Metal-organic frameworks for hydrogen storage: progression in synthetical methods on physical and chemical properties

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Abstract: Metal-organic frameworks (MOFs) with their flexibility give rise to various types that help to improve the capability of MOFs in hydrogen storage. In this article, the synthetical methods as a crucial factor in the advancement in MOFs application are detailly presented. These methods contribute to incrementing the adsorption capacity and the stability of MOFs. The tactic for this approach is mainly increased by the exchange and modification of the metal ion and ligand of the complex. The metal ion increases adsorption enthalpy, while the ligand increases surface area and pore volume. Apart from adsorption enthalpy, stability is another critical property for MOFs in hydrogen storage. The modification and alteration of the structural feature of the MOFs are two main approaches for this target. Chemical stability is primarily related to the adsorption enthalpy, which uses the same methods including the exchange of metal and ligand. The physical stability raised by using penetrated system increases the interaction strength in the MOFs. These techniques discuss the future application in areas such as the working capacity and thermostability of the MOFs. The detailed mechanisms and effects for these general types of synthetical methods are presented. Also, data and analogy with the expected use for these types of the synthetical pathway to evaluate the suitable circumstances to adopt these methods. In the end, reasonable improvements to these methods introduce interpretation to select the appropriate technique for future investigation in MOFs development.

Keywords: synthetical methods; hydrogen storage; metal-organic-frameworks.

1. Introduction

The alternative energy source has become the focus of modern chemistry and biological science. Hydrogen is one of the most promising green energies that could replace the current fossil fuels. Despite its apparent advantages, technological difficulties remain the major drawback for commercial applications. While with the development of material science, nanomaterials have been invented to solve the low density of hydrogen. Many nanomaterial types developed, including active carbons, metal-organic frameworks, and zeolites. These materials use adsorption to attract hydrogen molecules on their surface, thus increasing the density of the hydrogen stored and significantly reducing the cost of hydrogen storage from the conventional methods due to the flexibility, high surface area, and pore volume. MOFs is the promising candidates for hydrogen storage.

It is essential to analyze why MOFs could be the possible choice among many others. The most obvious reason is the flexibility of alternating the structure and components of the material. The unit cell consists of metal ions and ligands surrounding the ions and linkers molecules linking the complexes ions from each other. This property allows scientists to conveniently modified the material for testing and improving the MOFs, creating thousands of different configurations. So, the invitation process is significantly accelerated. MOFs produced since 2022 that obtain different components and structures. This property makes the MOF one of the most advanced materials in multiple areas, including hydrogen storage. Furthermore, compared with active carbons, MOFs generally have more vital stability. Due to their flexibility, the chemical selectivity and inertness of the MOFs can be easily extended. The effect of the impurity in the air can be prevented by modifying the MOFs, while active carbon requires more specific engineering to obtain the same stability without changing its adsorption capacity. Also, the MOFs have a relatively high adsorption enthalpy compere with carbon, further stabilizing the hydrogen. Not only does it exceed the active carbon, but it also gains advantages compared to zeolite and has more substantial chemical stability, despite MOFs' weak thermos and

mechanical stability. Water stability is an example, as removing water causes a significant amount of energy, while MOFs can reduce that significantly [1]. Although its native disadvantages of weak thermos and mechanical stability, the recent development in synthetical provides an acceptable solution by altering the structure and components of the MOFs.

The development of MOFs in hydrogen storage is significant in two parts. First, with the improvement in surface area, pore volume, and stability, the material can achieve the standard for hydrogen storage at low temperatures and high pressure. For example, at 77K, 100bar MOF-5, the most traditional one, obtains a volumetric capacity of 31.1g/L, and the newly developed IRMOF-20 has 33.3g/L. These data distinctively demonstrate the achievement of hydrogen adsorption capacity that is essential for the application of MOFs in this field [2]. Apart from adsorption capacity, another noticeable property of hydrogen storage is the stability of the material. The pressure and chemical resilience directly determine life expectancy. The stability of the material is also a significant factor required in real-life applications.

