields.

3.2 Microwave and ultrasonic synthesis techniques

Microwave (MW) irradiation has revolutionized the synthesis of inorganic and organic solid-state materials, offering advantages such as reduced crystallization times, precise control over phase and morphology, and uniform particle size distribution. This electromagnetic radiation technique, widely employed in synthetic organic chemistry, has found applications in the synthesis of zeolites and MOFs in both solid-solid and solution-based approaches. Crystals produced through MW synthesis exhibit similar physical and textural properties to those obtained via standard hydrothermal methods [15]. Notably, the first MOF successfully synthesized using MW irradiation was MIL-100, showcasing comparable yields to traditional methods. This study underscores the potential of MW irradiation for achieving faster synthesis of MOF materials. Some microporous coordination polymers are exclusively accessible through MW irradiation, highlighting the efficacy of this method in MOF synthesis [16]. Microwave technology, cutting-edge science and technology, skilfully utilises water as its central medium. In this technique, scientists focus on complex physical phenomena in aqueous solutions, such as ionic motions in polar solvents, interactions between molecules, and the behaviour of solid-state ions and electrons. By precisely controlling the frequency and intensity of electromagnetic radiation, microwave researchers can explore in depth the interactions between these microscopic particles and electromagnetic waves. This approach not only provides a new tool for probing the nature of matter but also opens the door to innovation in many fields. MOF-5 [17], Cr-MIL-101 [18], and Fe-MIL-100 [19] are among the metal-organic coordination polymers synthesized using this pioneering technique.

Sonochemistry, an emerging field of science and technology, applies high-intensity sound waves to chemical processes. This method is favoured for its straightforward and economical nature, as well as being a more environmentally friendly way of operating. With the aid of ultrasound, researchers can prepare MOF materials more efficiently, which are of interest because of their unique structures and potential applications.

Ultrasonic chemistry involves the use of sound waves in the ultrasonic range of 20 kilohertz to 10 megahertz to alter the physical properties of molecules. By adjusting the frequency and intensity of the ultrasound waves, scientists can precisely control the course of chemical reactions, allowing for fine-tuning of molecular structures [20]. This methodology serves as a top-down strategy for creating nano-sized metal-organic coordination polymers. While no direct chemical reactions occur with the ultrasonic radiation interacting with the molecules, the introduction of ultrasound to a liquid result in the generation of alternating pressure patterns, leading to the formation

of cavities or small bubbles within the solvent. As these bubbles expand and collapse during cavitation, hot spots within the liquid emerge, reaching temperatures of approximately 5000 °C and pressures around 500 atm within microseconds [21]. These extreme conditions promote chemical reactions to take place. Utilizing this cavitation process, MOFs such as [22], and MOF-177 [23] have been successfully synthesized via the ultrasonic method, offering specific advantages over traditional synthetic procedures.

3.3 Electrochemical synthesis method

Electrochemical synthesis is a technique for organic synthesis by electrochemical means, in which old bonds are broken and new bonds are formed by the transfer of charges and the interconversion of electrical and chemical energies of organic molecules or catalytic media at the "electrode/solution" interface [24]. The electrochemical synthesis method is based on the electrolysis of organic compounds and the exchange of electrons between the raw material of the organic compound and a metallic electrode to obtain MOF materials. The essence of this method is to promote the reaction through the electron gain and loss, several conditions need to be met: 1, a DC power supply that can be continuously and stably supplied; 2, a metal electrode that can meet the electron transfer; 3, a suitable solvent medium that can complete the electron transfer. Among them, the electrode is the most important. It is the place where the electron transfer is implemented and plays the role of reaction base and catalyst. Electrochemical synthesis methods can avoid the use of toxic or dangerous oxidizing or reducing agents. Not only that, because there are only raw materials and products in the reaction system, this makes the products easy to separate and highly pure. And because of the simplicity of the equipment required, large-scale production is possible by electrochemical methods. For example, in a pioneering study, scientists prepared Cu-MOF for the first time in a methanol solution by precisely controlling the reaction conditions. They used a copper plate as the anode, a metal whose unique properties enable it to generate an electric current during electrolysis. Meanwhile, the tricarboxylic acid acts as the cathode, which undergoes a reduction reaction under electrochemical action. By tightly regulating the electrolysis voltage and electrolysis time (12 to 19 volts and 1.3 amperes), the researchers observed a successful synthesis of a copper-based porous framework material with a blue-green lustre in 150 minutes [25]. Other MOFs, such as Zn-imidazolate [26] and HKUST-1 [27], were also successfully synthesized using this innovative electrochemical method.

