Metal organic framework for hydrogen storage

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Abstract. Hydrogen is considered to be a clean energy alternative to non-renewable fossil fuels. Hydrogen storage using metal-organic frameworks (MOFs) has received more attention in recent years. Their higher pore volume, high density of interaction sites, and a wide variety of structures contribute to their greater versatility. MOFs for hydrogen storage was discussed in this article, including their mechanism, preparation, and factors. In this study, several conventional and distinct methods for the synthesis of MOFs were demonstrated in detail, including slow diffusion, hydrothermal (solvothermal), electrochemical, mechanochemical, and microwave-assisted methods. In addition, hydrogen can be adsorbed by physical and chemical adsorption. In particular, physical sorption is facilitated by relatively low heat and pressure by van der Waal's force. To increase the uptake of hydrogen storage, strategies to improve MOFs by altering pore structure and isosteric heat were addressed. The article discusses how MOFs have the potential to meet DOE targets for hydrogen storage and explains why that is so through examples and comparisons.

Keywords: Hydrogen storage, metal-organic frameworks, preparation.

1. Introduction

Nowadays, the environmental problems that carbon fuels bring are increasing dramatically and we are eager to find new sustainable fuels. Hydrogen has the highest specific energy of any fuel, making it the most promising candidate for the replacement of the current carbon-based energy sources. On a weight basis, hydrogen contains almost three times the energy content of gasoline. However, the volumetric energy density is very low unless being compressed, so it requires energy-intensive compression and liquefaction in the process of hydrogen translation and storage. Therefore, the research of materials for hydrogen storage becomes an active area. However, none of the materials like tanks, valves, regulators, piping or mounting brackets have achieved the expected target. Among the various porous materials, MOF is popular due to its high specific surface area and its versatile structures in chemistry. MOF consists of metal ions connected with organic ligands, there are a lot of micropores being created so that the hydrogen gas can attach to it. A remarkable number of MOFs have been reported ranging from small surface area and low uptake capacities to the big surface area with large uptake capacities [1]. In general, the porosity of MOFs is higher than that of any porous carbon. MOF-5, for example, has 60% open space, so organic molecules, and gases can be introduced inside it for storage. Unlike other porous materials, MOFs have pores without walls as they just contain struts and intersections. Therefore, the surface area of MOFs is much higher, taking MOF-5 as an example again, its surface area can be achieved to 3800 m^2/g. Several researches have been made on the hydrogen adsorption with MOFs from different parts to use it further in the future with many experiments. A study of MOFs with fluorine atoms shows fluorination enhances the adsorption of hydrogen by physisorption [2]. And it can adsorb hydrogen of 1.2 bar at 77K [3].

This review mainly introduces the preparation, mechanism and factors which affect the adsorption energy of MOFs in hydrogen adsorption.

2. Preparations of MOFs

Since MOF is consist of metal and organic blocks, creating a 3D crystalline structure that can absorb various organic elements. MOFs can self-assemble through a mixture of building blocks and can achieve highly complex sponge-like structures. Several conventional and distinct synthesis methods include slow diffusion, hydrothermal (solvothermal), electrochemical, mechanochemical, and microwave-assisted.

2.1. Slow diffusion or evaporations method

Slow diffusion or evaporations can be done at room temperature and do not need extra heating. The solution and reagents are mixed and allowed to slowly evaporate, then letting the crystals form when critical concentration is achieved [4]. These can create single-crystal metal-organic frameworks. The benefits are that the method is rapid, efficient, scalable, and environmentally friendly. One can easily control the MOFs' size, dispersity, and morphology. One example of a slow diffusion MOF is MOF-5 and IRMOF-6, which Li et al. have shown to prepare through the diffusion of $Zn(NO_3)_2$ and H_2BDC in DMF/chlorobenzene. Hydrogen peroxide can be added to assist in forming binding to SBU. They have single-crystal ray structures and large BET surface area and high chemical stability [5].