In this article, the development in metal-organic frameworks (MOFs) will be discussed explicitly for the varying synthetical technique supporting this trend. a discussion of the improvement in adsorption capacity and stability will be considered by the advancing methods adopted. Also, an Evaluation of synthetical methods with these properties and the future development of these techniques in room temperature conditions will be stated. The report will present a clear insight into each synthetical methods

2. The Synthetic Modification of MOFs

Firstly, with the development of MOFs in hydrogen storage is the advance in structural feature modification. This advancement gives rise to high porosity, adsorption enthalpy, and stability. The major contributor to this advancement is the post synthetical modification. The four main post synthetical modification techniques are metal-based, ligand-based, metal and ligand-based, and guest-based modification. This part focuses on the first two types applied in hydrogen storage.

2.1 Metal-Based Modification

On the one hand, metal-based modification in hydrogen storage generally includes exchanging original metal or doping the new one into the center of the original one.

2.1.1 Partial metal exchange

The most widely used application is the mixed-metal system using one or more other metals to part exchange with the original metal to enhance the performance and stability of the MOFs. The synthetic method is to put the MOFs into the solution containing the subject metal for a controlled time determined by the percentage of exchange required. The transformation will change the conformation and properties of the original MOFs depending on the portion that may retain new properties and uses. For instance, the exchange of the Cu-BTC alters surface area, thus the gravimetric capacity for H_2 storage. Concerning the reactivity of the metals, Cu and Zn are two metals that suit the purpose of hydrogen storage. The Cu-BTC has a BET area of 945 m^2/g, while the Zn-Cu-BTC has a 1940 m^2/g BET area which increases twice that previously. Furthermore, the gravimetric capacity of Zn-Cu-BTC is 1.63 wt%, 59.8% higher than the Cu-BTC's 1.02 wt% [3]. About the experimental data, Zn and Cu are generally more suitable for hydrogen storage because their chemical stability is better than other common choices. Also, the pore volume can increase. Using Co to exchange ZIF-8 with the ratio of 70:30. The results are an increase in the Hydrogen uptake by 23% [4]. Overall, the metal exchange will increase the hydrogen uptake capacity.

2.1.2 Metal doping

Metal doping does the pathway increase the surface area but also doping. The doped metal increases the surface area of MOFs and the contact point between hydrogen and metal ions. This dope will improve the hydrogen uptake capacity and the thermostability of hydrogen physisorption. MOF-

519 modification with Li doping is one example. Since Lithium has a strong polarity that will attract the hydrogen better than the transitional metal while also obtaining an appropriate reactivity and adsorption enthalpy for hydrogen storage. The Li-doped MOF-519 massively increases the adsorption enthalpy from 0.116eV to 0.264eV for the first hydrogen. The rise in adsorption enthalpy increases the hydrogen uptake. This improvement led to a 20% increase in the working capacity for Li-MOF-519 compared to the MOF-519 shown in Fig.1 [5]. Moreover, the expanding adsorption enthalpy of Li doping also increases the isosteric heat 0.61kj/mol higher than MOF-519 at 77K, 1bar shown in Fig.1(b). The combination of the two effects demonstrates the increase in the working capacity of the MOF. Even so, it still causes a reduction in pore volume and surface area. Since the occupation of the metal ion inside the space of MOFs. Generally, metal doping increases both the hydrogen uptake capacity and the working capacity of the MOFs.

