Synthesis and engineering of porous metal-organic frameworks to store hydrogen

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Abstract. Hydrogen energy is a clean and efficient renewable energy with water as its only combustion by-product, and the research on hydrogen energy has also attracted extensive attention in the world industry and academia. Despite the gradually extensive usage of hydrogen, the efficient storage of hydrogen remains a bottleneck, which hinders its further large-scale application. As a volatile fuel, hydrogen needs to be stored safely and efficiently. Porous metal-organic frameworks persist in high specific surfaces, high pore volume, and modifiable pore structure, which shows broad application prospects in gas storage, especially hydrogen storage. To explore how to design MOFs to improve their hydrogen storage performance, this paper introduces various synthesis methods for MOFs. The strategies for engineering the MOFs and improving their hydrogen storage capacity are comprehensively summarized. The enlarged specific surface area and enhanced combining enthalpy of MOFs are decisive factors for achieving better hydrogen storage performance. Compared with high-pressure compressed hydrogen and low-temperature liquid hydrogen, MOF may become the alternative next-generation mainstream hydrogen storage technology in accomplishing safe and efficient hydrogen storage.

Keywords: MOFs, hydrogen storage, MOF material modification.

1. Introduction

Hydrogen is a green, sustainable fuel with high energy density, a promising substitution for the depleting carbon-based fossil fuels. The storage method was considered a main technical difficulty in obstructing hydrogen from being applied in our daily life. Compressing and refilling a large volume of gaseous hydrogen is neither an economic nor safe choice. In the past few decades, MOFs, a permanent and highly porous material, have drawn considerable attention to storing hydrogen through a more efficient approach, in which MOFs could adsorb hydrogen repeatedly under moderate temperature and pressure. Numerous micropores in MOFs offered sufficiently large pore volume and surface area, capable of enclosing the guest hydrogen molecules by physisorption on the pore surface. The U.S. Department of Energy (DOE) had published goals for storing hydrogen, which reached an efficiency high enough for the practical replacement of currently used fossil fuels. By 2025, the target was 5.5 wt% under -40 to 60 °C and 100 atm. NU-100 had an excess hydrogen storage capacity of 9.95 wt% under 77K and 56 bar for MOF hydrogen storage. However, due to the weak hydrogen adsorption enthalpy, this capacity at cryogenic temperature tended to decline by multiples under room temperature. Few of the MOFs could reach the DOE target at this moment [1]. Synthesis and modifications on MOFs to obtain a higher hydrogen storage capacity were continually designed and tested by researchers, mainly focusing on enlarging the specific surface area and binding enthalpy of MOFs, along with optimization of synthesis cost and stability of the framework. Currently, one of the most powerful MOFs, $V_2Cl_{2.8}$ (btdd) could store 1.64 wt% hydrogen under moderate conditions (298 K and 100 bar), already exceeding conventional compression storage under the same conditions [2]. This paper aims to discuss the synthesis methods for MOFs and further adjustments to the framework to enhance hydrogen storage performance, providing a state-of-the-art insight into advanced MOF materials in hydrogen storage and hopes to facilitate future hydrogen economy development in clean energy industries, as well as offer guidance for the next-generation MOF material designing principles for later researchers.

2. Synthesis methods of MOFs

2.1. *Hydrothermal/solvothermal synthesis*

The most commonly used synthetic method for the preparation of MOF compounds is the hydrothermal/solvent thermosynthetic method. This method can efficiently synthesize materials with a single crystal structure. The hydrothermal method is to place the aqueous solution containing the well-proportioned and weighed reactants in a reaction kettle containing a polytetrafluoroethylene lining and crystallize for a period of time at an autogenous atmospheric pressure and a given temperature. The solvothermal method mainly uses an organic solvent instead of deionized water. Due to the change in the properties of the solvent (density, viscosity, etc.) The reactants are dispersed in the solvent and become more active, the reaction occurs, and the product is formed more slowly [3]. The obtained product has good dispersibility, which helps control the dimensions of particles and final shapes. At the same time, diverse candidates of organic solvents participate in the construction of frameworks in the solvothermal process; their polarities and functional groups will induce various MOF materials with new structures. In addition, the hydrothermal/solvothermal method to synthesize MOFs is relatively simple to follow up, requiring a low level of complexity in equipment.

