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The design of metal-organic frameworks (MOFs) in hydrogen storage applications

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Abstract. Carbon-based energy, when incompletely burned, produces toxic gases, and the earth's environment is irreversibly negatively affected. As a kind of clean energy, hydrogen energy has abundant resources and can be recycled, which is the focus of attention in the 21st century. However, hydrogen production, storage, transport and safety are major problems for the industrialization and large-scale commercialization of hydrogen energy technology. As an emerging nanoporous material, metal-organic frameworks (MOFs) are formed by self-assembly of inorganic metal ions and organic ligands, which have many unique characteristics beyond traditional porous materials, such as the high reversibility and high adsorption and desorption ability of hydrogen gas, which endows MOF materials a broad prospect of application. This paper introduces the MOF materials' application in hydrogen storage and comprehensively summarizes the decisive factors of MOF materials' performance in hydrogen storage. The issue prospects and suggestions are also given accordingly for the future research and promotion of MOF-based materials in hydrogen storage.

Keywords: Metal-Organic Frameworks, Gas Adsorption, Hydrogen Storage, Energy Storage.

1. Introduction

The world's environment has suffered as a consequence of over-exploitation and excessive use of fossil fuels in recent years. The greenhouse effect is a great example, which brings a series of problems to the world, such as high temperatures, melting of glaciers, rising sea levels, increased pests and diseases, flooding of coastal land and so on.

Many countries realized that the development of a new resource is extremely urgent, and one of the potential replacements for fossil fuels is hydrogen. The advantages of hydrogen over carbon-based energy sources are clear. For one thing, it has abundant resources, and 75% of the mass in the universe is hydrogen compared to the amount reduced by fossil fuels, which means raw materials are easier to collect. Second, hydrogen has a far higher energy density compared to gasoline. By weight, the energy content of hydrogen is 3-4 times greater than that of gasoline (the low calorific value of hydrogen is 33.3 kWh kg, and that of gasoline is 11.1 kWh kg). Third, the product of combustion is water, which is non-toxic and pollution-free and can be recycled, unlike fossil fuels which produce carbon dioxide. It's a non-renewable energy source. In addition, the prospect of hydrogen is huge, and it can also be widely used in energy, transportation, industry, construction, and other fields[1]. However, hydrogen can brings huge convenience to us, the hydrogen storage and transportation are still a big challenge for the technology so far.

Metal-organic frameworks (MOFs) are a new type of hydrogen storage material and have been reported in recent years. It is composed of metal ions, and organic ligands, which have benefits including high porosity, a huge portion of specific surface area, a rich structure, high quality of pureness and crystallinity and an adjustable skeleton. It is among the promising materials for storing hydrogen. In the following article, the factors affecting the performance of MOFs, the characteristics and advantages of MOFs, and the types of MOFs as hydrogen storage materials will be discussed and analyzed. Meanwhile, the design and improvements of MOF materials for hydrogen storage in the future are suggested. It is hoped that this article can promote the application and development of solid hydrogen storage materials and provide constructive suggestions for environmental protection and effective utilization of energy.

Many countries are conducting research into hydrogen storage. Among them, The United States has elevated hydrogen energy to the height of its national strategy. Following the Hydrogen Project Plan released by the Department of Energy in 2020, it is estimated that the domestic hydrogen demand of the hydrogen industry in the United States will reach 41 million tons/year by 2050. The EU has always been committed to the development of clean energy. In 2020, the EU announced the establishment of the EU Clean Hydrogen Energy Alliance. It has made full use of its advantages and achieved fruitful results in hydrogen production, storage and transportation, hydrogen utilization, fuel cells, and other fields, forming a complete industrial chain. Japan has promoted the coupled and coordinated development of hydrogen energy with other energy sources. By combining renewable energy, unused energy, and carbon recovery and capture technology, Japan has realized a zero-emission hydrogen supply system throughout its life cycle [2].