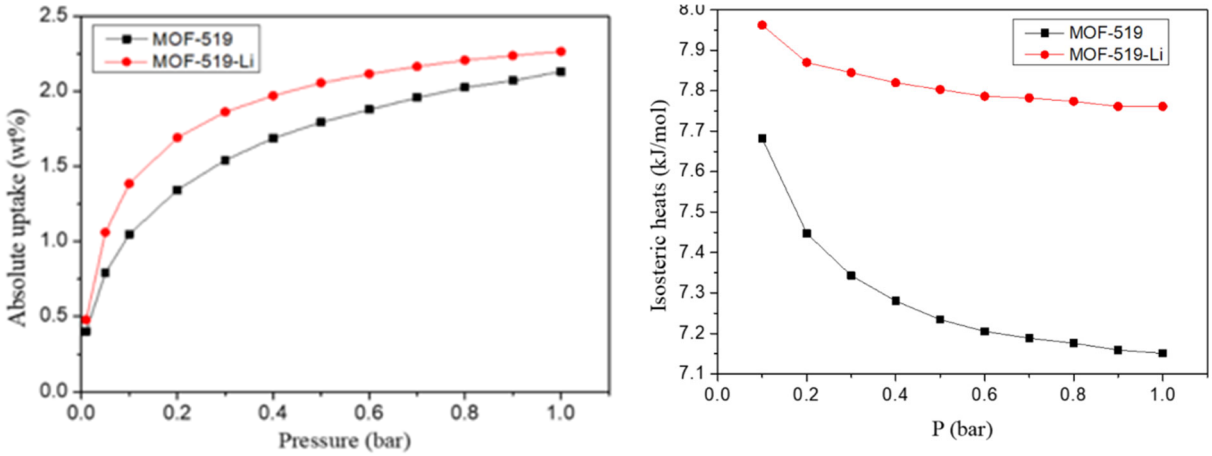


Fig. 1 (a) The adsorption capacity of MOF-519 and Li-doped MOF-519; (b) The isosteric heat capacity of MOF-519 and Li-doped MOF-519 [5].

2.2 Ligand-Based Modification

On the other hand, ligand-based methods to increase the hydrogen uptake capacity include modification and exchange. These mainly alter the surface area and pore volume to increase adsorption capacity.

2.2.1 Ligand modification

The Flexible ligand system retains a low density leading to larger pore volume and high surface area. The system increases the pore void ratio and maintains its porosity, enhancing the adsorption capacity [6]. The alteration of the ligand is applied to alter surface area and density. These shifts in properties will promote stability and hydrogen uptake capacity. The modified ligands are generally in the same functional group or with similar chemical structures and properties with different. For example, the modification of MOF-5 using morphology engineering of carboxylic acid linkers demonstrates the value of this strategy. New engineering achieves a leap in the density of MOF-5 compere with the commercial version of its presence in Fig. 3. The modified types' average density is 2x the original MOF. This modification increases the gravimetric capacity by 75% with the density. The result volumetric capacity is 30.5g/L exceeding the DOE2020 30g/L [7]. In addition, the process of synthesis and solvents causes a significant issue affecting their performance. In the main, forming an H bond with the MOF reduces the available capacity for hydrogen. The solution adopted solventless synthesis that prevents the solvent effect and achieved a noticeable outcome in the BET area suggested in Fig. 2 [8]. Overall, both methods involve in ligand modification are useful in hydrogen storage.

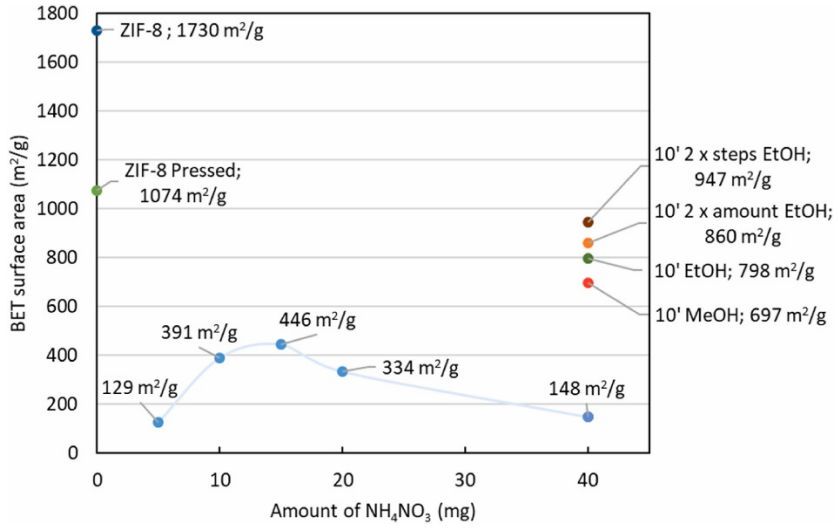


Fig. 2 The BET surface area of ZIF-8 changes with the amount of NH_4NO_3 [7].

