Metal-organic Frameworks (MOFs) on Hydrogen Storage and Purification

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Abstract. As a clean energy source, hydrogen shows promise as a potential substitute for non-renewable fossil fuels. However, the challenges with hydrogen include the difficulties in storing it feasibly and separating it from other gases mixed during industrial production. Metal-organic frameworks (MOFs) refer to crystalline substances that possess a significant porosity and expansive surface area, enabling them to effectively adsorb hydrogen via the van der Waals force. MOFs have been studied for ways to improve their surface area and hydrogen uptake capacities by various modification methods. This review discusses the key strategies for enhancing the hydrogen storage properties of MOFs to achieve the necessary increase in energy supply and the mechanisms behind the purification of hydrogen in practical use. Detailed discussions take place regarding synthesis methods, experimental testing results, and the mechanism behind the enhancement of hydrogen storage for each modification of MOF material discovered. Also, other parameters that may influence MOFs' hydrogen storage properties are demonstrated, together with the separating mechanism of purifying hydrogen from other gases and isotopes.

Keywords: hydrogen, metal-organic framework (MOF), hydrogen storage, hydrogen purification.

1. Introduction

Human activities are extremely likely responsible for the observed rapid global warming. This has led to climate change, which has caused significant environmental effects such as the vanishing of animal species, reduced agricultural productivity, and frequent severe weather conditions. Efforts to slow down climate change have gained momentum, with a focus on decreasing worldwide emissions of greenhouse gas. The United States Environmental Protection Agency stated that the burning of fossil fuels significantly adds to the release of greenhouse gases, making up to 76% of all human-caused emissions in the U.S. Therefore, to reduce the emissions of greenhouse gas, it is necessary to reduce fossil fuel usage, but this is not an easy task as fossil fuels are the major source of energy. For example, in 2017, fossil fuels accounted for over 85% of global energy production [1].

In recent years, experts from various fields, such as technology, science, economics, and policy-making, have focused on creating alternative energy sources. To be successful, these future energy sources must meet certain standards, including being environmentally safe, renewable, and accessible. Hydrogen is a great option for replacing fossil fuels. A hydrogen economy reason should be advocated because hydrogen is an environmentally friendly clean source of energy that produces minimal or insignificant amounts of greenhouse gases. Hydrogen has a very high energy density by weight, at 20 kJ/g, which is almost seven times than that of most fossil fuels. However, using hydrogen as an affordable and clean fuel is challenging because it is difficult to store and transport once it has been produced. The primary issue with hydrogen is its inadequate energy density by volume. Currently, the transportation industry relies heavily on refined petroleum fuels, but these fuels are becoming more expensive and scarcer. Hydrogen is a promising replacement for traditional fuels, but first, a storage method with a high energy density needs to be developed for it to be used as a transportation fuel [2]. However, the infrastructure costs of current storage methods like cryo-compression and liquefied storage are high, while their volumetric capacity is low [3].

Recently, a novel approach to hydrogen storage has been introduced where solid materials with porous structures are employed to enable the diffusion of hydrogen through either chemisorption or physisorption mechanisms. To encourage the development of this new approach, the US Department

of Energy (DOE) has established a goal to achieve a capacity of 40 g/L in terms of volume and 5.5 wt% om terms of mass for hydrogen storage under ambient temperatures and without excessively high pressure. Metal-organic frameworks (MOFs) appear to be capable of meeting these requirements, as they have sufficient porosity to accommodate significant amounts of hydrogen molecules and are versatile in facilitating adsorption. MOFs, which are materials consisting of inorganic nodes linked together by organic connectors, are porous and crystalline. They can be created and customized in numerous ways, resulting in a vast array of possible MOFs. As of now, scientists have synthesized approximately 70,000 MOFs, and there are hundreds of thousands more that have been projected but not yet produced. MOFs are highly porous, have large surface areas, and their pore geometry can be adjusted, which makes them useful for a range of hydrogen storage and purification applications [4].

In the remaining parts of this article, the overview of the mechanism behind the modification of MOF structures will be explained first. Then multiple modified MOFs, including MOFs in their composites and monoliths form or with inert metals and other substituted metal ions, would then be introduced and their advantages in hydrogen storage will be explained. After discussing the MOF materials in hydrogen storage, other parameters which would also affect their hydrogen storage capacities will be discussed. Finally, the mechanism behind MOFs used to purify and separate hydrogen would be demonstrated.

