Hydrogen Storage and Purification with Metal-Organic Frameworks

Zeyi Zheng *

Chemistry BSc, University College London, London, United Kingdom

* Corresponding author: zeyi.zheng.22@ucl.ac.uk

Abstract. Hydrocarbons like petroleum and gasoline produce several products, such as carbon dioxide, nitrogen, and sulfur oxides that are harmful to the environment and humans when they are combined with oxygen during combustion. For the sustainable growth of people and the environment and to decrease the demand for fossil fuels, the use of renewable resources like hydrogen should be encouraged. Because it is a completely non-toxic, powerful, clean energy source and has a greater combustion range than other fuels hydrogen burns more efficiently. As the demand for hydrogen has increased, scientists have discovered many ways to store and purify it efficiently. However, current technologies and materials for storing and purifying hydrogen still have certain problems, such as low storage efficiency, harsh storage conditions (e.g., temperature and pressure limitations), high production costs for high-purity hydrogen, and many steps and low efficiency. Therefore, in recent years, MOF-based nanomaterials and membrane separation technologies with very high specific surface area and porosity have become hot research topics. This paper focuses on the advantages and disadvantages of using hydrogen as a fuel, the principles and operational steps of metal-organic framework-based nanomaterials and membrane technology used to store and purify hydrogen, and some methods to address the limitations of hydrogen storage.

Keywords: Metal-organic frameworks (MOFs), hydrogen storage, hydrogen purification, membrane technology.

1. Introduction

Resources are getting harder to get as the population rises [1]. Land degradation, water pollution, air pollution, and other environmental problems might result from the continued over-harvesting and over-use of these non-recyclable resources. Compared to these fossil fuels, because of its large specific energy, flammability, efficiency, renewability, and capacity to be created and oxidized without emitting carbon dioxide, H_2 gas is a viable fuel, but as the demand for hydrogen increases, it needs to be stored in large quantities and purified with high efficiency [2]. MOFs are advantageous resources, because of their large surface area, and changeable and customizable porous structure. MOFs are extended into one-, two- and three-dimensional frames by means of metal and linker mating, which is connected to another metal. The framework itself can be extended indefinitely in any direction by way of the initial metal cluster. This original framework can be expanded to form polymer-like structures with spaces, channels, and porous sponge materials. The porosity of MOFs is defined as the ability to maintain a porous structure without the presence of a guest molecule; this means that when the guest molecule is removed in a vacuum, the pores of the material do not collapse and are a constant presence. Hydrogen can be adsorbed on MOFs by weak van der Waals forces [3]. MOFs can also be used to synthesize nanostructured membranes, which are used as selectable barriers that allow only some molecules to pass through the framework, thus separating the impurity gases [4]. Next are the advantages and disadvantages of hydrogen compared to other fuels, i.e., the reasons for choosing hydrogen as an alternative to non-renewable sources and its limitations.

2. Advantages and Disadvantages of Hydrogen as a Fuel

First, since water vapor is the only waste that hydrogen generates, it is an entirely clean and renewable fuel. It has two atoms (H_2) in its free form, and when it burns, these two atoms mix with oxygen (O) [1]. Figure 1 illustrates how hydrogen burns more effectively due to its extremely low density relative to other fuel gases and high diffusion rate, or rate of dispersion. A very wide range of flammability is shown in Figure 2, and under ideal combustion conditions, hydrogen will take far less energy to burn than other fuels do. Hydrogen leaks, though, since H_2 gas has very small molecules with low viscosity and therefore leaks easily. Leaking hydrogen can build up and reach a combustible concentration in a small area. Also, it contains a lot of energy by weight rather than volume, which makes it difficult to store because it requires a lot of hydrogen to do so at extreme temperatures and pressures. In terms of energy density, compared to other fossil fuels, hydrogen has an energy density of about 120 Megajoules per kilogram, which is about 3 times higher. Hydrogen has a higher energy density (33.6 Kilowatt hours) than others like natural gas, which only holds on roughly 15 Kilowatt hours of useable energy per kilogram [5].