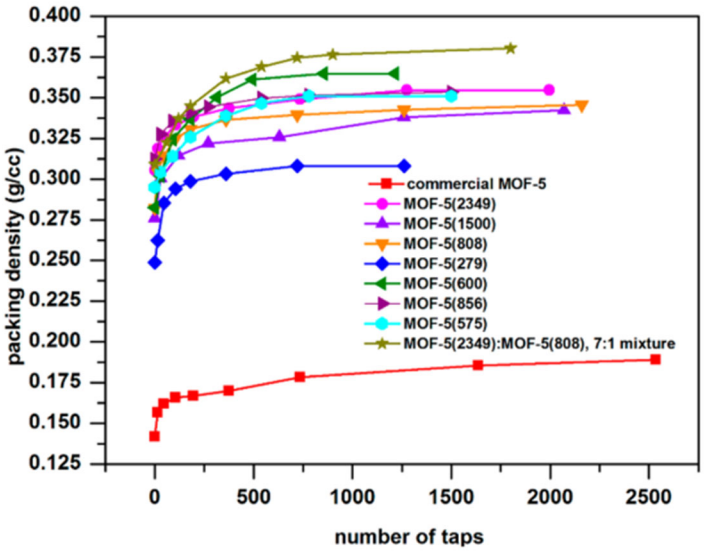


Fig. 3 The density of different types of MOF-5 changes with the number of trans [8].

2.2.2 Ligand exchange

Rigidification of ligand, turning the ligand by a single bond alters the ligand, primarily increasing the adsorption enthalpy and chemical stability [9]. Apart from the modification, the ligands exchange is also an investigation pathway. The ligand exchange alters parts of the original ligand to extend the surface area and pore volume. The mechanism simplifies to only the start and the end in Fig 4(a) [10]. The technique is to extend or alter parts that are inessential for chemical properties to increase the hydrogen uptake capacity. The example illustrated the experiment on the UiO-66 exchange. UiO-66 is a good MOF, with a gravimetric capacity of 3.37wt% under 77K and 4 bar. This study selects different side chains from CH_3 to $(OCH_2CH_3)_2$(L0 to L2 in Fig.4(a)). Results in Fig. 4 (b) and (c) suggest the performance of the UiO-66 variety under 303K and 77 K from 1-4bar. The best one is UiO-66$(OCH_2CH_3)_2$(L2), with a gravimetric capacity of 4.56wt% at 77 K 4bar higher than 3.37wt%. This MOF preserves these properties under 303K 4bar too. The inspection of the pore volume appears to be 1.6nm larger than the missing linker effect during synthesis. In the end, these combine to enlarge the surface area, thus the hydrogen uptake capacity.