2.2. Solvothermal or hydrothermal method

Solvothermal or hydrothermal reactions are made in an airtight container in autogenous pressure above the boiling point of the solvent [4]. Most MOFs are synthesized using this method. The temperature of the reactions can be raised to adjust bond formation; the temperature also affects the morphology of the crystals. This synthesis method can create a framework containing large rectangular channels and uncommon metal coordination. Orefuwa et al. found that IRMOF-8 crystals can be synthesized at 120 and 155 ^oC, with pore volumes of 0.603 cm^3/g STP and 0.693 cm^3/g STP. This method allows for a greater surface area [6].

2.3. Electrochemical method

Electrochemical is used for powders in industrial settings. The metal ion is made from anodic dissolution into reaction mixtures that contain the organic ligands and electrolytes. There is an advantage of this method is under mild conditions and slight temperature reaction. MOFs crystals can be synthesized continuously and in huge quantities using it. Examples include microcrystalline powders and films. Examples include HKUST-1 or Cu-MOF, which can be done through anodic electrosynthesis by applying oxidation potential and releasing Cu^{2+} ions in a solution with a BTC linker. The average size of the crystals is 0.5-5 μm and the surface area is 1820 $m^2\ g^{-1}$. Cu-metal organic frameworks have important uses in electrochemical hydrogen evolution reactions [7].

2.4. Mechanochemical method

The mechanochemical method uses mechanical forces instead of a solvent. It manually grinds the reagents and mixes them in automatic ball mills. Mechanical breaking of intramolecular bonds allows for the construction of new bonds. Coordination polymers can be formed in one to three dimensions by adding a small amount of solvent to the solid mixture. The benefits are the avoidance of organic solvents and minimal adverse effects. It also allows mass transfer, reduction of particle size, heat, and local melting. This accelerates the reaction time and is environmentally friendly. MOF-74 is synthesized through the mechanochemical method, using ZnO and 2,5- dihydroxyterephthalic acid (H4HDTA) with DMF as a solution. They have a high-density open metal sieve and high porosity for hydrogen capture [8].

2.5. Microwave-assisted method

Microwave-assisted methods can be used for making organic and nanoporous inorganic materials, such as metal clusters. Electromagnetic energy is converted to thermal energy, causing alignment

collisions between molecules and heating the sample. The process is high yielding with a short reaction time and low cost. It is very energy efficient and the power output, pressure, and temperature are adjustable. The microwave facilitates the molecule motions and leads to the formation of crystals with controlled shape and size by adjusting concentration and temperature. Microwave-assisted MOFs used for hydrogen storage include zirconium-based MOFs. This produces a highly crystalline octahedral-shaped crystal with comparable Zr-MOFs made with conventional methods. This type of MOF has high chemical and thermal stability and can be applied to catalysis, gas storage, and sensing molecules [9].

3. Mechanism of MOFs in hydrogen storage

MOFs can adsorb another component and allow adsorbate to be adsorbed in. These apply attraction forces like van der Waal's force, electrostatic force and hydrogen bonding. These forces can be included in physical adsorption and chemical adsorption. Physical adsorption often occurs at low temperatures. This includes van der Waal's interaction and electrostatic attraction. While chemical adsorption includes hydrogen bonding often occurs at high temperatures [10].

3.1. Van der Waal's interaction

Van der Waals' force is any dipole-dipole force inside molecules. This includes the weakest intermolecular force instantaneous dipole-induced dipole which occurs when very low electronegativity difference between atoms in covalent bonds. If it is polar, a permanent dipole exists and the strongest permanent dipole is a hydrogen bond that forms by H-F, H-Cl and H-O. This is the origin of the adsorption of hydrogen in MOFs. The higher the van der Waals force, the higher the adsorption energy and amount. From an experiment that commonly used IR spectroscopy shift to investigate the adsorption energy in different sites [11]. Inside hydrogen, it doesn't have a dipole. And the main origin of the force comes from polarization. Thus, the sites are important. Different adsorption sites are important to polarize hydrogen which is the main force between hydrogen and adsorption sites. For example, in the BDC-based Mg-MOF-74-25H_2 system, the positive charge in magnesium polarizes the hydrogen and the induced-dipole force helps the hydrogen adsorbed into the sites [2]. And the amount of adsorption reaches 1763 m^2g^{-1}which is quite large [2]. Since the force mainly comes from polarization, the adsorption is affected by the charge distribution and this affects binding strength at different sites. An experiment [2] indicates that the binding strength for MOF with aromatic ring linkers will be higher than without them and that more sites give higher adsorption due to the presence of more charge. The extra BDC linker contributes a 1.5 kJ mol-1increase in the binding strength. For higher charge density, open metal sites such as those of Mg^{2+} facilitate adsorption [2].

