Application of MOFs in Hydrogen Storage

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Abstract. This research analyzes the current energy problems and environmental problems and proposes to use hydrogen energy as a clean alternative energy source, which has high energy density and less pollution. After comparing the advantages and disadvantages of various hydrogen storage solutions, metal-organic frameworks (MOFs) are selected as the storage and transportation medium because of its large capacity, favourable reversibility, appropriate reaction conditions and relatively low density. The hydrogen storage mechanism of MOFs and the factors affecting its hydrogen storage capacity are introduced and discuss some methods to improve the storage features of MOFs. Three promising, MOFs, MOF-5, MIL-101 and NU-1501, are listed and their storage performance and specific structure are introduced. The current problems in the application and processing of partial hydrogen storage MOFs are proposed, and some feasible solutions and processing methods are introduced. Finally, the application prospects of MOFs are prospected and suitable development directions are proposed, which will be helpful for future research.

Keywords: List the; keywords covered; in your paper.

1. Introduction

Nowadays, with the continuous development of social technology, the demand for energy in modern society is also increasing. The lifespan of fossil fuels is limited. According to relevant calculations, oil resources will be exhausted after 2040 [1]. Burning fossil fuels not only emits a large amount of carbon dioxide causing the greenhouse effect but also causes serious environmental pollution due to substances such as sulfur and nitrogen in fossil fuels. Therefore, it is urgent to find alternative green energy. As an alternative energy source, the first condition that needs to be met is high energy storage efficiency. For reference, the energy of gasoline commonly used on transportation vehicles is about 42 MJ/Kg [2], and coal is about 20.8 MJ/Kg. At the same time, when choosing new energy sources, storage conditions, safety and cost issues should also be considered comprehensively. Renewable clean energy sources such as solar and wind power are not suitable for use in civilian transportation vehicles and this form of energy is difficult to store, which is often used for large-scale power generation. The energy storage material currently used on electric vehicles is lithium batteries, which have problems such as being greatly affected by temperature, limited energy storage capacity, and serious waste pollution.

Hydrogen is considered as one of the most promising candidates to replace fossil fuels. As a green fuel, it is a potential green fuel because its combustion product is only water and in the process of using will hardly cause pollution to the environment. Hydrogen has a high energy density of 141.86MJ/Kg [3], which is nearly three times that of gasoline. It is also easy to use as a raw material for fuel cells, and its energy conversion efficiency is higher than that of methane and natural gas. However, hydrogen as an energy carrier also has some drawbacks. Hydrogen has a very low density, even if high-pressure or low-temperature tanks are used for storage, the energy per unit volume is still lower than that of gasoline. Moreover, achieving these storage conditions requires expensive costs, making it difficult to achieve in vehicles. Hydrogen can reach satisfactory storage density in some metal hydrides such as lithium and aluminum hydrides, which have low operating temperatures and endothermic hydrogen release. However, these metal hydrides are usually very dense [4], which increases the weight of the vehicle and goes against the purpose of using hydrogen as a lower mass fuel under equal energy, they also have problems such as poor reversibility and slow dehydrogenation.

Metal-organic frameworks (MOFs) are porous polymer materials that use organic ligands to bind metal ions together, usually with more micropores and larger specific surface area, so when used as

an adsorption material, it can adsorb a very large amount of hydrogen, and has good thermal stability [5]. At the same time, due to the free choice of organic ligands and metal ions, various spatial structures can be produced, and some metal ions and organic functional groups can be used to modify MOFs, so that there are tens of thousands of MOFs materials, and the modification is convenient. These advantages make it an ideal class of hydrogen storage materials. According to the relevant research [6], MOF-5 is already very close to the performance and cost indicators of hydrogen storage materials for vehicles proposed by U.S. DOE in 2020. However, low mechanical strength, low temperature and relatively high hydrogen pressure are the main problems restricting the application of MOFs materials. Traditionally prepared MOFs are usually powdery materials, which will cause many problems during processing, including powder sedimentation, machine blockage, etc., and densification of MOFs, especially mechanical pressure, may lead to a damage of its microstructure, resulting in performance degradation. Laboratory measurements of MOFs performance are often performed at a temperature of 77 K, and increasing the temperature to room temperature will greatly reduce the hydrogen storage capacity of MOFs.