2.2. *Ultrasonic synthesis*

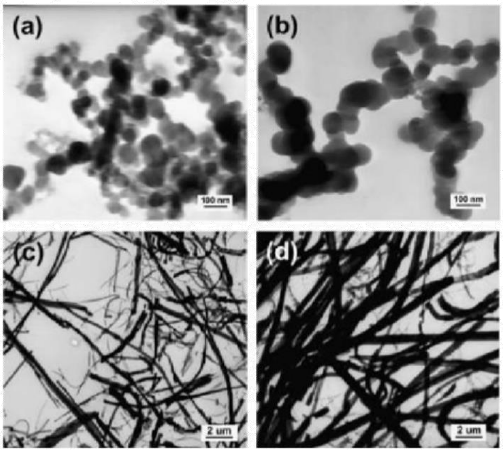
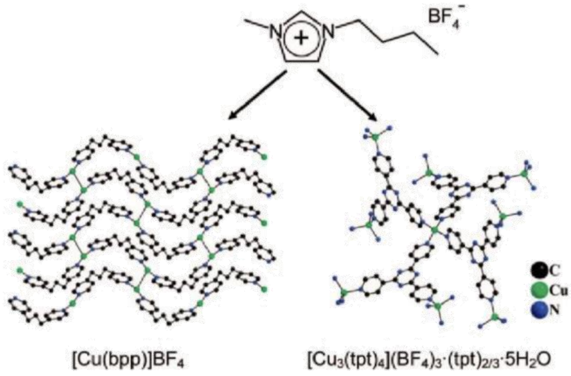


Figure 1. TEM images of Zn3(BTC)2 crystals synthesized by ultrasound at different reaction times (a)5min, (b)10min, (c)30min, (d)90 min [4].

Currently, the synthesis of organic products or nanoparticles commonly adopts the ultrasonic way, but the application of this method to MOF synthesis has been less reported. Ultrasonic synthesis, like microwave synthesis, enables the rapid synthesis of crystal samples. Under the condition of ultrasonic radiation, a local high temperature is generated inside the reaction system, and the inside of the solution is accompanied by the process of bubble formation, growth and bursting, which makes the solution very fast during heating and cooling. Ultrasonic synthesis can be performed under milder conditions. The nanocrystalline results synthesized by this method show that ultrasonic synthesis is an efficient and environmentally friendly method. It is found that with the different reaction times, the resulting size of nanoparticles lay within the range of 50 to 900 nm, and the particle size gradually enlarged with the addition of reaction time. The rod diameter reaches 700-900 nm when its reaction time is extended to 90 minutes (Figure 1) [4].

2.3. Ionothermal synthesis

The ionothermal synthesis method is to replace the solvent with an ionic liquid in the process of synthesizing MOF materials. Since the ionic liquid used in this method has a low melting point, is not volatile, and is a good solvent for various compounds, this method has attracted widespread attention as an effective method for synthesizing MOF compounds. The first time reported in the literature use ionic liquids to synthesize MOF materials is Kun Jin, Xiaoying Huang et al. using the solvent [bmim][BF_4] (bmim=1-butylene) Cu(bpp)BF_4 (bpp=(4-pyridyl)propane) material with two-dimensional structure was synthesized by using 3-methylimidazole [5]. The BF^{4-} anion introduced into the lengthened 1D polymer can function as a charge compensation, while $bmim^+$ was left in the solution. Publications by Daniel N. Dybtsev et al. also reported the application of ionic solvent [bmim][BF_4] to fabricate MOF materials with a three-dimensional structure. Figure 2 shows both structures [6].



[Cu(bpp)]BF_4 [$Cu_3(tpt)_4$]$(BF_4)_3\cdot(tpt)_{2/3}\cdot5H_2O$

Figure 2. Synthesis of 2D and 3D structured MOFs using ionic liquids[6].

2.4. Electrochemical synthesis

The electrochemical synthesis method is to put an anode with a metal plate as an electrode into an electrolytic cell containing organic ligands and a solvent under the action of a direct current voltage (sometimes, an electrolyte with strong conductivity is added to the electrolytic cell to improve the conductivity of the solvent.), MOF samples were synthesized after a period of time. Compared with other methods, electrochemical synthesis has the following advantages: 1. Frameworks can be rapidly produced under room temperature; 2. No metal salts are added to the solvent in the whole manufacturing process, so NO^{3-}, Cl^- can be eliminated along with solvent recycling; 3. Theoretically, the full utilization of organic ligands can be achieved, and the yield can be improved. Joaristi et al. synthesized various MOFs including Cu-BTC, ZIF-8, MIL-100(Al), MIL-53(Al), and NH_2-MIL-53(Al) via anodic dissolution in electrolytic cell and found that MOF yield and morphology are affected by reaction parameters such as solvent, electrolyte, voltage, current density, and temperature [7].