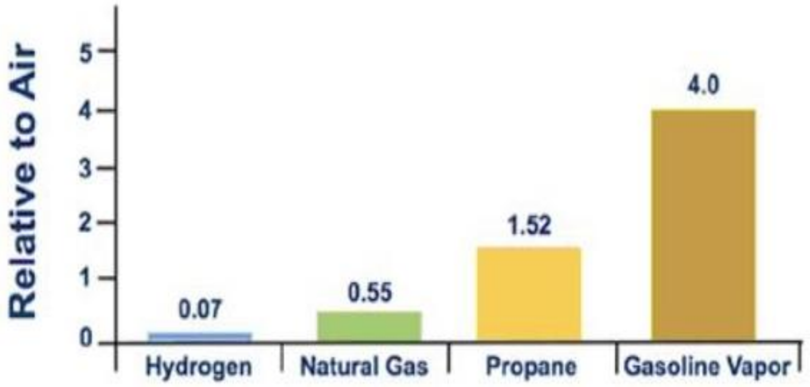

Figure 1. Relative Vapor Density [5].

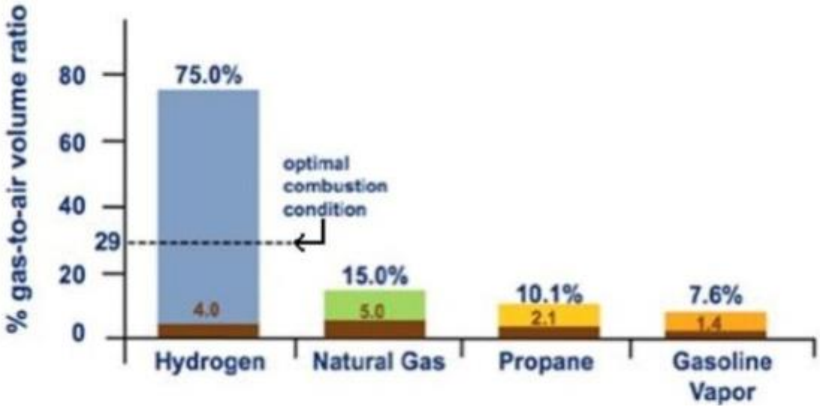

Figure 2. Flammability Range [5].

3. Hydrogen Storage with Metal-Organic Frameworks

Crystal-based porous materials known as metal-organic frameworks are frequently utilized to store H_2. These crystals must allow hydrogen to diffuse through them in order to store them. The rate of adsorption, which is a very quick process that often only takes a few seconds, is dependent on the rate of hydrogen diffusion in the MOFs and the size of the crystals, whereas its adsorption on MOFs is reliant on physisorption [6]. Physisorption materials (MOFs) interact with H_2 by the van der Waals force, a relatively weak connection. Only a few benefits include the complete reversibility of physisorption materials compared to chemisorption ones and the incredibly straightforward and rapid kinetics of adsorption/desorption. Moreover, physisorption produces less heat than chemisorption because H_2 has a lower enthalpy of adsorption, and for storing hydrogen, physisorption is regarded to be more appropriate. Inorganic metal clusters and organic linkers self-assemble to form microporous crystalline MOFs. Because of the different combinations of these core elements, the Wide-ranging characteristics of MOFs include several that are unmatched by those of other materials, including large surface area, overall pore volume, variable pore sizes, excellent tenability, and structural diversity. At 78 Kelvins and pressures up to 3.5 Megapascals, the link between pore volume and hydrogen adsorption surface area was first studied in activated carbon. It was demonstrated that the relationship between surface area and hydrogen uptake was linear. Although numerous MOFs demonstrated hydrogen uptake above the US Department of Energy's objectives, only high adsorption values were frequently seen at 78 Kelvins. For instance, MOF-19 has an exact surface area of 3100-4630 square meters per gram, a pore size value of about 2.70 cubic centimeters per gram, a hydrogen uptake of 6.18 percent by weight, and other characteristics [7]. Despite its high weight density, the adsorption at an ambient temperature of MOFs is restricted by its low interaction energy with hydrogen. For instance, MOF-5, a stable and extremely porous cubic framework is created by joining inorganic Tetrazinc Oxygen (6+) groups to an octahedral array of [O2C-C6H4-CO2] (2-) (1,4-benzene-dicarboxylate) groups (Figure 3). Because the linkers are separated from one another and open to sorbate molecules from all sides, the MOF-5 structural motif and similar compounds offer the best surfaces on which to adsorb gases [8].