3.2. Electrostatic force

The electrostatic force is a repulsive or attractive force between particles caused by an electric charge. In the presence of giant electronegativity or non-neutral ionic bonds, electrostatic attraction occurs [10]. Some experiments demonstrated that the carbonyl group contributes more to electrostatic attraction. ZIF-90 with carbonyl group, for example, shows a marked decline in adsorption without electrostatic force [10]. The corrected diffusivity falls from 6.52×10^{-7} to 3.05×10^{-5} which decreases a lot. The same as the van der Waals force, the higher the electrostatic force, the higher the adsorption amount.

4. Factors of MOF used in H_2 storage

4.1. Surface area

Adsorption sites are identified through their surface area. Adsorbate molecules of the gas phase take up more free space when the surface area is larger. As shown in Fig.1, the MOF-177 with the

greatest volumetric surface area has a volumetric surface area of 19.6 weight percent at 77 K and 2.0-2.5 MPa. [13] Based on all the measurements, the gradient of 1.9×10^{-2} mg m^{-2} is relatively constant through the origin, indicating that the greater the surface area, the greater the hydrogen storage capacity [14].

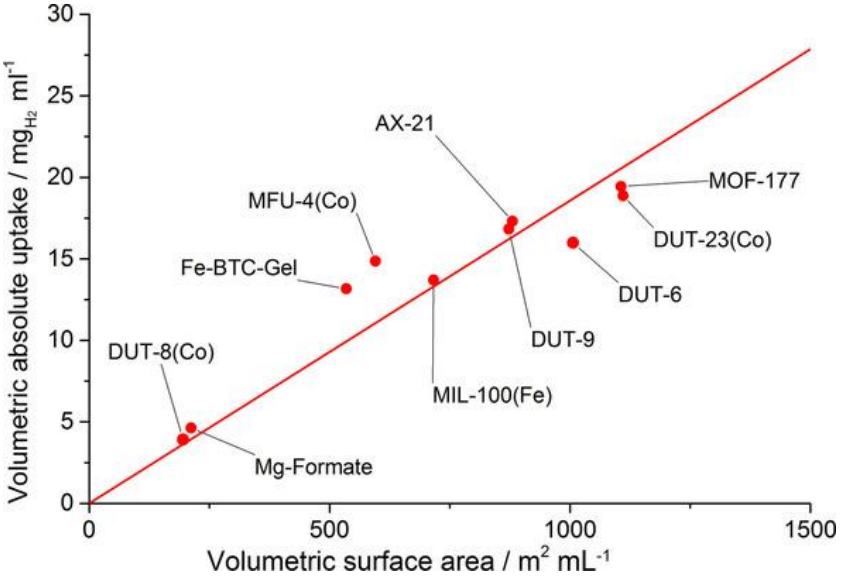


Figure1. The relationship between volumetric surface area and volumetric absolute uptake [12].

The rht-MOF-7, NU-125, and NOTT-112 are Cu (II)-based MOFs with rht structures, however, because of different linker lengths, their cage sizes are different, as shown in Table 1, which results in different BET areas and hydrogen uptake capacities. During the transition from NOTT-112 to rht-MOF-7, the absolute gravimetric delivery capacity increased from 4.7wt% to 9.1wt%. A linear relationship exists at 77 K as well as 100 bar between greater pore volume, area of BET, and greater H_2 gravimetric deliverable capacity. Exceptions do exist. In the following passage, we will discuss how to improve your surface area [15].

Table 1. The pore size, BET area and gravimetric capacity of three MOFs (rht-MOF-7, NU-125 and NOTT-112) in hydrogen uptake [15].