3. **MOFs for hydrogen storage**

3.1. MOF activation strategy

Typically, MOF is activated by either (1) thermal extraction based on experimental data or (2) displacement of guest with an easily boiling solvent during temperature rise [8]. However, when the framework is activated and then emptied by guest exchange, the replacement usually deforms the framework structure depending on the solvent applied. Especially the MOF skeleton, which forms hydrogen bonds, will undergo significant alternation in the molecular structure of the solvent [9].

Powder X-ray diffraction data should be able to detect possible conformational changes caused by the displacement of guest molecules. Once the molecules inside the frameworks exchange with the low boiling solvent, MOF activation in room temperature evacuation, heat evacuation, or supercritical CO_2 treatment will be carried out. However, there are times when the frame structure collapses during thermal tests. MOFs containing mesopores tend to lose porosity by the activation process. Usually, the selected conditions for MOF activation are relatively mild [10].

4. Modifications on MOFs to enhance hydrogen storage capacity

The specific surface area of MOFs could be an influential factor in the hydrogen uptake at cryogenic gas sorption temperature of 77K. The pore volume is generally proportional to the specific surface area. Based on experimental data and calculations from a diverse range of MOFs with high porosity, the excess hydrogen uptake at 77K under high pressure seemed to be almost directly proportional to the BET surface of the framework. The hydrogen uptake would become less correlated to the specific surface area at room temperature due to the low adsorption energy between the surface and hydrogen. As for the pressure influence on this surface area correlation, at 77 K and 1 atm, the hydrogen uptake continue to show positive relationship with surface area of 100 to 2000 m^2g^{-1}. For MOFs with larger surface areas, this correlation will diminish. It had to be speculated that the maximum area H_2 could fully cover at 1 atm is 2000 $m^2\ g^{-1}$. The BET surface area of the highly porous MOF measured under different H_2 pressures is shown in Figure 3. H_2 would show more preference for the sites with high affinity, dependent on pore size or open metal sites under low pressure [1]. To summarize, increasing specific surface area and pore volume could be a feasible method to enhance hydrogen storage by MOFs at cryogenic gas sorption temperature and high pressure, but not sufficient to improve the storage under room temperature and pressure.

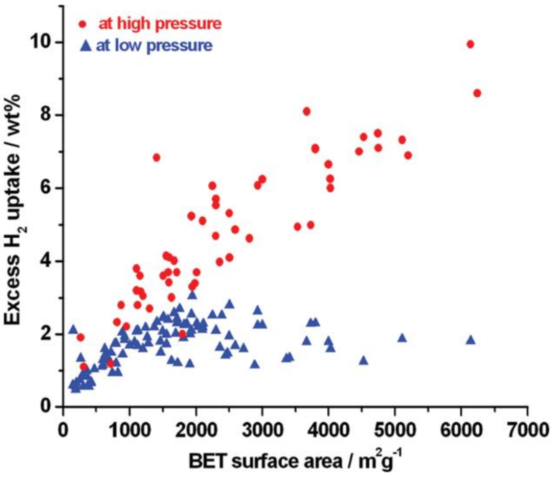


Figure 3. Excess hydrogen uptake at 77K and different pressure versus BET surface area for some highly porous MOFs [1].

The DOE has suggested a prospect for hydrogen storage of 5.5wt% at moderate temperature and pressure. However, even with super high porosity, MOFs can hardly achieve this target. The most favorable binding enthalpy for hydrogen adsorption falls within the range of 15 to 25 KJ mol^{-1}, whereas most MOFs bind with hydrogen with a low enthalpy near 5 KJ mol^{-1}. Although satisfying hydrogen adsorption could be achieved at 77K, the hydrogen storage capacity under moderate temperatures might decline to less than 1/10 of the cryogenic value due to this weak hydrogen adsorption. A positive correlation between the amount of hydrogen adsorbed and adsorption enthalpy had been demonstrated [1]. Increasing the adsorption enthalpy through enhanced interaction between the hydrogen and MOFs could be an effective method to improve hydrogen storage capacity.