2. The methods of hydrogen storage

Gas hydrogen storage, liquid hydrogen storage, and solid hydrogen storage are the three main types of hydrogen storage that are currently being researched and used [3]. Among them, high-pressure gaseous hydrogen storage is the most common type of gas hydrogen storage. Liquid hydrogen storage can be separated into two categories which are low-temperature liquid hydrogen storage and organic liquid hydrogen storage. Physical adsorption and chemical adsorption are two different types of solid-state hydrogen storage [4].

2.1. Gaseous hydrogen storage

Pressure is used to liquefy high-pressure gaseous hydrogen storage and transfer it to a gas cylinder for storage, which has already received extensive use. This technique has the advantages of simple structure, quickly blowing within hydrogen and low energy consumption. However, the density of stored energy and security is low. The materials can be classified into four types by their cylinder materials [5].

2.2. Liquid hydrogen storage

Low-temperature liquid hydrogen storage works by liquefying the hydrogen to enable high-volume density storage of hydrogen in compact storage containers while liquid hydrogen storage techniques are still in the experimental stage [6]. Organic liquid hydrogen storage refers to the hydrogenation reaction to immobilization of hydrogen in aromatic organic compounds and, simultaneously, to form a stable liquid of organic hydrogen compounds. Their advantage is that they can store higher densities of hydrogen and are safe and easy to transport. The disadvantages are also obvious: high running costs, large energy consumption and harsh operating conditions.

2.3. Solid-state hydrogen storage

Solid-state hydrogen storage is mainly under mild conditions; the hydrogen is stored in a specific surface area of the material to realize the reversible suction and stripping, which is an ideal hydrogen adsorption storage method [7]. However, the amount of hydrogen storage at room temperature is much lower than the commercial application level, and the adsorption material preparation is also quite expensive [8]. Carbon-based hydrogen storage materials, metal-organic skeleton (MOF) materials, covalent organic compound (COF) materials, inorganic porous materials and others are the primary types of physical adsorption hydrogen storage materials. Chemical hydrogen storage materials primarily consist of hydride hydrogen storage materials, metal-alloy hydrogen storage materials, and liquid organic hydrides. Among them, as emerging hydrogen storage materials, The benefits of MOFs include their high porosity, low density, significant specific surface area, regular pores, controllable pore size, variety of topology, and tolerability.

3. The typical types of MOFs

The typical classical MOF materials include IRMOFs, ZIFs, MIL and UiO etc.

IRMOFs are the first MOFs material that can keep the pore structure from collapsing even after removing the guest solvent molecule in the pore. This series of materials is formed by oxygen coordination in the roots of Zn^{2+} and terephthalate. The series of materials have the same topological structure and good thermal and chemical stability.

ZIF series consists of Zn^{2+}, Co^{2+}, and other metal ions with tetrahedral coordination ability and imidazole groups in the coordination of nitrogen atoms. Compared with traditional porous materials, ZIFs series materials have the advantages of higher yield, adjustable pore size and shape, and diverse structure and function.

MIL series is produced by the coordination of Al^{3+}, Cr^{3+}, Fe^{3+}, and some metal ions combined with oxygen in dicarboxylic acid ligands, which typically have strong solvent and heat resistance. The three that most exemplify this are MIL-53, MIL-100, and MIL-101, which have the same crystal structure. The skeleton of this kind of material is flexible and can undergo large reversible deformation under external stimulation, which is called "breathing".

The UiO series is composed of Zr^{4+} combined with organic ligands and has high stability. The most typical representative is UO-66. $Zr_6O_4(OH)_4$ is a secondary structural unit, and the structure is highly symmetric. Because of the strong interaction between the octahedral core of Zr and the carboxyl oxygen in the ligand, it has good water and thermal stability and has attracted extensive attention in catalysis, adsorption, and separation.

4. Factors that influence MOFs' capacity to adsorb hydrogen

Inherent factors and external factors are the two main categories of variables that determine the hydrogen adsorption characteristics of MOFs. At low pressure (mainly 77 K), the heat of adsorption (Qst) of hydrogen and MOFs mainly affects the uptake of excess H_2 [9], While at medium pressure (up to 3 MPa), the SSA of MOFs, wherein the two are linearly correlated[10], becomes the major factor to consider.