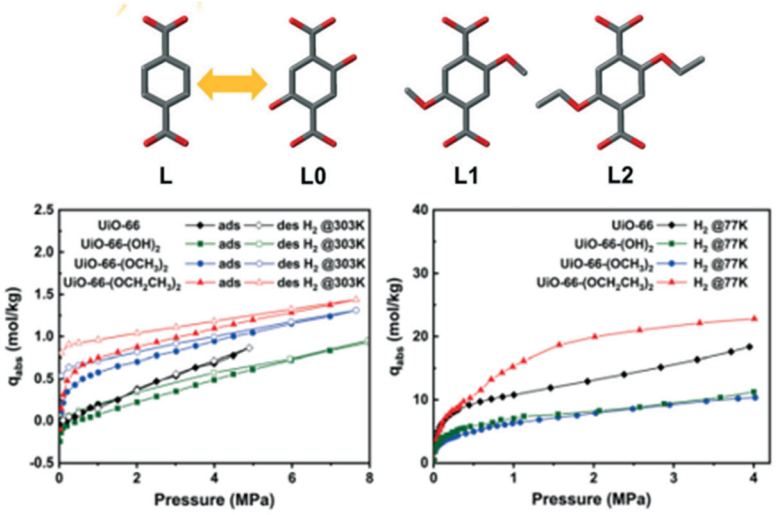


Fig. 4 (a) The modification of ligand of UiO-66, L is the original one, L0 is $(OH)_2$, L1 is $(OCH_3)_2$, L2 is $(OCH_2CH_3)_2$; (b) The quantity of hydrogen adsorbed by different types of UiO-66 under 77K (c) The quantity of hydrogen adsorbed by different types of UiO-66 under 303K [10].

2.3 The Evaluation of Metal-Based and Ligand-Based Methods in MOFs Modification

In general, the post-synthesis methods advance the recent development of MOFs and contribute to the surprising outcome of MOFs in hydrogen storage. On the one hand, the metal-based pathway mainly results in more vital interaction with hydrogen by increasing the percentage of metal ions and its contact point with hydrogen in metal doping. Also, partial exchange with new metal ions could alter the structure hence the porosity and surface area. This technique can modify currently existing MOFs with certain drawbacks in structures. On the other hand, the ligand-based pathway can increase the surface area and pore volume for the ligand modification that alternates the original ligand from the existing MOF. This method will not change the configuration of the material. Instead, it will increase the surface area and pore volume, which will also lead to an overall increase in capacity, despite the ligand exchange changing the configuration of the MOFs. In this case, the metal ions will be remained with the ligand switched. It will be a considerable method when constructing new MOFs from a known metal ion. So, the properties of the metal ions can become better developed. Overall, metal-based methods are more suitable for thermostability of hydrogen storage and increasing the strength of the material or alternating its structure. The ligand-based methods extend the material's surface area and pore volume better.

3 The Improvement in the Stability of MOFs for Hydrogen Storage by Synthetical Methods

The stability of MOFs is an essential parameter in the measurement of the hydrogen storage ability of a material. The MOFs must withstand high-pressure conditions used for hydrogen storage at the current stage and are chemically inert to avoid transformation. The development of stability helps MOFs adapt to these conditions. The alternation in crystalline structure and reactivity of the ligand/metals of the MOFs are keys to stability.

3.1The Improvement of Chemical Stability

Many MOFs obtain a high surface area and interaction strength with hydrogen but do not perform specificity under a mixed environment. One possible solution is the modification of the original MOF with a low exchange rate ligand and high valance metal ions.

3.1.1 Metal exchange

For high valance metal ions, the evidence for their water stability and low toxicity are suitable to provide a pathway for green and large-scale production. [1] This outcome is due to the chemical stability these high valance metal ions rose and contributes to their resilience to impurity in the application. It also increases the working capacity due to more hydrogen adsorbing at low temperature and pressure stages. These exchanges increase the energy barriers for hydrogen to desorb from the surface of the MOFs. In particular, the synthetical pathway will be similar to the partial metal and ligand exchange in 2.1.1 and 2.2.2. The experiment was conducted by MOF-5 exchange with zinc loaded in a cylindrical steel holder with various pressure to test these exchanges' effects [11]. The result suggests that the modified version can effectively separate many impurities, such as ammonia and oxygen, under cycle tests. [12] These data suggest the modification increase the chemical stability of MOF-5 under a mixture of gas. The improvement will significantly reduce the effect of impure gas contact during transferring and storage, thus reducing the cost of the MOFs in the application.