4.1. Elongation of ligands

An elongated organic ligand could provide a larger pore volume and specific surface area for hydrogen to accommodate. Only certain types of framework could take a couple with ligand extension, while most

MOFs with long ligand chains might easily collapse after desorption of hydrogen or lose surface area due to interpenetration (Identical framework structures entangling physically). Suh and team members reported doubly-interpenetrated pyrite framework SNU-1 [Zn_4-O(NTB)$_2$] and SNU-77 [$Zn_4O(TCBPA)_2$].TCPBA is an elongated product from NTB by adding one benzene ring into each of the chains of tricarboxylate ligands. Both structures are stable upon heated to 400 ºC and permanently porous. SNU-77 could transform guest-free structure by rotational motion in response to heat applied or desorption of hydrogen guest molecules. This may contribute to its exceptionally high stability in storing gas molecules. The BET area for SNU-77 (3670 m^2 g^{-1}) was significantly higher than SNU-1, which is 1120 m^2 g^{-1} [1]. Publication by Schoedel et al. reported that SNU-77 had a hydrogen uptake of 9.9 wt% under 77K and 90 bar [11].

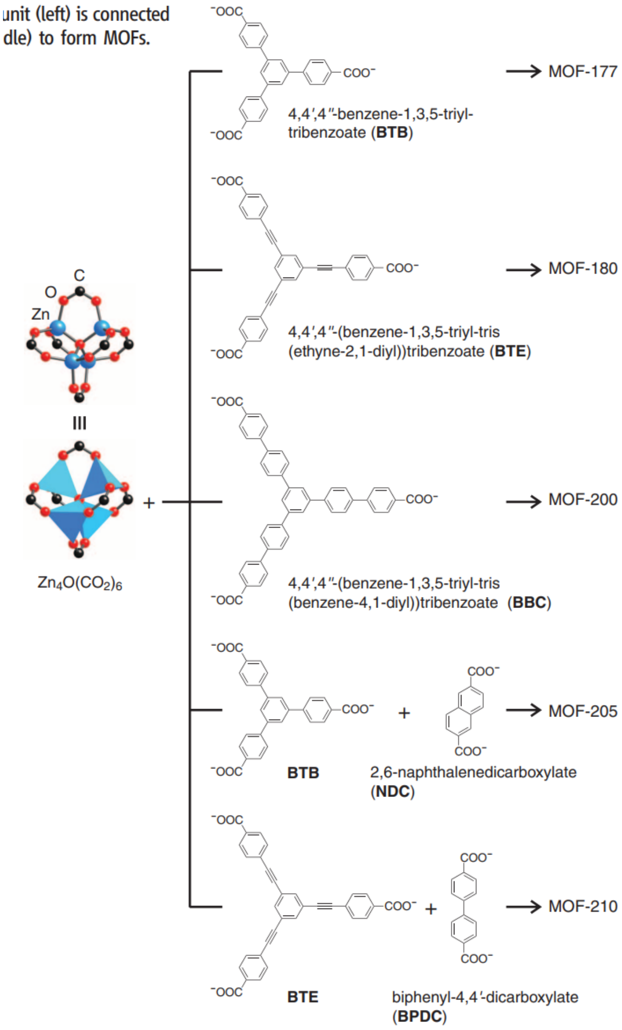


Figure 4. Reaction scheme for the MOFs with elongated ligand [12].

Several non-interpenetrating elongated frameworks built by octahedral $Zn_4O(CO_2)_6$ and ligands of tribenzoate or dibenzoate were reported by Hiroyasu Furukawa's team in 2010 [12]. MOF-177, MOF-200, MOF-205 and MOF-210 all possessed higher BET surface area and hydrogen uptake than MOF-5, which adopted terephthalic acid as ligands, attributed to the extension of organic chains by alkyne or benzyl groups (Figure 4). MOF-200 and MOF-210 have been considered some of the most powerful MOFs to store hydrogen. MOF-210 had a storage record of 176 mg/g (17.6 wt%) at 77 K and 80 bar, talented by its extremely high surface area of over 6000 m^2 g^{-1}. MOF-200 presented the highest performance for room temperature hydrogen storage (3.7 wt%) in absolute capacity at 298 K and 100 bar. However, the solvothermal synthesis for ligand elongated MOFs with ultrahigh surface area, and porosity could be energy costing. A high temperature was required to be applied for a long time (i.e., 95°C for 72 h) [13]. (Wen Ren, 2021) The practical application of these MOFs to store a large quantity of hydrogen might hardly be an economic choice relying on current preparation procedures.