Using MOFs as a material for hydrogen adsorption to realize the storage and transportation of hydrogen is an ideal solution for the use and storage of hydrogen energy, which may help to solve the current global energy shortage and environmental pollution. This research will focus on three types of relatively advanced MOFs, namely MOF-5, MIL-101 and NU-1501, and introduce their respective microstructures and compositions, as well as their excellent performance in hydrogen storage. And starting from the hydrogen storage MOFs applied to vehicles, the problems existing in most MOFs are pointed out and their solutions are discussed.

2. Application of MOFs in hydrogen storage

The adsorption process of MOFs is mainly physical adsorption, so the factors that affect the adsorption performance are mainly the surface area and pores of the material. The hydrogen storage capacity of MOFs materials at low temperature and high pressure is proportional to the specific surface area of the material. With the increase of the specific surface area of MOFs materials, there are more hydrogen adsorption sites, so the hydrogen storage capacity also increases. In addition, since the interaction energy between hydrogen and the surface of the material is very low, the small pore size can overlap the electric potential fields from the pore walls on both sides, and enhance the interaction potential in a disguised form. The ideal pore size allows the hydrogen molecules to form a monolayer on opposite pore walls, maximizing the van der Waals forces acting on the hydrogen molecules, resulting in optimal hydrogen-skeleton interactions. Besides, the unsaturated metal sites in MOFs materials can provide favorable binding sites for hydrogen molecules, hydrogen molecule can directly combine with open metal centers, thereby increasing the isothermal of hydrogen adsorption and thus the materials have a high hydrogen storage capacity at low pressure, the introduction of doped metal ions in the MOFs material can provide unsaturated metal sites. The type of organic ligands and the interconnected ligand skeleton are also beneficial to improve the adsorption performance.

Generally, the adsorption performance of MOFs can be quantitatively analyzed by BET surface area and porosity. Higher porosity helps to reduce the distance between active sites and promote the diffusion and mass transfer of adsorbed substances, while larger BET surface area can increase the number of active sites and improve hydrogen storage. This research summarizes some MOFs materials that have been proved to have good prospects by calculation or experiment.

2.1 MOF-5

Li et al. proposed a method using zinc as an active metal ion and a dicarboxylate linker to give supertetrahedron clusters when capped with monocarboxylates [7], as shown in Fig. 1. During this period, the complex forms a highly porous three-dimensional structure, which has a larger pore volume and surface area than most zeolites, so it has quite ideal gas adsorption properties. Li's team

named it MOF-5, and used XRD to explain the structure of MOF-5: its terminal group is composed of Zn4 (O) (CO2)6cluster, and the specific structure is that in every ridge of the regular Zn4O tetrahedron, there is a -CO2 group connected, in which two O atoms are connected to the Zn atoms at both ends respectively, and the connection between the terminal groups is completed by terephthalic acid. The synthesis of MOF-5 is of great significance, because the framework structures synthesized before are very unstable and had no utility [8], unable to maintain a stable porosity, and the microstructure collapses once the guest molecules are lost, which greatly hinders the development in this field of study. But MOF-5 was more stable, its morphology and crystallinity have no change in the heating at 300℃ for 24 h, which can be recognized in XRD.