MOFs	rht-MOF-7	NU-125	NOTT-112
cage size	8.1, 10.3, 16.6 Å	11,15,16,24	13, 13.9, 20 Å
BET area m^2/g	1950	3230	3440
gravimetric capacity wt%	4.7	8.5	9.1

4.1.1. Mixed ligands

An organo-ligand framework is defined as one that contains two organic ligands or one that can be built from a ligand with two functionally distinct groups [16]. Matzger and co-workers have demonstrated that they can develop high porous MOFs by using mixed ligands. As part of UMCM-1, which is $[Zn_4O(BDC)(BTB)_{4/3}]$ octahedral SBUs are connected to BTBs and BDCs. When BDC was changed to thieno[3, 2-b] thiophene-2,5-dicarboxylate (T2DC) instead, the framework with a different topology, UMCM-2 is formed, $\{[Zn_4O(T2DC)\ (BTB)_{4/3}]\}$. At 77 K as well as 46 bars, it shows higher hydrogen uptake (excess 68.8mg g^{-1}). The crowded pore environment of the MOFs causes the channel size to change. This makes it easier for them to uptake hydrogen at low pressure since they have the highest hydrogen affinity [15].

4.1.2. Catenation and interpenetration

The catenation occurs when two or more identical frameworks are entangled physically These interconnected pores have a bimodal distribution of pore sizes, consisting of both microscopic and large pores. Therefore, the volumetric surface area increases, and the density increases. Rafael Balderas-Xicohténcat and his co-worker developed the CFA-7 network, a first-of-its-kind interpenetrated one in MFU-4's family. In Fig. 2, we see the secondary building units of MFU-4. The MFU-4 structure is cubic, and the CFA-7 has a reduced free volume due to hydrogen in the wall material of the large pores. The results are shown in Fig.2c, showing that CFA-7 with a lower specific surface area has double the volumetric storage capacity of MFU-4. A study shows that interpenetrating porous materials can increase their volumetric capacity [16].

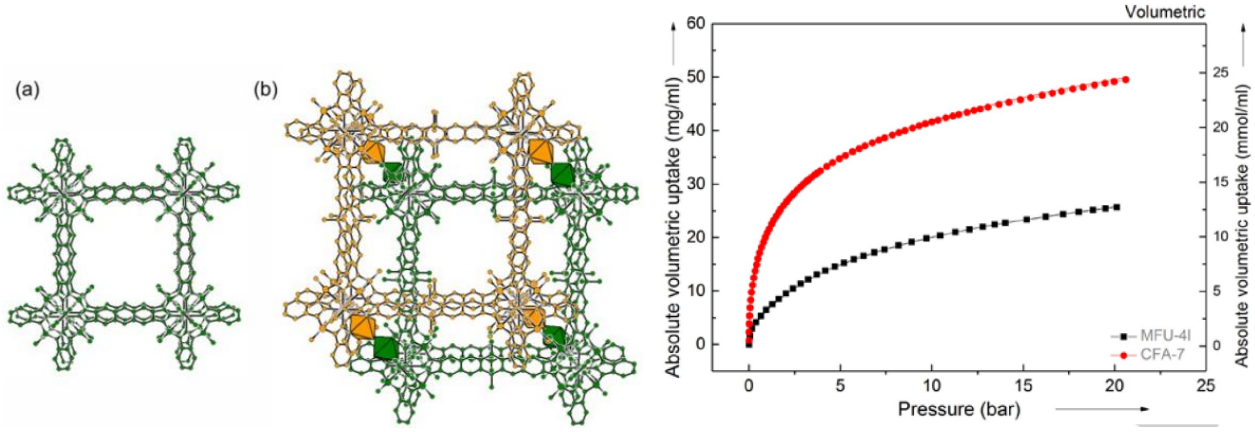


Figure 2. (a) the structure of MFU-4 (b) the structure of CFA-7 (c) absolute volumetric hydrogen isotherm of two MOFs (MFU-4 and CFA-7) [16].

4.1.3. Elongation of ligands

Elongation of ligands is defined as adding more extended organic ligands to MOFs. An elongated ligand can increase surface area and make MOFs more stable. According to Yaghi and coauthors [15], there are several Zn_4O-based MOFs that are noninterpenetrating qom networks (Fig.3). MOF-200 is structurally similar to BBC, which is an elongated version of BTB used to synthesize MOF-177.