4.2. Addition of interface

Graphene oxide (GO) has been employed as an oxygen-functional and highly-stable material incorporated with MOFs to enhance porosity. It could generate additional pores on the interface of GO and frameworks. From the research conducted by Liu S et al. in 2013, the incorporation of 9 wt% GO increased hydrogen storage from 2.81 wt% in pristine Cu-BTC to 3.58 wt% in Cu-BTC/GO composite under conditions of 42 bar and 77 K [14].

From Figure 5, Ren W's team divided the composite structure into 4 regions, and they revealed that most additional guest hydrogen molecules were accumulated at the interface area of Cu-BTC and graphene oxide layer [13]. The simulated accessible surface area and pore volume for the composite with interface layer were higher than the pristine framework. They also reported a slightly decreasing trend in hydrogen adsorption along with the increase in the number of GA layers, possibly induced by the layer stacking, which could cause a reduction in the surface area. A thinner layer of graphene oxide was considered a more favorable choice to maximize hydrogen uptake.

A very recent study carried out by Chengbao Liu in 2022 proved that the GO incorporation with MIL(Fe)-100 could highly improve room-temperature hydrogen storage performance as well, from 0.86 wt% in MIL-100(Fe)-M to 2.02 wt% in MIL-100(Fe)/GO-M at 298 K and 50 bar, ascribed to a considerable amount of hydrogen (41.31%) adsorbed by the interface space [2].

MIL-100 Fe shared some similar characteristics with Cu-BTC. Both of them had very economic and high-yield synthesis approaches that could be applied to large-scale production, and also a problem of low hydrogen storage capacity. The preparation scheme to generate a powerful hydrogen storage MOF/GO composite might not appear as energy-intensive as synthesizing a powerful hydrogen storage MOF directly. Converting pristine MOFs to composites could be a promising modification of a framework to design hydrogen storage applications with high capacity and low cost.

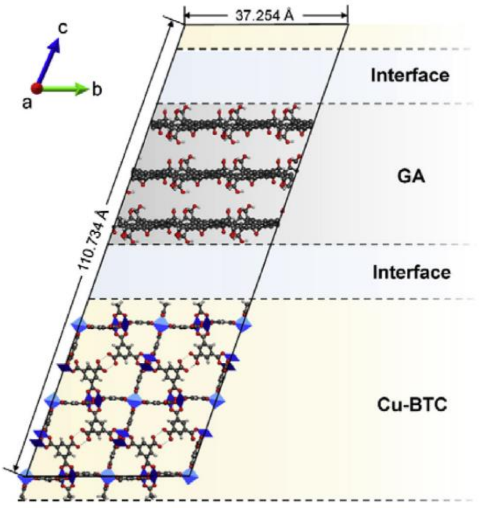


Figure 5. Four regions in the Cu-BTC/GA-3 composite [13].

4.3. Introducing metal ions

Metal ions are doped into the MOFs to make the pore surface more interactive with incoming hydrogen guests in an electrostatic or structural way. Hupp's team proved the doping impact on some zinc-based interpenetrated MOFs $Zn_2(NDC)_2(diPyNI)$ and $Zn_2(NDC)_2(diPyTz)$ by alkali metal ions including Li^+,

Na^+ and K^+. The hydrogen uptake for the doped MOFs all presented remarkable enhancement compared to the original MOFs. The average isosteric heat was proportional to the charge density of the embedded metal ions (Li>Na>K), implying the electrostatic interaction. Hupp et al. mentioned that the displacement of the interpenetrated framework by alkali ions possibly contributed to the enhanced hydrogen storage performance rather than direct access of the guest hydrogen towards the doped metal [15].