3.1.2 Ligand exchange

The low exchange rate ligand represents the chemically inert ligand. This property suggests the ligand will not be easily exchanged by others, thus increasing the reliability of the MOF and the life expectancy under normal and extreme conditions. This outcome is due to the chemical stability these high valance metal ions rose and contributes to their resilience to impurity in the application. The example of increasing stability applies to gas storage, including hydrogen storage is plenty. Using two different imidazolates as a linker and three hydrophobic ZIFs with chabazite topology in ZIF provides a great example. The result shows a low energy consumption with high energy efficiency for all gases (CO_2, H_2O, N_2, H_2) due to stability modification [9]. Modifying MOFs with high valance metal and carboxylic base presents perfect stability. If the metal also obtains redox ability, it will be promising for further research for applications in room temperature hydrogen storage.

3.2 The Increment in Physical Stability

The ability to withstand pressure is fundamental for the application of MOFs. The synthesis of an interpenetrated network could increase the strength of the material. The overlapping interaction of the two-layer increases porosity and the framework's strength by forming a stronger bond within the material. (Fig.5) The penetrated system is suitable for enhancing its mechanical and thermos stability.

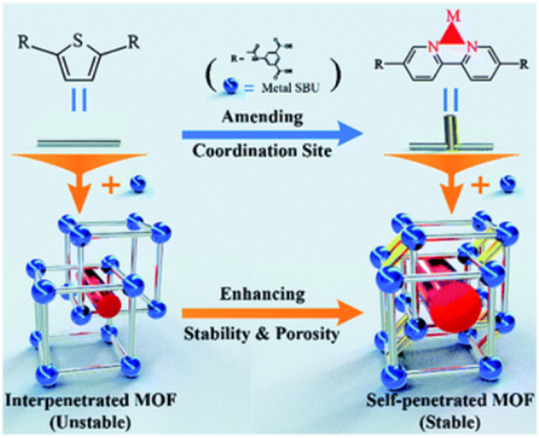


Fig. 5 The transformation between interpenetrated MOFs and self-penetrated MOFs [13].

3.2.1 Mechanical stability

The interpenetration system generates a more vital interaction between layers of molecules, increasing the strength and stability of the original structure. The increase in the mechanical stability can be presented by the "solvothermal reaction of $Zn(NO_3)_2$ and 4-(3,5-dimethyl-1*H*-pyrazole-4-yl) benzoic acid (H_2mpba)" [13]. During the reaction, three isomers are formed. The energetic calculation

revealed that the isomers with the interpenetrated network retain much higher chemical and physical stability tested by water impurity under high pressure. The result suggests an increment in resilience against rising temperature and pressure by adopting the interpenetration structure. This advancement will protect the MOFs from collision and increase their usability. Increasing usability and life expectancy can enormously reduce the cost of applying MOF in hydrogen storage and extend the available application condition. It also reduces the water impurity affecting the hydrogen storage in the application.

3.2.2 Thermostability

The thermostability is increased by forming the self-penetrated framework supported by the experimental data comparing a Tetragonal crystal. It can synthesize to form a self-penetrated framework. The result from the TG curve illustrates a slight weight loss in the MOFs of 1.7% ($0.5H_2O$) at 25-150 ºC. At 400 ºC, the MOF is thermally stable, and no more guest molecules are released [14]. The powder X-ray diffraction (PXRD) confirms its thermos properties by revealing its bulk identity. The identified pure bulk MOF is immersed in anhydrous MeOH. The PXRD proved that the MOF maintains its crystalline structure during solvent removal and thermal treatment, demonstrating its rigidity and robustness. The material also presents considerable adsorption for H_2 at low-temperature conditions due to its small pore volume. Overall, despite the reduction in the pore volume, the methods could significantly increase the MOF's thermostability that can be further investigated for room temperature hydrogen storage.

