Advances in metal-organic frameworks for hydrogen storage

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Abstract. With the advancement of science and technology and the rapid growth of the population, the global consumption of energy is increasing rapidly. Traditional fossil fuels are non-renewable resources, and their combustion emits large amounts of greenhouse gases, intensifying the pace of global warming. Therefore, people are looking for renewable resources as an alternative. Among them, hydrogen has attracted much attention due to its high energy density, the combustion product of water, and its wide range of sources. However, efficient and safe storage strategies are required to realize the wide application of hydrogen energy. One of the best materials for storing hydrogen at the moment is metal organic frameworks (MOFs), a three-dimensional porous structure material that has drawn interest because of its large surface area, tunability, and recyclability. For this reason, the preparation techniques for MOFs are initially summarized in this article. The fundamentals of MOFs' hydrogen storage were then described, along with the ways in which various circumstances affect how well they store hydrogen. In conclusion, pertinent ideas for modification were put out to enhance their hydrogen storage effectiveness and offer direction for the creation of materials for hydrogen storage.

Keywords: MOFs, synthesis, hydrogen storage, modification strategies.

1. Introduction

With rapid industrialization and overpopulation, the widespread use of fossil fuels has become the primary means of generating electricity. Over the past century, global energy consumption has increased eightfold, with fossil fuels dominating. This form of energy not only leads to huge greenhouse gas emissions, especially carbon dioxide but also produces a variety of environmentally harmful by-products [1]. In response to these problems, people began to look for new forms of energy to replace the traditional fossil fuels. As a kind of clean energy, hydrogen energy has many advantages. First of all, hydrogen is a very abundant resource. It can be prepared by hydrolysis, steam reforming, petrochemical and biomass gasification, and is very abundant on Earth. Secondly, hydrogen energy is environmentally friendly. After hydrogen combustion, the only waste produced is water vapor, without any harmful gas emissions and without negative effects on the atmosphere. In addition, hydrogen energy has the characteristics of high efficiency. However, efficient, reliable, and safe hydrogen storage strategies are essential to realize the wide application of hydrogen energy.

At present, the widely used hydrogen storage method is high-pressure gaseous liquid hydrogen storage. This is a more traditional and mature method that does not require any material as a carrier, only a pressure-resistant or adiabatic container. However, its hydrogen storage efficiency is very low, pressurized to 15MPa, the mass hydrogen storage density is not more than 3%, and there are huge safety risks, its liquefaction process needs to consume a lot of energy, the cost is high. In recent years, MOFs, as a porous material, are the most promising hydrogen storage materials due to their advantages of low density, large surface area, high porosity and high stability. Therefore, this paper summarizes the latest advances in MOFs for hydrogen storage.

2. Synthesis Strategies for MOFs

The synthesis of carboxylate-based MOFs usually involves the reaction of organic ligands containing carboxyl groups with metal ions or metal clusters in a solvent. Carboxylate ligands such as benzene dicarboxylic acid and homotrimellitic acid are widely used in the construction of MOFs due to their multi-coordination pattern and ability to form stable frameworks. During the synthesis process, the carboxyl group of the ligand can form a coordination bond with the metal center through deprotonation, which leads to the construction of a stable lattice structure. This type of MOFs is usually highly thermally and chemically stable [3].

Azo salt-based MOFs, on the other hand, utilize the special coordination ability of azo ligands. Such ligands can not only connect with metal centers through azo bonds but also interact with metal centers or other ligands through other functional groups. Azo-salt-based MOFs exhibit excellent performance, such as high porosity and tunable pore systems.

MOFs with mixed ligands are synthesized by using two or more different organic ligands in the same structure. This strategy allows the introduction of different functionalities in MOFs, such as increasing the active sites, modulating the pore properties, or changing their optical and electrochemical properties. The synthesis of mixed-ligand MOFs requires precise control of the ratio and addition order of the different ligands to ensure that the resulting materials have the desired structure and properties.

The method of using metal complexes as building blocks is another synthetic strategy. This approach usually involves macrocyclic complexes, which form a three-dimensional mesh structure by coordination with metal ions. Macrocyclic complexes not only provide stability to the structure but are also capable of forming more complex network structures by reacting with other metal ions through coordination sites within their macrocycles. For example, frameworks with open metal sites can be formed by self-assembly using nickel (II) macrocyclic complexes and linear dicarboxylic acids. The structures of these MOFs typically show excellent pore properties and structural stability, and the three-dimensional network structure remains intact even after the removal of the crystallization solvent. The synthesis of such MOFs can be further modulated by redox reactions, such as the ability to switch the oxidation state of the metal centers by a redox agent. The central metal of metal macrocyclic complexes can act as a catalytic center, while their macrocyclic structure can provide a microenvironment that affects the selectivity and rate of the reaction. MOFs with this type of structure can mimic the active site of an enzyme, thus playing a role in the field of biomimetic catalysis [4].