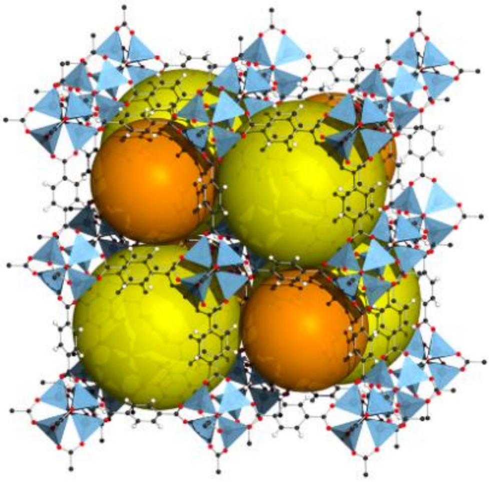

Figure 3. Crystal structure of MOF-5 [6].

4. Hydrogen Purification with Metal-Organic Frameworks

Large-scale hydrogen synthesis generates byproducts, so traditional H must be separated from these byproducts and purified. Hence, a method that is both inexpensive and energy-efficient must be developed to separate H_2 from less desirable products. Nowadays, membrane separation is a typical purifying technique, including pressure swing adsorption, vacuum swing adsorption, temperature swing adsorption, and cryogenic distillation. Due to their unique characteristics, such as limitless structural design and modular synthetic pathways for controlling their porosity and pore surface functioning, porous crystalline MOFs have emerged as a new type of molecular sieve membrane. MOFs can have changeable pore environments and pore sizes by carefully choosing the appropriate metal ions and organic linkers, which enables high efficiency of molecule separation than other conventional porous materials [9]. It has been found that membrane technology delivers continuous, low-cost, and energy-efficient high-purity hydrogen (Figure 4). It is especially useful for the separation and concentration of heat-sensitive compounds, such as antibiotics and other medications, fruit juices, enzymes, and proteins. At room temperature, there is very little loss of active components.

MOFs have evolved into molecular sieve membranes due to their limitless structural design and modular synthesis techniques that control their porosity and pore surface functioning. MOFs can have a wide range of pore sizes and pore environments, which makes the molecular separation more efficient than with other conventional porous materials. The careful selection of metal ions and organic connections is to blame for this. Due to the original flavor being preserved and the conventional physical separation technique, which uses no chemical reagents or additives and prevents product contamination, there is no phase shift and no chemical alterations. Since the molecular level separation of substances, which has excellent performance, cannot be replaced by common filter media, it also has good selectivity and is highly adaptable. The treatment scale can be large or small, continuous or intermittent, and the process is straightforward, user-friendly, and simple to automate. Because of the careful selection of metal ions and organic linkers, in contrast to other regularly used porous materials, MOFs can have a variety of pore environments and pore sizes, which enhances molecule separation. Four different types of mechanisms, the general mechanism of gas adsorptive separation by porous materials includes molecular sieving brought on by size and shape exclusion, thermodynamic equilibrium brought on by various adsorbate-surface interactions, the kinetic effect caused by variations in diffusion rates, and the quantum effect for light molecules in small micropores. In porous materials, separation is influenced by the average pore size, the kinetic diameter of particular gas molecules, and the pore's surface environment. The adsorption strength of H_2 gas is substantially lower than that of the other gases, and it should consequently have tiny micropores to let an adsorbent pass through [9].

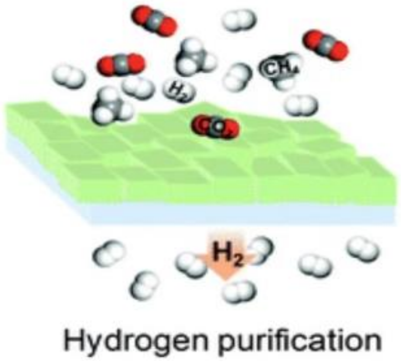

Figure 4. Hydrogen Purification [9].