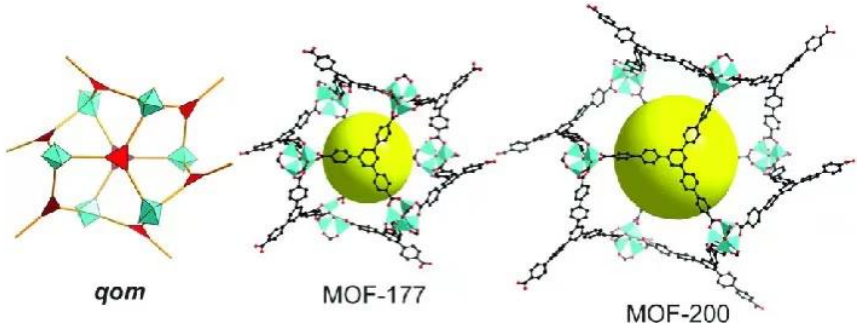


Figure 3. The structure of qom network, MOF-177 and MOF-200 [17].

As shown in Table 2, MOF-200 displays more surface area, leading to wider pores, so hydrogen uptake increases significantly [15].

Table 2. The comparison of surface area, pore volume and hydrogen storage capacity of MOF-177 and MOF-200 [15].

MOFs	MOF-177	MOF-200
Surface area (Langmuir)/m^2g^{-1}	5640	10400
Surface area (BET)/m^2g^{-1}	4750	4520
gravimetric capacity wt%	1.59	3.59

4.2. Isosteric heat

Adsorption isosteric heat is defined as the differential heat of adsorption at a given pressure and temperature [1]. As indicated by several results, the strength of the interactions between the adsorbent and adsorbate is also indicated. Even though hydrogen uptake capacities greatly depend on the pore volume of the material at high pressures, high isosteric heat greatly increases hydrogen uptake. The theoretical calculation study, for example, describes the effect of isosteric heat of adsorption based on the average value, instead of under low coverage by hydrogen molecules. Based on Bae and Snurr's research in 2012, using GCMC simulations to research hydrogen storage and delivery. They used MOFs from 1.5 to 120 bar, their optimal isosteric heat value is about 20 kJ per mole. However, the majority of MOF materials hold the range of isosteric heat capacities of 5 to 9 kJ per mole [1]. Several aspects can be improved to increase the isosteric heat.

4.2.1. Unsaturated metal site creation

Unsaturated metal sites are generated due to the existence of small solvent molecules such as dimethylformamide (DMF), water and ethanol. By heating or vacuum treatment, these small solvent molecules can be discarded and the unsaturated metal sites are revealed. In addition, in the heating process, the pore volume, and surface area are also increasing, while decreasing the material density [18]. MOF with open metal site mostly provides considerable hydrogen storage capacities, since the strong interaction occurs between the open metal site and hydrogen molecules which increases the isosteric heat of hydrogen adsorption. However, this high isosteric heat which dissociates metal hydrogen bond well is not favorable in hydrogen loading for fuel cells. The solution is to utilize open metal sites with low density. Usually, the high density of open metal sites contributes to the strong interaction forces and increases the isosteric heat, however, under the condition of extremely low temperature, weaker interaction positions are more important. These positions employ simply Van der Waals interactions or more specifically induced dipole interactions with hydrogen. According to the experiment result, for example, MOF-74-Mg has the open metal site with the highest density value of 8.3mmol/g, but 1.7wt% of hydrogen uptake capacity [19]. In contrast to the former result, MOFs with much lower density can adsorb 6~10wt% of hydrogen gas at 77 K and 100 bar [19].

4.2.2. Metal ions and ligands functionalization

These transition metals catalyst the adsorption reaction and stimulate the spreading of the hydrogen gases. The principle of this function is referred to as the spillover effect. The spillover effect demonstrates the process that which the metal ions and ligands attract the hydrogen molecules and spread them in the materials to help in adsorption.

Hydrogen gas is hard to adhere to the wall of the adsorbent by a simple physical reaction. However, the transition metals and ligands can adsorb the hydrogen gas easily because of the electron-withdrawing ability and then dissociate the hydrogen molecules into hydrogen atoms. The hydrogen atoms spill over to the surface of the materials and attach to it which largely increases the adsorption yield.