4.1. Inherent factors

Pore size is one of the innate factors that discourage hydrogen from being absorbed at high temperatures and low pressure, as it decreases the interaction of the hydrogen molecules and the pore wall [11]. Another vital factor in the adsorption performance of porous materials is SSA. In the situation of physical adsorption of hydrogen storage, a large SSA is required to increase the rate of excessive H_2 absorption. However, under low pressure, hydrogen will preferentially bind to areas with high affinity [12]. Therefore, H_2 molecules can't completely cover SSA. The metal center will also affect the hydrogen adsorption properties of MOFs. Metal atoms make up the skeleton of MOF, and the properties of metal centers determine the stability and hydrogen storage performance of MOF [13]. The metal center, as the charge center, attracts hydrogen molecules and induces adsorbed H_2 molecules to produce dipole moments, thus coordinating the adsorption of hydrogen molecules. Due to the energy stability of the ME-H_2 bond, transition metal ions in MOFs indeed significantly enhance their affinity for H_2 molecules compared to other types of metal ions [14]. Furthermore, the effectiveness of MOFs as hydrogen storage materials is mostly influenced by the organic ligands (organic linkers). Host-guest synergism and the interaction of host-guest hydrogen molecules with organic linkers are the main forces behind hydrogen adsorption. The host skeleton structure contracts as a result of hydrogen adsorption on the organic linker, changing the electron potential surface within the pore [15].

4.2. External factors

The structure and hydrogen storage capabilities of MOFs are also influenced by the temperature and solvent content during the synthetic process [16]. To prevent the generation of undesired by-products, which may continue to exist in the structure's pores even after the evacuation procedure and restrict the gas physisorption [17], a lower synthesis temperature can be used. This may be stated by two different mechanisms: (1)The solvent, which is present in the pores or associated with the metal ion of the framework, could significantly alter the structure of the framework, particularly the size, shape, and chemical environment of the pores, all of which influence the MOF's capability to store hydrogen; (2) during the calcination, the framework's pores widen, the block channels expand, and massive open metal sites are created, all of which have an impact on the MOF's capacity to store hydrogen[16].

5. Properties & Advantages of MOF materials for hydrogen storage

MOFs have three typical characteristics, and the first is porosity and large specific surface area. The longer the length of organic functional groups, the larger the pore size of the material and the larger the specific surface area. In actual hydrogen storage, MOFs with highly porous and comparatively tiny pore sizes are typically chosen. The second characteristic is the variety of both function and structure. The metal centers and organic ligands of MOF materials affect their structure and function. Nearly all metals are available as metal centers for MOFs materials, while Zn, Cu, and Fe are the most frequently utilized. The third property is the unsaturated metal site. The unsaturated metal spots need to be combined with some specific substances to satisfy the conditions for coordination. These solvent molecules can be eliminated through heating or vacuum processing, revealing the unsaturated metal sites that can subsequently adsorb and separate the gas.

In order to bypass the constraints of updated hydrogen storage techniques and achieve the ideal DOE value, it is very important to use porous materials for the physical adsorption of hydrogen storage [18]. MOF materials have various compositions, rich structures, strong heat and chemical stability, wide specific surface area, and extremely high porosity. Since most of the MOF materials contain unsaturated metal sites, which can be used in the molecular recognition process, they can be used for hydrogen storage. Furthermore, MOFs have good modifiability, which can be used to prepare highly selective adsorbents by regulating the types of central metal ions, the connection mode of organic ligands, and the grafting of specific functional groups according to the actual situation[19].