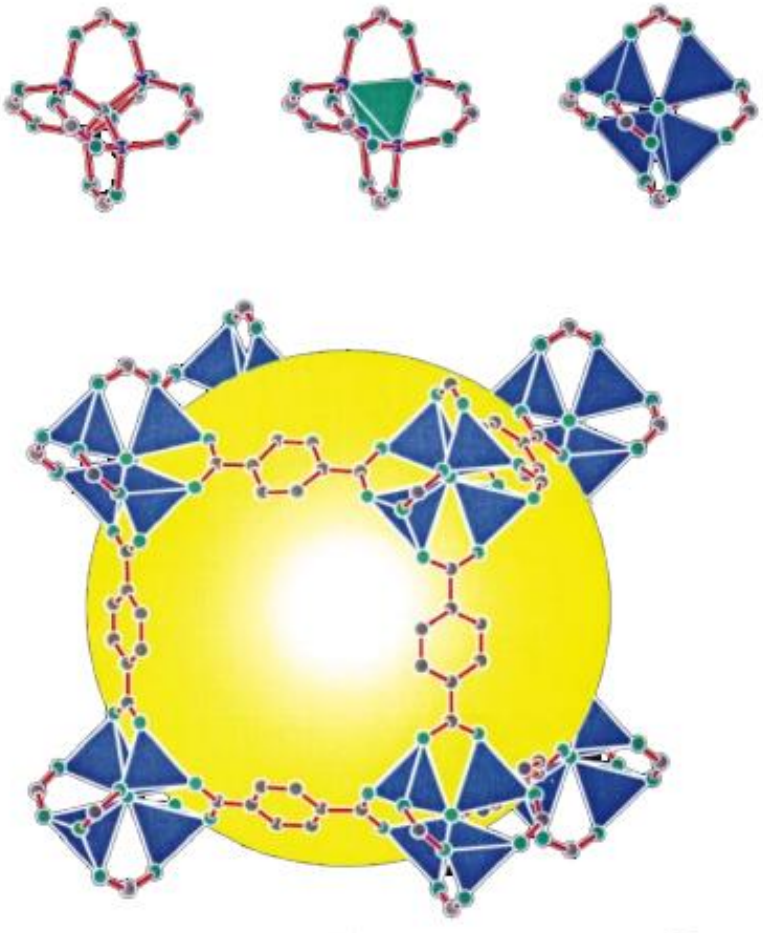

Fig 1. Structure of MOF-5 [7, https://doi.org/10.1038/46248].

After that, many studies had been done on MOF-5, and MOF-5 had shown many excellent properties. Rosi et al. conducted a detailed study on the performance of MOF-5, and INS spectroscopy analysis was carried out [9], the analysis results showed that compared with zeolite, MOF-5 had more binding sites with similar energy, which enabled it to have more hydrogen adsorption sites, and the types of binding sites are rich. The above studies explained the reason why MOF-5 has excellent gas adsorption performance, and pointed out the direction for the design of MOF materials, that was, the organic linking group played an important role in the gas adsorption process. As shown in Fig. 2, the study also tested that the adsorption capacity of hydrogen can reach 4.5wt% when the pressure is 20 bar and the temperature is 78 K, while at room temperature and the pressure is 10 bar, the number of H2 molecules absorbed by each formula unit could be reduced by about 9 times (from 17.2 to 1.9), showing that at ambient temperature and higher pressures great potential for adsorbing gases.