3. MOFs for Hydrogen Storage

3.1. Hydrogen Storage Mechanism

MOFs mainly store hydrogen through physical adsorption and chemical adsorption. Physical adsorption is realized by intermolecular van der Waals force or electrostatic force. Due to the porous structure of MOFs, they can provide a large internal space and internal surface. This mechanism has a modest enthalpy of adsorption, suggesting that hydrogen can be adsorbed and released effectively at lower pressures. The MOFs can adsorb a significant amount of hydrogen at low pressure at 77 K. However, as the temperature rises to room temperature, the amount of hydrogen adsorbed decreases significantly [5]. This is because the interactions between the hydrogen molecules and the MOFs' adsorption sites weaken with temperature. Chemisorption is due to the metal ions or organic ligands in MOFs stabilizing hydrogen storage inside the material by forming chemical bonds with hydrogen.

3.2. Factors Affecting Hydrogen Storage Properties

MOFs' ability to store hydrogen at high pressures and low temperatures is directly correlated with the material's specific surface area. Chahine's rule states that the specific surface area of the MOFs rises by 500 m^2/g, which corresponds to a 1% increase in hydrogen adsorption. Furthermore, the tiny pore size permits the potential field from the opposing wall to overlap, which in turn increases the interaction potential since the interaction energy between hydrogen and the adsorbent surface is very low. The ideal hole size would enable the hydrogen molecules to form a monolayer on the opposing pore wall, optimizing the van der Waals forces acting on the molecules and providing the best hydrogen backbone connections [6]. Given that the kinetic diameter of a hydrogen molecule is 2.89

One method to improve MOFs materials' ability to store hydrogen is to include metal ions into the material. It produces unsaturated metal sites in the MOFs, increasing the number of hydrogen molecule binding sites. Better hydrogen storage capability results from this increase in the binding strength between the hydrogen molecules and the doped cations. In contrast, undoped MOFs usually have a reduced capacity to absorb hydrogen. On the other hand, the MOFs materials' ability to store hydrogen is greatly enhanced by doping them with alkali metal ions. This is due to the significant hydrogen-affinity of the alkali metal ions, which result in stable complexes that strengthen the binding between the hydrogen molecules and the MOFs. By improving the stability and endurance of the MOFs materials, this doping strategy not only improves their hydrogen storage capabilities but also makes them more suited for real-world energy storage and conversion applications.

The efficiency of hydrogen storage in MOFs can be enhanced by doping metal cations to produce unsaturated metal sites and increase the binding strength between doped cations and hydrogen molecules. It has been discovered that the kind of ligand employed in MOFs is essential in establishing the electrical environment and specific surface area, both of which have an additional impact on the hydrogen storage capacity. Higher hydrogen storage capacity may be achieved by improving the interaction between hydrogen molecules and the MOFs framework by an increase in the aromaticity of the organic ligand. Thus, in order to get the best possible hydrogen storage performance, it is crucial to take into account the selection of both metal centers and organic ligands when designing MOFs for hydrogen storage applications.

Interpenetration of the organic ligand skeleton of the MOFs creates smaller voids and generates more adsorption sites per unit volume, thus increasing the adsorption capacity of hydrogen gas.

4. Strategies to Enhance Hydrogen Storage in MOFs

4.1. Lithium (Li) Doping

Compared to 9.1% wt% for the undoped MIL-101(Cr), Li-doped MIL-101(Cr) can hold hydrogen up to 10% at low temperatures and high pressure. This enhancement is explained by the fact that lithium doping makes the organic ligand more polarizable, which improves the interaction between the hydrogen molecule's charge and quadrupole moment [7].

In summary, the hydrogen storage capacity can be significantly improved at room temperature and relatively low pressure by Li doping and the development of MOF-based composites, which is of great scientific and industrial value to promote the practical application of hydrogen as a clean energy source. Future research should continue to explore more such strategies to realize efficient and economical hydrogen storage technologies to make the application of hydrogen energy in daily life possible. The advantage of lithium-doped MOFs lies not only in the improved hydrogen adsorption capacity but also in their ability to improve the interaction between MOFs and hydrogen molecules, making them more suitable for hydrogen storage under room temperature conditions. Through the introduction of lithium, not only the polarization of adsorption sites can be increased, but also the interaction force between adsorbent and hydrogen can be enhanced, thus improving the hydrogen storage efficiency. Lithium doping has the potential to greatly increase MOFs' hydrogen storage capacity, both experimentally and theoretically. This is especially true at ambient temperature and low pressure, which is crucial for the commercialization and radicalization of hydrogen energy.

Li doping and the creation of MOF-based composites may greatly increase the hydrogen storage capacity at room temperature and relatively low pressure, which is important from both a scientific and industrial standpoint to support the use of hydrogen as a clean energy source in real-world applications. Future studies should look into more of these tactics in order to develop affordable and effective hydrogen storage systems that will enable the use of hydrogen energy in day-to-day activities. Li-doped MOFs lies not only in the improved hydrogen adsorption capacity but also in their ability to improve the interaction between MOFs and hydrogen molecules, making them more suitable for hydrogen storage under room temperature conditions. Through the introduction of lithium, not only the polarization of adsorption sites can be increased, but also the interaction force between adsorbent and hydrogen can be enhanced, thus improving the hydrogen storage efficiency.