3.4 Mechanochemical synthesis approach

In the realm of green chemistry, the use of volatile organic solvents poses significant challenges as environmental pollutants [25]. To address this issue, a

mechanochemical synthesis approach has been proposed for the creation of porous Metal-Organic Framework (MOF) materials. This method offers two key advantages: synthesis under solvent-free conditions to eliminate organic solvents and shortened reaction times (typically 10–60 minutes) resulting in quantitative yields [26]. By applying mechanical force, physical changes and chemical reactions can be induced, giving rise to the concept of mechanochemical or solvent-free synthesis.

3.5 Liquid phase diffusion method

Liquid-phase diffusion method refers to the selection of organic ligands and metal salts dissolved in two immiscible solvents, and then one solution is added dropwise to the other solution, the two solutions in contact with each other through the slow diffusion of mutual reaction and ultimately precipitate crystals [27]. Compared with other preparation methods, this method is easy to operate and simple. Yanwei Sun's team used this method to fill a certain concentration of CoCl₂ aqueous solution in the porous alumina carrier, and then submerged it in gallic acid-containing aqueous solution after freeze treatment and reacted it at 80°C for 6 hours to obtain a dense and continuous Co-gallate MOF membrane.

3.6 Solvent evaporation method

Solvent evaporation synthesis is a method that promotes the growth of crystals in a solution by continuously evaporating the water in the solvent to bring the solution to a state of supersaturation. The mother liquor is constantly replenished during crystal growth to ensure that there is enough material for the crystals to grow. Growth can be maintained at a constant temperature, with the control of evaporation to control the degree of supersaturation of the solution, the obtained crystal composition is uniform, and the growth process is stable, conducive to the growth of doped crystals. However, when the corrosive solvent is discharged, the evaporation rate is difficult to control, and local high supersaturation occurs to make the crystals cross and grow. For example, Zhang et al. successfully synthesized Cu(II)-lanthanide(III) MOF by solvent evaporation [28].

3.7 Ionothermal synthesis way

Ionothermal synthesis is a novel method of preparing inorganic materials using ionic liquids as both solvents and potential structure-directing agents [29]. The isothermal method was proposed to distinguish it from the hydrothermal method, and its most prominent feature is that the materials can be prepared at atmospheric pressure. Ionic liquids, a new type of solvent material, have found a place in many fields of scientific research because of their unique and powerful polar properties. It is a liquid compound assembled from intramolecularly charged ions and usually

presents a stable liquid state at or near room temperature (less than 100 ° C). Such ionic liquids offer significant advantages over conventional solvents, such as their ability to be dissolved at lower pressures (only a few thousandths of atmospheric pressure) without generating excessive vapour pressure. In addition, these substances exhibit extremely high thermal and chemical resistance, making them stable under extreme conditions.

Using these ionic liquids with excellent properties, Cooper's research group conducted experiments using ionothermal synthesis. By precisely controlling the reaction conditions, they successfully synthesized two novel ionic liquids, SIZ-1 and SIZ-6. SIZ-1 is an ionic liquid with high solubility and excellent thermal stability, while SIZ-6 demonstrates significant improvements in chemical stability and thermal responsiveness. These results expand the range of potential applications of ionic liquids as solvents and offer new research directions and material options for fields such as materials science, chemical engineering, and environmental science. With a deeper understanding and application of such compounds, we can expect to see more innovative chemical reactions and technological breakthroughs shortly [30].

4. Conclusion

At the intersection of academia and industry, in-depth research on the design and construction of metal-organic frameworks (MOFs) and their diverse applications has become a powerful driving force for the continuous advancement of materials science. This interdisciplinary research has not only greatly enriched the knowledge of materials, but also spawned a wide wave of innovation. In this review, the author delves into the close connection between the structure and properties of MOFs. This is in a way a useful resource for researchers, who can refer to the MOF synthesis methods summarized in this paper to choose their experimental methods and experimental directions. This review is a careful compilation of a variety of synthesis methods that have proven to be remarkably effective in guiding the design and synthesis of novel MOF materials. Researchers can make some adjustments and optimizations to the synthesis process so that they can fabricate MOFs with different framework structures and topological properties. This review summarizes some of the structural merits and excellent properties of MOFs, and these unique structures and properties have enabled MOF materials to show great potential and value in a variety of fields, such as the separation, storage, and purification of gases, and the preparation of crystals.

Although researchers have successfully synthesized many new MOF materials, the field of MOF materials still has a very broad exploration space and considerable exploration value. Therefore, continued research efforts on new materials and potential new uses of already developed materials are very important. Fundamentally, the innovative design and improvement

of MOFs is not only an important means to address environmental challenges but also a key way to solve societal challenges such as energy shortage and pollution. With the continuous advancement of technology and the emergence of innovative thinking, we have reason to believe that the prospects for greater progress of MOFs in a wide range of fields are immense.

In summary, the design concepts and synthesis strategies of MOFs have become one of the core topics of modern materials science. Through continuous efforts and research, scientists are expected to discover and develop new MOFs that are more efficient, environmentally friendly and functionalized, thus bringing more benefits to human society.

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