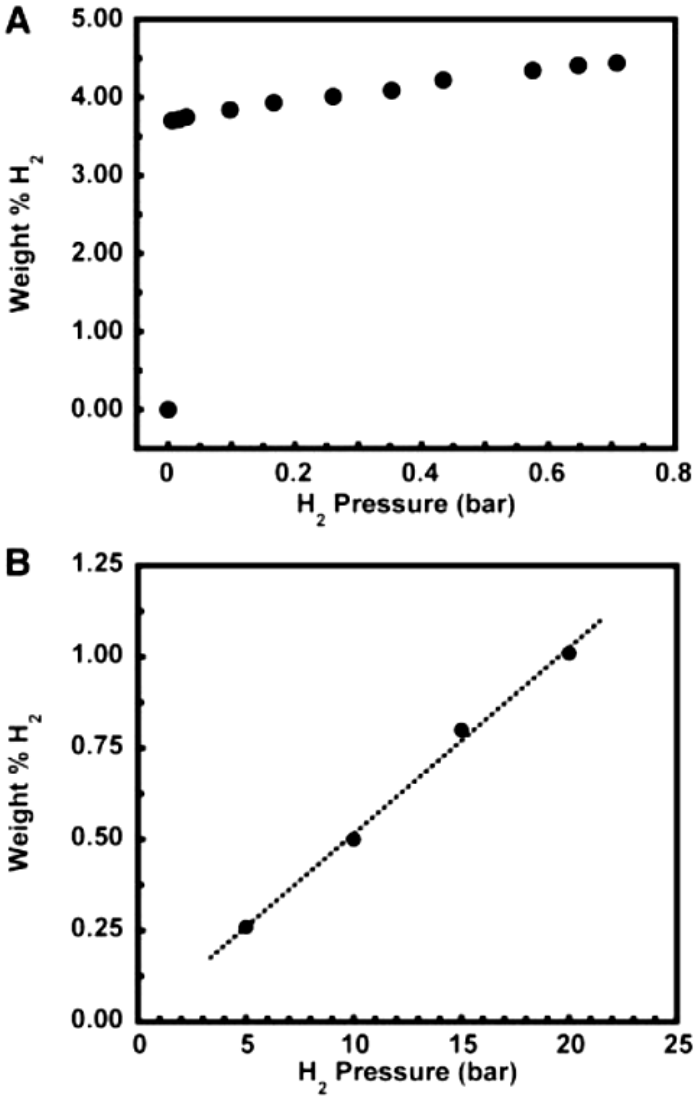

Fig 2. Hydrogen adsorption isotherms of MOF-5 at
(A) 78 K and (B) 298 K [9, https://doi.org/10.1126/science.1083440].

2.2 MIL-101

Compared with other MOFs, MIL-101 has higher porosity, more importantly, it also has good chemical and hydrothermal stability, and has a rigid structure. Which makes it stand out from various of MOFs. Férey et al. used targeted chemistry and computational design to predict the existence of MIL-101 and designed its crystal structure [10], where MIL represents their institution, Materiaude l'Institut Lavoisier. According to their design, MIL-101 is composed of a metal trimer and used 1,4-benzene dicarboxylate (H2BDC) as an organic ligand, and the latter can be cross-linked to obtain a super tetrahedron (ST), which is the MOF's secondary building unit. Each inorganic trimer has three octahedrons, containing a metal atom in the center of each octahedron, two of which are combined with water molecules, and the third is determined by the preparation conditions to be combined with a halide or hydroxide ion. Each octahedron is connected laterally by the carboxyl groups of two BDCs on both sides, that is, there are 4 connections between each molecule at the two sides, and there is a total of six bidentate carboxylic linkers in a trimer. All octahedrons are linked by the μ3O oxygen atom and assembled into a secondary building unit. In the construction of the secondary structural unit, the trimer is on the four vertices of the super tetrahedron, and the organic ligands build the edges to form a microporous structure. The secondary structural units are connected by vertices to form the final structure. Latroche et al. measured the hydrogen adsorption capacity of MIL-101, which can reach up to 6.1wt% [11], as shown in Fig. 3.