Yang et al. in 2006 reported that hydrogen storage for IRMOF-8 improved from 0.4-0.5 wt% to 1.8 wt% by mixing physically with Pt and activated carbon (Pt/AC had 1.0 wt% storage capacity) under room temperature 298 K, high pressure of 10 MPa and catalyst/MOF weight ratio of 1:9. Yang also discovered that further improvement in hydrogen adsorption to 3 wt% in IRMOF-1 and 4 wt% in IRMOF-8 could be achieved by building a sucrose carbon bridge, which enhanced the contact between MOF and doped metal particles. The hydrogen adsorption enthalpy at room temperature for modified IRMOF-8 was raised to 20-23KJ mol^{-1}, which was the highest record by the moment of this publication [16]. The smaller size of Pt nanoparticles worked better for this improvement [17].

Chengbao Liu 2021 recently discovered that lithium doping could apply to the MIL-100 (Fe) /GO composite and give rise to a dramatic improvement of 135% in hydrogen adsorption, possibly resulting from the direct interaction between Li^+ and hydrogen and the Li^+-induced dipole moment interaction within hydrogen and framework [2].

There have been plentiful applications such as MOF-177/Pt, MIL-101/Ni and MIL-100/Pd. The preparation of doped MOF was not as complex as the organic synthesis steps, generally by soaking the MOF within the organic solution of metal salts. However, the solvent molecules might continually coordinate with the doped metal ions and are hardly removed by activation, which strongly limits the metal ions' polarization effect. Introducing Sc, Ti, and V ions that would not easily bind with solvent molecules might contribute to higher efficiency in MOF metal doping [1].

4.4. Engineering of the metal sites

Metal centers unsaturated by coordination are defined as active metal sites, providing a chance for direct M-H bonding during the adsorption process. One common method to construct MOFs with active metal sites is using a building block coordinated by solvents such as SBUs, followed by thermal evacuation, which will eliminate solvent molecules and decrease the coordination number on metal sites [1].

A recent study in 2021 by David E. et al. investigated the M-H pi-back bonding of unsaturated metal sites in MOF of $V_2Cl_{2.8}$ (btdd), shown in Figure 6. The btdd had achieved hydrogen uptake of 1.64 wt% under room temperature and 100 bar, already exceeding compression storage under the same conditions. The adsorption enthalpy reached 21 KJ mol^{-1}, highly consistent with speculated most favorable range of 15-25 KJ mol^{-1}. Enhanced MOF-guest interaction in $V_2Cl_{2.8}$ was mainly contributed by M-H bonding between coordinately unsaturated vanadium (II) and hydrogen, which had been proved by neutron powder diffraction and infrared spectroscopy. Vanadium (II) was weakly pi-basic, capable of initiating pi-back bonding interaction with hydrogen. The Energy Decomposition Analysis gave specific enthalpy values for sigma-donation from H-H σ orbital (HOMO) to the empty dz^2 orbital of vanadium (19.34 KJ mol^{-1}), and pi-back bonding from partially filled d orbital of vanadium to H-H σ^* orbital (LUMO) (12.58 KJ mol^{-1}) in fully relaxed MOF [18].

To a confident extent, the active metal sites were expected to raise the enthalpy of hydrogen adsorption on MOFs. The average value of isosteric heat for MOFs with active metal sites was 7.8 KJ mol^{-1}, higher than frameworks without active metal sites (6.8 KJ mol^{-1}), calculated by Suh's team in 2012 [1]. The high enthalpy of M-H bonding facilitated the hydrogen adsorption process to be more thermodynamically favorable. In addition, reduced coordination numbers in unsaturated metal sites brought the desired effect of increasing specific surface area and pore volume. One possible enhancement was to insert a greater density of unsaturated metal sites in MOFs and design each site so that it could bind more than one hydrogen molecule.

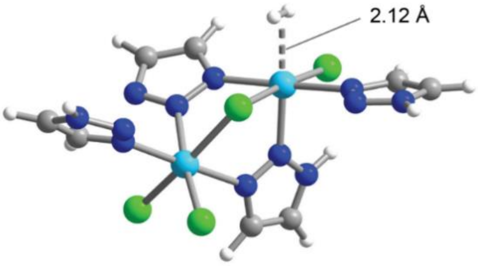


Figure 6. Structure of two vanadium clusters in MOF $V_2Cl_{2.8}$ by electronic structure calculation. Square pyramidal vanadium (II) center with hydrogen and octahedral vanadium (III), overall three triazoles, one triazolate, and four chlorides as ligands [18].