2. MOFs in Hydrogen Storage

MOFs are composed of inorganic nodes, such as metal or metal oxide, linked by organic connectors. The size of the pores in MOFs can be altered to be a good fit for the size of hydrogen molecules, which allows hydrogen to easily enter their structures. MOFs are permanently porous and have incredibly extensive specific surface areas, with a maximum of 6000 m^2/g. Additionally, their strength, flexible structure, thermal stability, and adjustable pore sizes make them excellent candidates for storing hydrogen. By adding various functional groups to their organic linkers, MOFs' chemical and physical properties can be altered. There are various types of functional groups, linkers, and nodes available that can be combined in different ways to form distinct topological nets. Also, MOFs can be modified after synthesis by replacing metal atoms in the node or incorporating additional functional groups. This results in an enormous number of potential combinations of functional groups, linkers, nodes, and topologies, which means that there are countless possible MOFs [5].

Ma et al. have proposed MgH_2-trimesic acid-TM MOF (TM=Co, Fe) hybrid composites to improve pure MgH_2's sorption kinetics [6]. The group synthesized two types of MOFs employing metal ions (Co (II), Fe (II)) and organic linker trimasic acid (TMA). To be more specific, the MOF composites were formed by introducing TMA-TM (TM = Co, Fe) MOFs that have been effectively made in deionized water at 298 K into MgH_2 by ball milling. The dehydriding kinetics together with the thermodynamics of pure MgH_2 and these MOF composites were comprehensively examined using the Pressure Capacity Temperature (PCT) test. The result from PCT tests exhibited that compared to the pure MgH_2's PC isotherm, which showed the single sloping plateaus without obvious hydrogen desorption plateau at 598, 623, and 648 K, the PC isotherms of the composites showed the single flat plateaus and distinct hydrogen desorption plateau without decreasing of H_2 pressure at all testing temperatures. In another word, during the process of hydrogenation and dehydrogenation, MgH_2-TM MOF (TM = Co, Fe) has superior hydrogen adsorption and release kinetic compared to pure MgH_2. Also, α-Fe and Mg_2Co phases were detected through X-ray diffraction in MgH_2-Fe MOF and MgH_2-Co MOF composites after re/dehydrogenation. The MOF composites' rate of sorption is accelerated by the significant catalytic efficiency of evenly distributed nanoparticles of α-Fe and Mg_2Co over the particles of Mg/MgH_2 with big size. The reason why the MOF composites have a better hydrogen storage performance compared to pure MgH_2 is because of the advantageous effect of α-Fe and Mg_2Co nanoparticles during the (de) hydrating cycles.

Madden et al. have reported that densified HKUST-1 monoliths can achieve both excellent gravimetric and volumetric hydrogen storage capacities [7]. The high-density monoHKUST-1 was synthesized using the sol-gel method. This reaction was initiated by the creation of primary MOF particles with a crystalline structure. After that, the team used a centrifuge to separate the original solution and then proceeded to cleanse the resulting MOF gel three times to eliminate any unreacted precursors. The synthesis of monoHKUST-1 was achieved by allowing MOF gel to air-dry at room temperature overnight. High-density monoHKUST-1 is evaluated to have excellent performance for hydrogen storage. The densified monoHKUST-1 can hold 46 g/L of hydrogen when used in a combined pressure-temperature swing gas delivery system (ranging from 25-50 bar and 77K to 5 bar and 160K). At an operating pressure of 25 bar, it can deliver 41 g/L, while at 50 bar, it can deliver 42 g/L. Compared to benchmark materials, the performance of densified monoHKUST-1 represents that the operating pressure criteria for hydrogen gas delivery can be reduced by at most 80%. The remarkable hydrogen storage and sorption performances of densified monoHKUST-1 are due to its unique high-density structure and the distinct synthesis procedure which produces monoHKUST-1 with porosity retention after being shaped and benchmark volumetric BET area respectively. Also, because the dense configuration of monoHKUST-1 can creates a layer of oxidation on the outside surface that restricts the contact of particles with moisture, the monolith's outstanding performance can be maintained even after exposing to the atmosphere for an extended period of time.

Molefe et al. have suggested that the cross-linked polymer of PIM-1 and [MIL-101(Cr)] monolith has the potential in storing hydrogen due to its extraordinarily porous character of the hybrid material [8]. The group successfully synthesized PIM-1/MIL-101(Cr) monolithic composite by physically combining MIL-101(Cr) powder and PIM-1 in tetrachloroethane solvent. This MOF monolith can easily be produced because tetrachloroethane exhibits a high ability to dissolve PIM-1, which made it easier to combine with MIL-101, form a homogeneous mixture, and generate monolithic gels. The resulting monoliths showed increased specific surface areas and extraordinary hydrogen absorption capabilities with the maximum loading of MOF (80 wt%) representing the most desirable characteristics. The hydrogen uptake capacity of this composite containing MIL-101(Cr) at levels of 40% and 60% was determined to be very close to the anticipated values by using the formula for estimating BET surface area. On the other hand, the hydrogen absorption at 80 wt% loading was found to be 1.73 wt%, indicating an increase of 7.5% from the predicted quantity of 1.61 wt%, due to a larger measured surface area than predicted. This difference in the measured and anticipated surface areas could be because of two possible reasons. Firstly, when the MOF loading was high and the sample was almost saturated, it is possible that the external surface area has increased, resulting in some of the surface of the MOF crystal being exposed. Secondly, the initial mesoporosity observed in the pristine PIM-1 powder caused by re-formation may have disappeared, which increased the inherent microporosity. This helped the physical properties of the MOF work together more effectively. PIM-1's usage as a binder was proven to be favorable because it failed to exhibit any evidence of blocking the MIL-101(Cr) micropores.