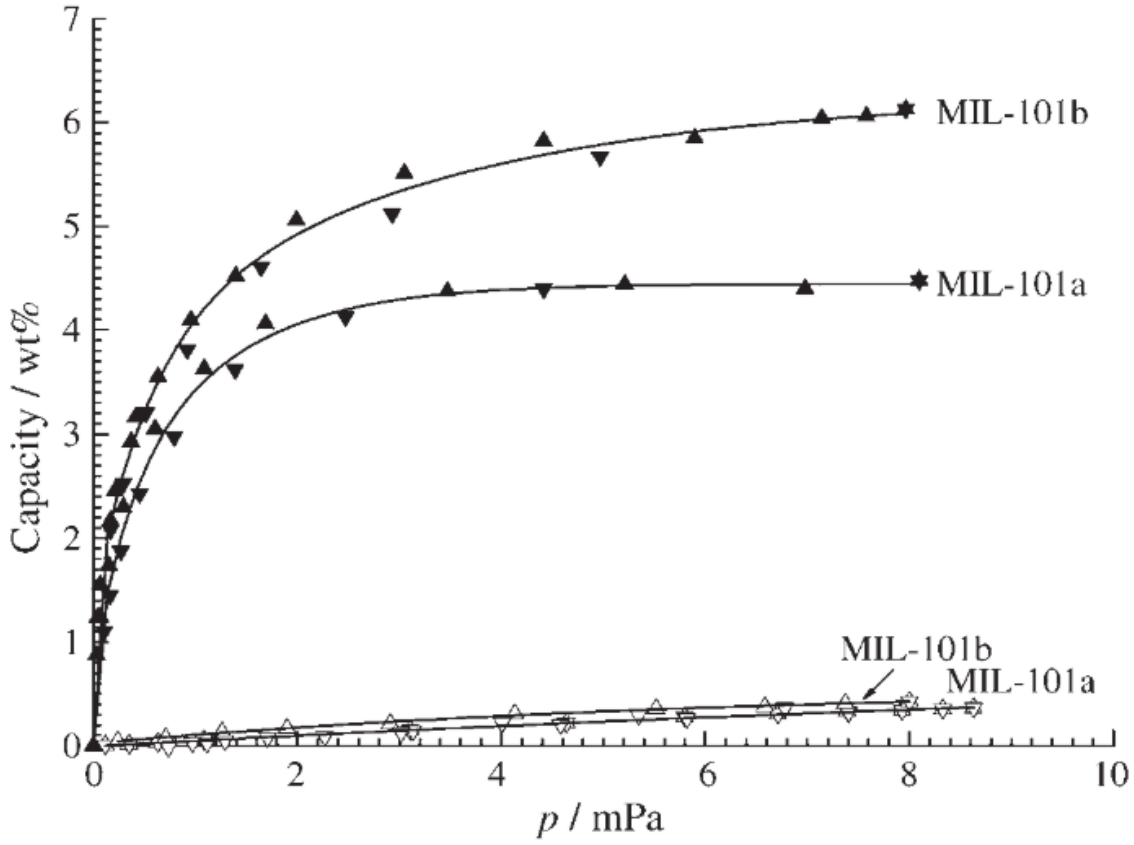

Fig 3. Isotherms of Adsorption (point-up triangles) and desorption (point-down triangles) of MIL-101a and MIL-101b at 298 (empty symbols) and 77 K (full symbols), MIL-101b was activated by additional treatment steps [11, https://doi.org/10.1002/anie.200600105].

Generally speaking, the trivalent metal used in MIL-101 is Cr. At present, there are many ways to replace the trivalent metal atoms in it and obtain the same structural form, which is called "isomorphism" [12]. These isomorphs can be characterized using the same research methods and formulas. Commonly used candidate elements are usually elements around Cr, such as Fe. Compared with Cr, MIL-101(Fe) has better biological safety, but its synthesis is more difficult, because its synthesis reaction is extremely sensitive to parameters and prone to transformation, so a single phase is usually not available. In addition, there are isomorphs replaced by Ti, V, Al, etc., all of which have their own unique properties.

2.3 NU-1501

In order to obtain MOFs materials with both high gravimetric specific surface area and volume specific surface area, Chen et al. obtained NU-1501-M based on NU-1500 by using the simulated synthesis method [13]. It is a 3-periodic acs-MOF having one type of open hexagonal channel, where M refers to metal atoms, currently using Al or Fe. It has high porosity and specific surface area, and the pore size is about 1.4nm, which is relatively small, good hydrothermal properties, and easy to modify. After analyzing NU-1501-Al, it is found that its experimental total pore volume calculated based on N2 is 2.91 cm3/g. And it has a very large gravimetric BET area, reaching 7310 m2/g, which reaches the top after satisfying the four BET consistency criteria. This is mainly because the largest pore of NU-1501-Al is much smaller than other MOFs and only one main pore exists. The iron-based analog of NU-1501 (NU-1501-Fe) has similar BET area and adsorption curve. As shown in Fig. 4, its ultimate hydrogen storage capacity can reach 14.2wt% under the optimal combination of temperature and pressure. These excellent properties make NU-1501-M an extremely high-quality material for storing and transporting hydrogen. At present, there are still few studies on this MOF,

but considering its high designability and great adsorption potential, it can be predicted that it has broad prospects.