6. The existing challenges, suggestions, and outlook

6.1. Challenges

Although MOFs materials have made a lot of progress in hydrogen storage, they still cannot meet the current DOE hydrogen storage index; storage and transportation are the biggest problems in the hydrogen energy industry chain. Due to the special nature of hydrogen, it is difficult to ensure the safety and cost of hydrogen storage and transportation by current means. Firstly, hydrogen is light in weight and low in density, so high-pressure storage and transportation containers are needed to improve the density and efficiency of hydrogen. Secondly, the liquefaction temperature of hydrogen is low. Hydrogen can only be liquefied at -253℃ under atmospheric pressure, resulting in high energy consumption, high evaporation loss, and high cost. Moreover, the atomic radius of hydrogen is very small and can pass through most invisible pores, even very thick steel plates, so the storage tank requirements are very strict; Finally, hydrogen is active and unstable, and it is more likely to burn and explode than other gases [20].

The above is an overview of how hydrogen itself is difficult to store. On top of that, MOF materials also face some challenges. MOF materials can only be used in the form of loose powder, which could occur problems incorporated into the related apparatus structures. Its engineering challenges are mostly caused by three factors: packing density, heat and mass transport, and the ability of adsorbent materials to store hydrogen. When the MOF materials enter a tank with pipe fittings, several challenges may be encountered. First, their low packaging density will compromise their bulk capacity. Second, when charged and discharged, powdered MOF compounds could potentially contaminate pipe fittings. Third, they are loose powders that are easily blown around, making handling difficult [21]. In addition, high synthesis cost and low yield are common problems in the manufacture of MOF materials, which also serve as the primary restraints on the industrial application of MOF materials [22].

6.2. Suggestion

The first is to improve the stability of MOFs materials. Usually, the structure of pellets, beads and monoliths is relatively stable and can be uniform in packaging, and it can increase the packing density to the greatest extent while reducing wasted space and reducing wear[23]. Secondly, the improvement of moisture stability, because traces of water will be produced during the process of industrial hydrogen, and with the current state of human technology, it is difficult to completely eliminate it. This might leads to the structural decomposition of MOF materials, for instance, the low structural resistance of MOF-5 towards atmospheric moisture, which invariably leads to lower hydrogen sorption efficacy and poor repeatability, which would impede the utilization of MOF-5 from many aspects[24]. In addition, the experimental result demonstrates that the low thermal conductivity would decelerate the refueling of hydrogen adsorption processes. The framework of most MOF materials would change or collapse due to instability after removing the guest molecule so far, so it is necessary to further improve the stability of MOF materials to broaden their ability and life as adsorption materials. The final goal is to enhance MOF material synthesis and make an uncomplicated, high-yield, and low-cost synthesis method. High cost and low yield are the key factors that restrict the large-scale industrial production of MOFs [22]. If the method of MOF synthesis can be successfully improved, It will build a strong foundation for the widespread use of MOF materials.

6.3. Outlook

In the past decades, there have been synthesized more than 20,000 various types of MOF materials. MOF materials will have innumerable opportunities as a result of the diversification of MOF materials and the progressive emergence of composite MOF materials. It can not only develop new energy to meet more people's needs and bring business profits but also solve the increasingly serious environmental problems facing the earth. Therefore, the development of functionally diversified MOF and composite MOF materials and their utilization in various industries would significantly foster cross-disciplinary growth.

7. Conclusion

In this review, with the deterioration of the earth's environment, the development of new energy is imminent, and hydrogen energy is anticipated to become the heavyweight energy in the 21st century. As one of the materials used to store hydrogen with broad application potential, MOFs are still in the early stage of research but compared with traditional porous materials, MOFs basically inherit the characteristics of traditional porous materials and improve the specific surface area, porosity and structural composition on this basis. It is believed that with the deepening of research, The functionality of MOFs materials will be improved even more. The challenges faced by MOFs materials include packing density, heat and mass transfer, the hydrogen storage qualities of the selected materials, and the methods that have been used in synthesis etc. In the future, the stability of MOFs materials should be further improved, including structural stability, water stability and thermal conductivity, adsorption properties, hydrogen storage properties, and improved synthesis methods, so this would have a significant influence on the effectiveness of the MOF-based hydrogen storage system in order to accomplish the goals of high stability of the structure, good heat capacity, and good hydrogen storage efficiency, etc.

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