3.3 The Evaluation of Two Methods

The alteration of the metal ions and ligands can increase the chemical stability primarily by increasing the adsorption enthalpy. This method can both extend the adsorption capacity and the chemical stability. The most suitable candidates for ligand and secondary linkers are highly conjugated carbon. These groups obtain a higher electron density that can attract the hydrogen more intensively, thus increasing the energy barriers for replacement from other chemicals. Also, the conjugated system can act as a good pi-donor and sigma-donor in the complex ion. As the low exchange rate ligand, this property results in more muscular strength for the coordinate bond. There will be a more vital electrostatic interaction from the metal ion center to the ligand and hydrogen for high valance metal ions. This increases the adsorption enthalpy and the chemical stability in a similar pathway.

In terms of physical stability, structural features become the primary factor. Since the ligand and organic linkers originally had weak mechanical and thermos stability. The alternation in the structure of the MOFs becomes the leading solution for this problem. For mechanical stability, the interaction strength between molecules becomes the essential factor-the more overlapping, the stronger the strength and resilience against an outside force. So, interpenetration becomes multiple systems to synthesize. The additional layer of overlap significantly increases the strength of the structure. So, interpenetration systems are considered to become the technique to increase mechanical stability. The self-penetration system is preferred for thermostability due to the increased porosity and the contact area of metal ions in the MOFs. The metal ions can attract more molecules, and a larger surface area is obtained with increasing porosity; the resilience against high temperature is improved by an average increase in adsorption enthalpy in general; they help to maintain more hydrogen on the MOF during high temperatures. Thus, increasing the thermostability.

In application, molecular modification can be used to solve the problem of impurity, which is one of the major concerns for the application in real life. The structural shifting can be used to increase the life expectance reducing the cost of usage. It can also reduce the risk of transformation and withstand higher pressure extending the range of MOF applications. Last but not least, the thermostability of the MOFs can be improved by both methods. A combination approach might be the most effective way to achieve this goal which is one of the most fundamental issues before the industrialization of MOFs.

4. Summary

MOFs are one of the most promising materials in the field of hydrogen storage. This article suggests the effect of fixability and its structural diversity as two main factors behind the advancement in MOFs, especially the synthetical methods of MOFs. Also, the complex compounds do not have significant limitations in selecting the metal and its ligands to form a new complex. This specialty gives rise to the synthetical pathway base on modification and exchange for metal ions and ligands to increase the adsorption capacity discussed in the paper. Alternatively, stability, in general, is another main target for MOFs development. The same methods, including changing different component molecules, are also appropriate for this application, mainly on the chemical side. It is worth mentioning that the shifting in the crystal structure can also be conducted for stability in terms of mechanical and thermal.

Overall, with the cutting age synthetical methods, properties improving the hydrogen storage performance can be installed into one signal MOF. This advancement allows the MOFs to obtain further leads in the race to commercialize hydrogen storage and the usage of hydrogen. In recent, with the achievement in the adsorption capacity and stability. The application of MOF under low-temperature conditions is turning more mature. The research into the thermostability and the production of MOFs gradually become the target for future research. Just like the contribution of these synthetical techniques to the current achievements, they will remain fundamental since thermostability for hydrogen storage is related to the adsorption enthalpy, working capacity, and the correct release of hydrogen. The structural and molecular features will be considered using the same metal and ligands methods. The difficulty will be focused on the limitation of the metal ions, which have around 15-20 kJ/mol adsorption enthalpy. This value is not sufficient for the room temperature application. So, doping might not be the best method.

Moreover, the contribution from ligand and secondary linkers is generally weaker than metal ions ranging from 5 kJ/mol-11kJ/mol. The improvement in their performance is critical for the next leap in MOF in hydrogen and other gas storage. One possible solution might be an increment of the conjugation of the ligand to increase the electrostatic attraction upon hydrogen molecules. Apart from thermostability, industrialized production will be another issue before real-life application. The synthetical methods are the central part itself. Research for the cheaper and more effective synthetic process is the most urgent target in this field. This goal will require simplifying the synthetical process, thus making the process more economically sustainable and accessible for the high-tech factories, accompanied by automatic control of the time and ingredients added. The future for MOFs in hydrogen storage will be successful.

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