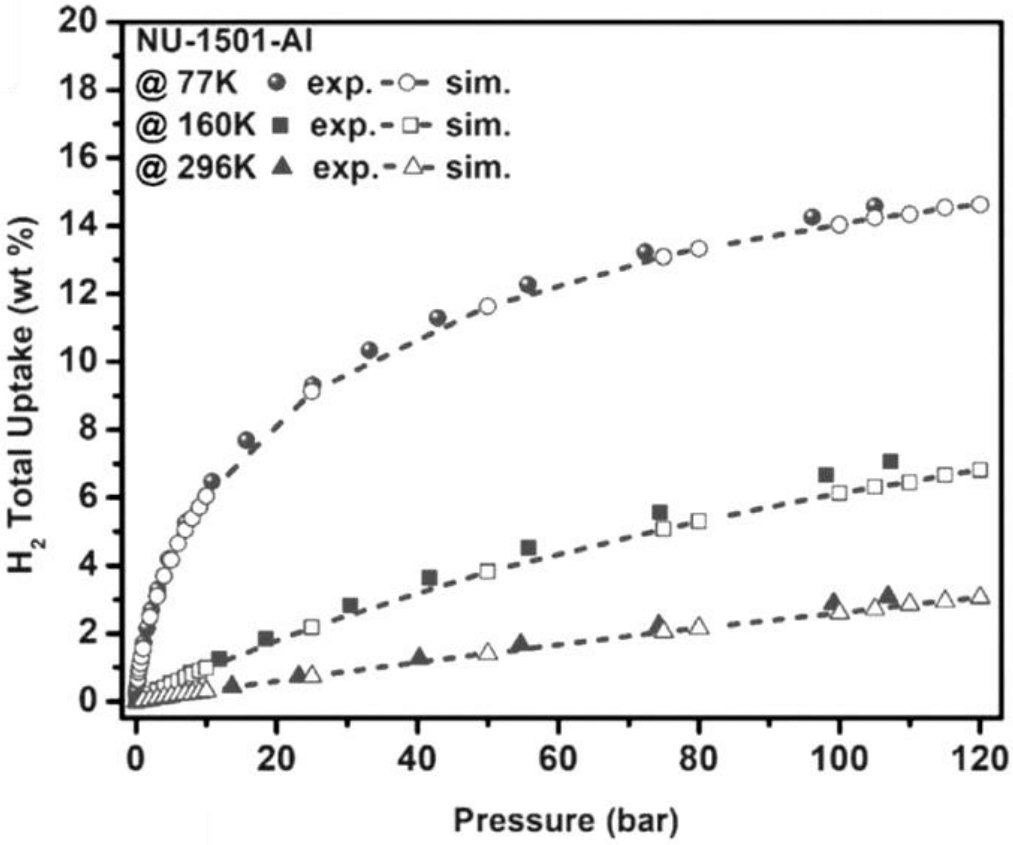

Fig 4. H2 storage capacity of NU-1501 [13, https://doi.org/10.1126/science.aaz8881].

3. Problems in the application of MOFs

As mentioned above, MOFs materials usually exist in powder form, and their current problem is weak mechanical properties. In the application of various materials, mechanical properties are an important indicator, especially for industrial manufacturing and processing. Strong mechanical strength and elasticity mean that the material can withstand some external deformation forces, such as stretching, abrasion and alternating stress, without changing its own properties. This is very important for the processing of materials, because the processing of materials is always accompanied by force and deformation. The weak mechanical properties of MOFs mean that its performance may be greatly reduced in some traditional processing processes, so they are not suitable, and MOFs are chemically sensitive to additives such as binders, so it is necessary to find new processing methods.

One way to increase the mechanical strength of MOF powders is to intersperse them with structurally more stable materials. Carbon-based materials such as activated carbon, carbon nanotubes, and graphene are rich in sources, stable in structure, have good thermal conductivity, and have the structural characteristics of adsorption and storage of hydrogen. Choosing these materials which are relatively stable through the intercalation structure can improve the structural strength of MOFs. They are used as a raw material for intercalating MOFs to improve the structure of MOFs. As shown in Fig. 5, it has been shown that carbon-based materials interpenetrating MIL-101(Cr) can improve the structural strength of MOFs, and by incorporating other microporous materials such as carbon nanotubes into MOFs [14]. It is also possible to adjust the pore size and increase the microstructure pore volume of MOFs, which enhanced hydrogen adsorption capacity.