Liu et al. have proven that incorporating graphene oxide (GO) into the Li^+ doping MIL-100(Fe) composite results in a more efficient substrate for storing hydrogen [9]. Overall, MOFs are thought to store more hydrogen at ambient temperature when doped with Li^+. During the research, Li^+ doped both MIL-100(Fe)/GO composite and MIL-100(Fe) were prepared through impregnation. The result indicated that the hydrogen storage capabilities of both MOFs can be substantially improved at 298 K through Li^+ doping. Li^+ doped MIL-100(Fe)/GO demonstrated highly improved hydrogen adsorption performance (2.02 wt%) at 50 bar and 298 K in comparison to Li^+ doped MIL-100(Fe) (0.86 wt%). The reason behind this improvement can be linked to the better bonding between hydrogen and MOF or the isosteric adsorption heat which was aided by a greater amount of ultramicropores and conveniently reachable adsorption sites by the evenly dispersed Li^+ ions within the pores. The enhanced ability of Li^+ doped MIL-100(Fe)/GO in storing hydrogen can be explained mechanistically using Grand canonical Monte Carlo (GCMC) simulations. The experimental results

showed that a substantial number of Li^+ ions dispersed between GO and MIL-100(Fe) facilitates a large amount of hydrogen uptake by the addition of hydrogen adsorption sites.

Xu et al. synthesized Pd-modified MOF-808 series materials (Pd@MOF-808) which have extraordinary thermal stability and great potential for hydrogen storage [10]. By employing trimesic acid as the ligand, Zr(IV) as the central ion, and Pd as the modifier, the simple solution method effectively created the core-shell and penetrated structures of the MOF. Various measurements and tests were employed to describe the properties. Through Thermogravimetric Analysis (TG) analysis, Pd@MOF-808 material has excellent thermal stability over 350 °C because of the addition of Pd nanoparticles. Experiments on photocatalytic hydrogen production have revealed that the MOF has high hydrogen production, which can reach up to 236 μmol/gh. In addition, the 10 wt% core-shell structure of the MOF exhibits hydrogen storage properties of 8.11 wt%, 4.48 wt%, and 2.59 wt% when exposed to a pressure of 4 MPa for 77 K, 195 K, and 300 K. Similarly, the MOF with penetrated structure demonstrates a maximum hydrogen adsorption capacity of 8.20 wt%, 5.01 wt%, and 2.61 wt% at the above conditions. Also, the hydrogen storage performances exhibit an increasing trend with pressure. Moreover, an examination of the thermodynamics reveals that Pd@MOF-808 with penetrated structure has a maximum hydrogen adsorption enthalpy of up to -1.378 kJ/mol, which suggests great potential for practical use in hydrogen storage. The primary cause of the rise in hydrogen storage is due to the addition of Pd nanoparticles to the initial physisorption of MOF-808, which introduces some chemisorption. This increase in adsorption enthalpy results in increased hydrogen storage.

Huynh et al. have reported that substituting metal in MIL-88A MOF can improve the storage of hydrogen [11]. To make MIL-88A a practical option for hydrogen storage at normal conditions, its storage capacity needs to be improved. This study aimed to investigate how replacing Fe with transition metals with three valence electrons, such as Sc, Ti, V, Cr, and Mn, affects the performance in storing hydrogen of MIL-88A. Using van der Waals density functional theory (vdW-DFT) calculations, the researchers explored the best ways for the hydrogen molecule to bond with M-MIL-88A (M = Sc, Ti, V, Cr, Mn). The bonding between V-MIL-88A and hydrogen was discovered to be the best, with binding energy measuring 17 kJ/mol. The researchers also used GCMC simulations to show that substituting different transition metals affects also the amount of hydrogen uptake because of the modification of the interaction between H_2 and MIL-88A. Of all the metal options, Sc-MIL-88A exhibited the greatest excess and absolute H2 uptake values for volumetric and gravimetric measurements. At room temperature, the excess values Sc-MIL88-A can hold were increased compared to Ni, Fe, and Co metals by up to 32% and 18% in terms of weight and volume, respectively. The improved ability to store hydrogen is due to the modification of the considering metals, which have altered the way hydrogen molecules are adsorbed, resulting in better storage performance compared to Fe and Co-MIL-88A.