5. Discussion

5.1. Disadvantages of MOFs in Hydrogen Storage

There are some limited operating conditions, that MOFs are sensitive to changes in temperature and pressure, which can affect their hydrogen storage capacity. Different MOFs' large-pressure adsorption of hydrogen capacities are shown in relation to their surface areas. Most often, the relationship between pore size and specific surface area is linear. Thus, a bigger particular surface area and a larger pore size should be produced in MOFs for boosting the adsorption of hydrogen capabilities at 78 Kelvins. Although none of the MOFs currently meet the suggested U.S. Department of Energy (DOE) threshold at room temperature, the H_2 storage capacity drops precipitously with temperature. The MOFs are physisorption-based materials for storing hydrogen, and they have very weak interactions with hydrogen molecules. The Quantitative sensory test in porous MOFs ranges from 59 kilojoules per mol. For improving the H_2 storage performance to room temperature, the heat of hydrogen adsorption in the MOFs needs to be greatly enhanced. Effective room temperature storage and release require an average heat of H_2 uptake of approximately 15 kilojoules per mol [10]. Its use in actual contexts is constrained by the fact that they are often only stable across a small range of operating conditions. The adsorption and desorption kinetics of MOFs are also slow. The rate at which hydrogen can be stored or released may be constrained by the lengthy process of hydrogen adsorption onto MOFs and subsequent hydrogen desorption. In applications where quick response times are necessary, this can be a serious restriction. Moreover, MOFs can be expensive to create, which might be a drawback in situations where the price is a crucial consideration.

5.2. Solutions to Improve the Capacity of Hydrogen Storage.

5.2.1. Elongation of Ligands

MOFs can be extended indefinitely in either direction, as was noted in the introduction. The long organic ligands used to create MOFs have a tendency to collapse when the guest molecules are removed. A structure with a reduced surface area or even one that is nonporous is commonly produced by the longer ligands interpenetrating the framework. Yet, numerous studies have shown that using extended ligands can increase the surface area with a particular framework topology. Using [Zn_4O $(CO_2)_6$] octahedral secondary building units and tri-carboxylates, [$Zn_4O(NTB)_2$] (SNU-1)94 and [$Zn_4O(TCBPA)_2$] (SNU-77) were created [10]. NTB was used in the former and TCPBA in the latter. Tris (40-carboxy biphenyl) amine, an extended version of NTB, is referred to as TCBPA. Both frameworks display single-crystal to single-crystal transformations, mostly rotating motions in response to the removal of the guest molecules, high permanent porosity, great heat stability (up to about 400 degrees Celsius), and guest-dependent luminescence. SNU-77 has a substantially greater Langmuir surface area (about 4180 square meters per gram) than SNU-1 (about 1120 square meters per gram).

MOF-177 and MOF-200, two Zn_4O-based MOFs, are non-interpenetrating qom networks. BBC created MOF-200, an extended version of BTB used in the synthesis of MOF177. According to studies on N_2 gas sorption, MOF-200 has extremely high surface areas, measuring 10 400 square meters per gram (Langmuir) and 4520 square meters per gram (BET area), while MOF-177 has surface areas measuring about 5640 square meters per gram (Langmuir) and 4750 square meters per gram (BET area) [10].

The pore diameter along the caxis was shown to drastically increase with ligand elongation, going from 10.0 in NOTT-100 to 32.0 in NOTT-102. The shortest ligand-derived framework the NOTT-100 has the smallest pore size and BET surface area. NOTT-102, which has the longest ligand, produced the largest pore volume and BET surface area. There have also been reports of reticular series topologies with hex carboxylate ligands. These MOFs feature metalorganic polyhedral ligands having C3 symmetry and three coplanar is phthalate moieties. The supercritical CO2 drying procedure used to create activated NU-100 results in a material with an ultra-high high BET surface area of roughly 6143 square meters per gram and a pore size of about 2.8 cubic centimeters per gram. At 56 bar, NU-100's excess H_2 uptake was about 100 square meters per gram, and at 70 bar and 77 Kelvins, it was 164 square meters per gram. Compared to other MOFs that have been published so far, these values have the largest surplus and are second only to MOF-210 in terms of overall H_2 uptake. The development of a unique 3,24-connected network, which significantly lowers the opening of pores and precludes network interpenetration, accounts for the stability of such MOFs from extended hexatonic ligands. This strategy successfully increases the surface area of the MOFs without compromising their stability [10].