5. Conclusion

The traditional synthesis of MOFs is to heat a solvent mixed with organic ligands and metal salts for half to two days. Although this method is suitable for high-quality crystalline material production, the time-consuming reaction and low yield can be undesirable. Therefore, it is important to develop synthetic methods that can speed up the reaction and reduce the solvent, such as hydrothermal/solvothermal synthesis, ultrasonic synthesis, ionothermal synthesis, and electrochemical synthesis. The activation and methods of MOFs mainly include the guest exchange with low boiling solvent followed by thermal evacuation. As for the modifications to obtain a higher hydrogen storage capacity, strategies like elongation of ligands, metal doping, and the introduction of the interface layer, as well as open metal site engineering, have been widely adopted on versatile MOF candidates, targeting a greater pore volume, specific surface area and binding interaction. The intrinsic properties of each individual MOF, such as interpenetration, stability or solvent impact, play a more decisive role in deciding if these modifications could work as well as external temperature and pressure conditions. For future prospects, a more economical and efficient synthesis approach for MOFs that already exhibited satisfied hydrogen storage capacity might be worth investigating. A combination of different adjustments could be tested on any MOF that might show multiple enhancements in hydrogen adsorption. The DOE goal might hopefully be achieved by a specialized MOF with super high surface area, pore volume and open metal sites embedded by the interface layer and metal nanoparticles.

References

[1] Suh, M. P., Park, H. J., Prasad, T. K., & Lim, D. W. (2012) *Chemical reviews*, 112(2), 782-835.
[2] Liu, C., Shen, D., Tu, Z., & Li, S. (2022). *International Journal of Hydrogen Energy*, 47(8), 5393-5402.
[3] Choi Jonglak, Gillan Edward G. *Inorg. Chem*, 2005, 44, 7385.
[4] Khan N.A , Jhung S.H. *Coordination Chemistry Reviews*, 2015,285:11-23.
[5] Jin, K.; Huang, X.; Pang, L.; Li, J.; Appel, A.; Wherland, S. *Chem. Commun*, 2002:2872–2873
[6] Dybtsev D.N.; Chun H.; Kim K. *Chem. Commun*, 2004, 1594–1595.
[7] Martinez Joaristi, A., et al., *Crystal Growth & Design*, 2012,12(7):3489-3498.
[8] Dybtsev, D. N.; Yutkin,M. P.; Samsonenko,D. G.; Fedin, V. P.; Nuzhdin, A. L.; Bezrukov, A. A.; Bryliakov, K. P.; Talsi, E. P.; Belosludov, R. V.;Mizuseki, H.; Kawazoe, Y.; Subbotin,O. S.; Belosludov, V. R. *Chem. —Eur. J.* 2010, 16, 10348.
[9] Millange, F.; Serre, C.; Guillou, N.; Ferey, G.; Walton, R. I. *Angew. Chem., Int. Ed.* 2008, 47, 4100.
[10] Nelson, A. P.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T. J. Am. *Chem. Soc.* 2009, 131, 458.
[11] Schoedel, A., Ji, Z., & Yaghi, O. M. 2016 *Nature Energy*, 1(4), 1-13.
[12] Furukawa H, Ko N, Go YB, Aratani N, Choi SB, Choi E, Yazaydin AO, Snurr RQ, O'Keeffe M, Kim J, Yaghi OM. 2010 *Science.* Jul 23;329(5990):424-8.
[13] Ren, W., Zhuang, X., Liu, Z., & Li, S. 2021. *International Journal of Hydrogen Energy*, 46(24), 13097-13105.
[14] Liu, S., Sun, L., Xu, F., Zhang, J., Jiao, C., Li, F., ... & Schick, C. 2013. *Energy & Environmental Science*, 6(3), 818-823.
[15] Mulfort, K. L., Wilson, T. M., Wasielewski, M. R., & Hupp, J. T. 2009. *Langmuir*, 25(1), 503-

508.
[16] Li, Y., & Yang, R. T. 2006. *Journal of the American Chemical Society*, 128(3), 726-727.
[17] Wang, L., Stuckert, N. R., Chen, H., & Yang, R. T. 2011. *The Journal of Physical Chemistry C*, 115(11), 4793-4799.
[18] Jaramillo, D. E., Jiang, H. Z., Evans, H. A., Chakraborty, R., Furukawa, H., Brown, C. M., ... & Long, J. R. 2021. *Journal of the American Chemical Society*, 143(16), 6248-6256.