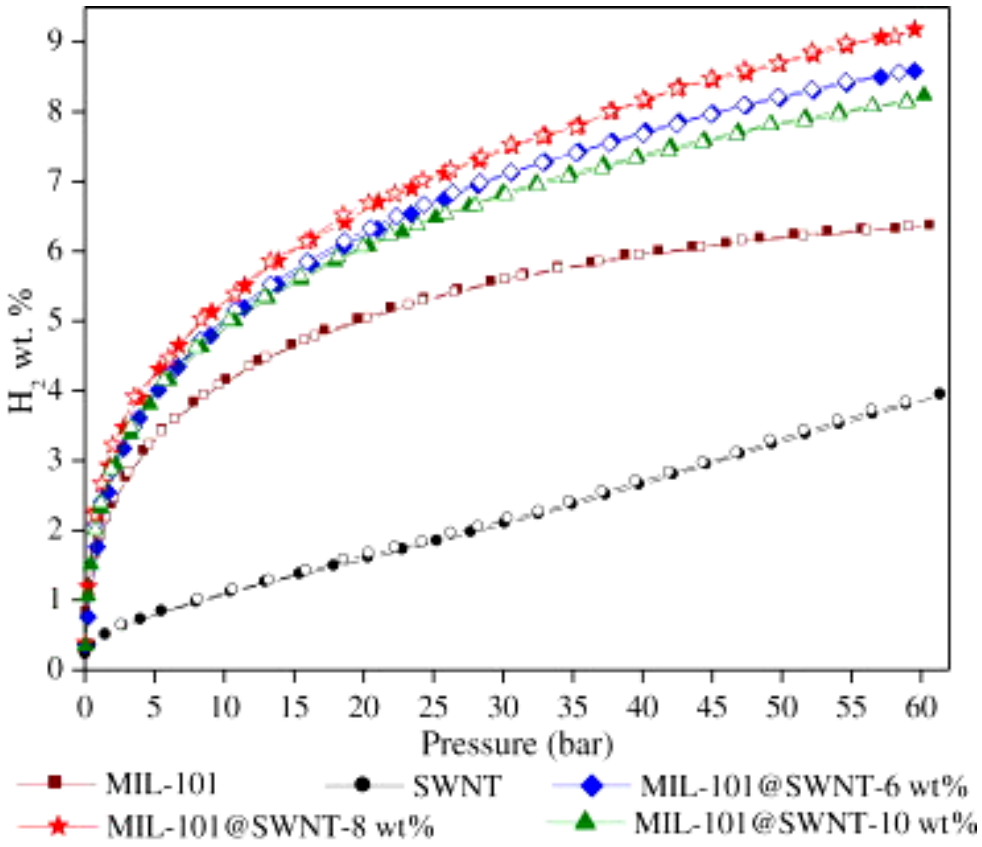

Fig 5. Hydrogen adsorption-desorption isotherm of MIL-101 incorporated with different concentrations of SWNT [14, https://doi.org/10.1016/j.ijhydene.2011.03.109].

In addition to improving the performance of MOF powder, it is also necessary to adjust the molding process of MOFs. Obviously, powdered MOFs materials cannot be directly applied, and the powder must be processed and shaped up. Granulation is one of the important molding methods, which is to combine powder into roughly spherical particles. Wet granulation uses a liquid dispersant as a medium to bond powders together to form granules. Valekar et al. used amorphous-phase mesoporous ρ-alumina to mold MOFs particles [15], and found that this method can maintain good adsorption performance, but its mechanical properties have little improvement. In contrast, dry granulation has higher density and mechanical strength, but at the same time causes a decrease in adsorption performance. This is because dry granulation usually achieves molding by pressing the powder, during which the MOFs structure will be destroyed, so it is necessary to tradeoff between adsorption performance and mechanical performance and achieve a balance.

4. Conclusion

This research focuses on the progress of MOFs materials in hydrogen storage, among which MOF-5, MIL-101 and NU-1501 have good prospects, although MOFs materials have made a lot of progress in hydrogen storage, especially at low temperatures, but the hydrogen storage capacity at room temperature is low, which still cannot meet the current DOE hydrogen storage target. There are still many challenges to be overcome for MOFs as a practical hydrogen storage material. In order to increase the hydrogen storage capacity of MOFs at room temperature, it is necessary to increase the interaction between hydrogen molecules and the material framework. At present, various strategies have been adopted to increase the interaction between hydrogen and the MOFs framework, such as increasing the specific surface area of the material, reducing the pore size, and doping guest metal ions. At the same time, it is necessary to overcome some shortcomings of MOFs materials, the core of which is the strength and molding of MOFs. It is more feasible to use guest materials to interpenetrate or use composite materials.

In the future, the research direction of MOFs materials will mainly focus on the practical application of hydrogen storage at room temperature. An ideal MOF material should have a large surface area and porosity. In addition, it also needs to have good reversibility, long life, fast adsorption and desorption kinetics and so on. For large-scale application, lower cost and environmental pollution are also directions that need to be considered. All in all, the current research on MOFs is still in the experimental stage, and there is still a long way to go before its practical application.

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