Some parameters, including temperature and pressure, can also significantly impact the hydrogen adsorption of MOFs. Firstly, overall, the adsorption capacity of MOFs negatively correlates to temperature, due to the fact that the overall volumetric capacity of MOFs has been observed to decline with rising temperature [3]. Physisorption would decrease with the rising temperature, because of the rapid decreasing of van der Waals force with increasing temperature. On the other hand, different from physisorption, chemisorption would increase with rising temperature in some cases. Due to the extra activation energy that higher temperature gives to the molecules, the adsorption process can be conducted more effectively [12]. Secondly, until equilibrium, the hydrogen adsorption performance of MOFs increases with pressure linearly. Under pressure swing conditions, some pristine MOFs' adsorption isotherms are measured. MOF-5, a MOF compound with a cubic structure, is observed to have the greatest total volumetric capacity but the least gravimetric capacity, therefore lowest usable volumetric capacity. As a result, usable capacity can only be partially predicted by total capacity under pressure swing condition [3].

3. MOFs in Hydrogen Purification

Regarding using hydrogen energy in practice, the purification of hydrogen using MOFs also plays a major role. Several other gas molecules, including CO_2, N_2, and CH_4, and other isotopes are frequently blended during the commercial manufacture and industrial production of hydrogen energy [3]. Thus, to effectively separate hydrogen from the gas mixture is important for hydrogen purification. However, the conventional gas separation and purification processes based on distillation are extremely capital- and energy-intensive. On the contrary, membrane-based gas separation mechanisms by using porous material (including MOFs) save about 90% of the energy that the distillation process required [13].

The majority of research concentrated on MOFs' use as membranes for hydrogen purification. A membrane is a thin transparent film that is frequently employed in gas separation and purification processes. Normally, membranes serve as selective barriers, permitting specific molecules to pass through. For membranes that MOFs acted in hydrogen purification, the two main gas separation mechanisms are solution-diffusion and molecular sieving. For the solution-diffusion mechanism, the molecule with the smallest size has a faster diffusion rate. Also, for the molecular sieving mechanism, the main influencing factor is molecular size. Because the kinetic diameter of hydrogen is much smaller than any other gas molecule, these two mechanisms can be successfully applied in hydrogen purification. Considering its stability both thermally and chemically with regular microporous structure, zeolitic imidazolate framework (ZIF) series membrane materials are frequently used to separate and purify hydrogen gas. ZIF series often employed to separate hydrogen gas are ZIF-7 (3 Å), ZIF-8 (3.4 Å), and so on [14]. Deuterium (D_2), a stable form of hydrogen, has various scientific and commercial uses, but due to its low abundance, it is necessary to separate it from other isotopes. However, conventional methods like molecular sieving described above are not suitable for separating isotopic H_2/D_2 because they have similar sizes, thermodynamic properties, and shapes. Instead, a kinetic quantum molecular sieving mechanism which relies on the quantum effects during the adsorption and release process of H_2 and D_2 in narrow pore systems has been proposed. This separating technique takes advantage of the fact that the H_2 molecule has a larger effective collision cross-section due to its higher zero-point energy, which results in facing a higher barrier for diffusing through the pores in comparison to D_2. This difference in diffusion could be used for separating H_2 and D_2 through kinetic sieving [13]. ROQFUA07 and RUBLEH are proven to be ideal MOFs in D_2/H_2 separation due to the greatest ideal membrane selectivity and best membrane performance respectively [15].

4. Conclusion

At present, MOFs are recognized as a novel kind of nanoporous materials that have garnered a lot of attention in materials chemistry. It is evident that MOFs offer distinct benefits over other traditional porous materials and will have a noteworthy impact on the development of porous compounds in the future. The use of high surface area MOFs for hydrogen storage is making advancements and progress, which can potentially decrease the dependence on fossil fuels. It has been proven that intensive modifications can be applied to the MOF structures to increase the amount of hydrogen that can be absorbed, including creating composites and densified monoliths, doping with metal ions and nanoparticles, adding inert metals, and substituting metals. Understanding the effects of these techniques can make the optimization of MOF easier. MOFs' hydrogen adsorption ability is also affected by other parameters such as temperature and pressure. Additionally, MOFs exhibited use in hydrogen purification by both separating hydrogen from other molecular gases and separating deuterium from other isotopes. For further practical application and industrial use, MOFs will likely be produced through a simple, effortless, eco-friendly, and cost-effective process. Therefore, MOFs will be synthesized on a large scale to meet the demand. The challenges and directions for further research indicate a promising future for MOF chemistry.

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