The effect of Li doping is related to the specific structure and composition of MOFs, and different doping strategies may be required for different MOFs. In addition, lithium doping may affect the stability and cycling performance of MOFs, which needs to be further explored and optimized in future studies. Meanwhile, although lithium doping improves hydrogen storage performance, the cost-effectiveness of the doping process and the feasibility of the process are also important factors for its industrialization. Future research should be devoted to optimizing the synthesis process of lithium-doped MOFs to improve their stability and hydrogen storage performance, while production cost and environmental impact also need to be considered.

4.2. Improved Crystal Stacking

Theoretical studies indicate that the maximum stacking efficiency for homogeneous spheres is 74%, but in practical applications, the efficiency of randomly stacked spheres typically does not surpass 63%. Different particle shapes, such as tetrahedra, exhibit varying efficiencies in random stacking compared to ordered solid arrangements. Research in this area has focused on examining the relationship between stacking density and hydrogen adsorption properties by synthesizing MOFs with specific crystal shapes and sizes. Studies have shown that significant improvements in volumetric hydrogen storage performance can be achieved through the optimization of MOF-5 crystal size and morphology. In contrast, commercial MOF-5 powders have demonstrated enhanced performance in terms of both packing density (with an increase of up to 100%) and compaction density (increased to 33%) [8]. For the automotive industry, these findings suggest that higher hydrogen storage requirements can be met through careful design and optimization of MOFs, making hydrogen-fueled vehicles a practical and clean energy option. Future research efforts should prioritize optimizing the preparation process of MOF materials, enhancing their stacking efficiency, and increasing their interaction force with hydrogen to achieve higher hydrogen storage density and improved cost-effectiveness. By doing so, the potential of MOFs as a sustainable and efficient hydrogen storage solution can be fully realized.

4.3. Hybrid MOFs

Despite the significant potential of MOFs for hydrogen storage, there are still limitations in their efficiency. To overcome these limitations and optimize the performance of MOFs, researchers have begun to combine them with other complementary materials. These combinations can enhance the efficiency of MOFs through various mechanisms, including dissociation, physical adsorption, and chemisorption. By introducing complementary materials such as graphene oxide (GO), the structural and functional properties of MOFs can be improved. For instance, researchers have synthesized MOF composites using molecular sieve template carbon (ZTC) and UiO-66 (Zr) with PIM-1 as an adsorbent. The introduction of PIM-1 effectively prevented pore clogging by interacting with the hydroxyl groups of UiO-66 (Zr), leading to a significant enhancement of the surface area up to 2,433 m^2/g. Adding 80 wt% of ZTC filler significantly improved the stability and H_2 uptake of the ZTC-based materials [9]. This finding highlights the enhancing effect of rGO, which not only improves the physical properties of MOFs but also enhances their hydrogen storage performance. The study of MOF-650 further demonstrates the application of DFT and GCMC theories in the evaluation of H2 storage properties. By adding Mg/Ca and B(OH) co-substituted linkers to the structure of MOFs, the H_2 adsorption rate was enhanced by 20%, showing higher H_2 storage potential. This structural tuning suggests that the less electronegative part contributes to the increased H_2 adsorption. Overall, these findings demonstrate that combining MOFs with complementary materials and tuning their structures can significantly enhance their hydrogen storage efficiency.

On the other hand, Pd/MIL-101 nanocomposites, which were prepared by the solvothermal method, displayed a decrease in surface area. However, the addition of Pd improved the H_2 storage properties of MIL-101 and increased its thermal stability. In the design and optimization of hydrogen storage materials, the synergistic effect between MOFs and metal centers in metal-organic skeleton structures is particularly significant, particularly in the interaction between CO_2 and H_2 [10].

5. Conclusion

Against the urgent backdrop of addressing the global energy crisis and environmental pollution, this article offers a comprehensive overview of the significant advancements made in hydrogen storage using MOFs. It delves into the essential properties of MOFs, the various strategies employed in their synthesis, and their potential applications in hydrogen storage. Emphasis is placed on the modification and optimization techniques used to enhance the performance of MOFs in hydrogen storage, including Li doping and crystal stacking improvements.

Although MOFs have a lot of potential for storing hydrogen, there are still obstacles that must be removed before widespread use can occur. The most important ones are MOFs' stability, cycling capabilities, and hydrogen storage effectiveness at room temperature and air pressure. The particular surface area, pore size, metal locations, and organic ligand selection of MOFs are critical factors affecting their hydrogen storage capacity.

Future research should prioritize enhancing the hydrogen storage capabilities of MOFs through innovative structural design. This includes the development of novel ligands and metal centers, as well as exploring composite materials. Additionally, optimizing the chemical composition and physical structure of MOFs, along with exploring novel doping strategies and crystal stacking techniques, are essential. These efforts not only aim to improve the efficiency and safety of MOFs for hydrogen storage but also aim to pave the way for the development of efficient and cost-effective hydrogen storage technologies. This will further facilitate the widespread utilization of hydrogen as a clean energy source.

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