5.2.2. Catenation and Interpenetration

Because it is improbable that hydrogen molecules will not experience any attractive forces from the pore walls when they are extremely close to the center of the pore, MOFs with big pores are not suitable for storing hydrogen. As a result, these frameworks are unable to absorb significant amounts of hydrogen. A substance will store hydrogen more effectively if it has a large volume of micropores and little porosity. Despite the fact that the volume of hydrogen that has been adsorbed grows, the material's substantial surface area remains unaffected. The number of large voids should be able to be decreased by interpenetrating the framework. Catenation's interpenetration phase causes a maximum displacement between the catenated frames. Another form of catenation called interweaving involves very little movement between the catenated frames. In one case, the H2 storage performance of the identical framework's catenated and non-catenated versions was directly compared. At 1 bar and 77 Kelvins, the catenated form of Cu3TATB-2 (TATB -3) = 4,40,400-s-triazine-2,4,6-triyltribenzoate) was found to adsorb 1.9 percentage by weight of H2, this represents an improvement of around 0.6 percent by weight over the compounds' uncatenated version. In experiments, the catenation enhances the thermal stability of the material.

6. Conclusion

In conclusion, this paper focuses on the advantages and disadvantages of hydrogen as a fuel and storage, as well as the principles, limitations, and some solutions for storing and purifying hydrogen in metal-organic frameworks. Hydrogen has been chosen as a fuel because of the negative environmental and human impact of the extraction and combustion of non-renewable fuels. However, the increased demand for hydrogen has raised the question of how to store it more cost-effectively and efficiently, and it is hoped that in the future it will be possible to store and purify hydrogen even at room temperature and high pressure.

References

[1] www.pirelli.com. (2022). Hydrogen as a fuel: the pros and cons. [online] Available at: https://www.pirelli.com/global/en-ww/road/hydrogen-as-a-fuel-the-pros-and-cons.

[2] Denchak, 2022 M. (2022). Fossil Fuels: The Dirty Facts. [online] NRDC. Available at: https://www.nrdc.org/stories/fossil-fuels-dirty-facts#:~:text=Disadvantages%20of%20Fossil%20Fuels%201%20Land%20degradation%20Unearthing%2C.

[3] Archana, K., Asif, A., Jose, D. and Sujith, R. Metal-Organic Framework-Based Nanomaterials for Energy Conversion and Storage. Micro and Nano Technologies. 2022, 589 - 607.

[4] A review on current trends in potential use of metal-organic framework for hydrogen storage. international Journal of Hydrogen Energy, 2021, 46 (21), pp.11782 – 11803.

[5] H2tools.org. (2016). Hydrogen Compared with Other Fuels | Hydrogen Tools. [online] Available at: https://h2tools.org/bestpractices/hydrogen-compared-other-fuels.

[6] Rivard, E., Trudeau, M. and Zaghib, K. Hydrogen Storage for Mobility: A Review. Materials, 2019, 12 (12), p.1973.

[7] Sun, Y., Wang, L., Amer, W.A. et al. Hydrogen Storage in Metal-Organic Frameworks. Journal of Inorganic and Organometallic Polymers and Materials, 2012, 23 (2), pp.270 – 285.

[8] Rosi, N.L. Hydrogen Storage in Microporous Metal-Organic Frameworks. Science, 2003, 300 (5622), pp.1127 – 1129.

[9] Lim, D.-W., Ha, J., Oruganti, Y. Purification and separation of hydrogen using MOF-based materials. Materials Chemistry Frontiers, 2021, 5 (11), pp.4022 – 4041.

[10] Langmi H W, Ren J, North B, et al. Hydrogen storage in metal-organic frameworks: a review[J]. Electrochemical Acta, 2014, 128: 368 - 392.