According to the research [20], they studied the correlation between metal ions, organic linker and hydrogen adsorption capacity by spillover, using MOFs of MILs and IRMOFs which have the similar surface area and chemical formula units. The result shows that when the adsorption isotherms are measured under the condition at 298K and up to 7.3 MPa, the hydrogen storage capacity of 0.55wt% was obtained on the IRMOF-1(i.e.MOF-5), this shows an improvement contributor of 1.96 in comparison with the parent IRMOF-1.

4.2.3. Pore Size

An easy way to determine the relationship between the hydrogen gas capacities and the surface area is to determine hydrogen adsorption by a physical reaction. High hydrogen adsorption capacities can be achieved by increasing the surface area and pore volume, these two factors are related to the pore size. In addition to increasing the surface area, large pores also reduce interaction forces and isosteric heat. By overlapping the potential adsorption sites on the walls, the adsorbent can enhance

its interactions with hydrogen gas molecules. In the porous materials where physisorption and weak van der Waals forces are dominant, the storage density is largely due to the size of the pores. As the distance gets smaller (which indicates the pore size), the stronger the negative forces between the adsorbate and adsorbent, so the repulsion forces are increasing due to the smaller distance.

5. Conclusions

Hydrogen adsorption using MOFs has been investigated a lot these years due to hydrogen can be a suitable fuel and less pollution. MOFs are a safe and efficient system for hydrogen storage and receive great attention from the scientific community as they can have various uses in the H_2 fuel cell, including electric cars. In this article, preparation, mechanism and factors that affect the adsorption of MOFs in hydrogen storage were mainly reviewed. MOFs can be synthesized by slow diffusion, hydrothermal, electrochemical, etc. These materials have been worked for hydrogen storage by either chemical or physical adsorption mechanisms including Van der Waal's attraction and Electrostatic attraction. To provide a higher volume to increase hydrogen uptake, adjusting surface area and isosteric heat can be implemented. To be specific, elongation, catenation, and mixed ligands can alter the surface area to increase hydrogen uptake. In terms of isosteric heat, unsaturated metal sites, metal ions and pore size also contribute to the high hydrogen uptake capacity. However, these are various concerns that should be apprehended in hydrogen storage MOFs. MOFs can be sensitive to air moisture and can degrade in the presence of water. Performance is also affected by structured defects: a collapsed framework can block pore storage. To make it more applicable, industries put their concern on how to make it stable even under extreme conditions.

References

[1] Myunghyun Paik Suh, Hye Jeong Park, Thazhe Kootteri Prasad, Dae-Woon Lim, Hydrogen storage in metal-organic framework, Chem. Rev. 112 (2012) 782 - 835.

[2] Trang Nguyen-Thuy, Phong Le-Hoang, Nam Hoang Vu, Thong Nguyen-Minh Le, Tan Le Hoang Doan, Jer-Lai Kuo, Toan T. Nguyen, Thang Bach Pha and Duc Nguyen-Manh.Hydrogen adsorption mechanism of MOF-74 metal-organic frameworks: an insight from first principles calculations. The Royal Society of Chemistry. 10 (2020) 43940 - 43949.

[3] Da-Shuai Zhang, Ze Chang, Yi-Fan Li, Zhong-Yi Jiang, Zhi-Hong Xuan, Ying-Hui Zhang, Jian-Rong Li, Qiang Chen, Tong-Liang Hu & Xian-He Bu.Fluorous Metal-Organic Frameworks with Enhanced Stability and High H2/CO2 Storage Capacities.Scientific Reports. 3 (2013) 3312 - 3319.

[4] Raptopoulou, Catherine P. Metal-organic frameworks: Synthetic methods and potential applications. Materials 14, (2021) 310.

[5] Li H., Eddaoudi M., O'Keeffe M., Yaghi O.M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. Nature .402 (1999)276 - 279.

[6] Orefuwa, Samuel A., Hongwei Yang, and Andrew J. Goudy. Rapid solvothermal synthesis of an isoreticular metal–organic framework with permanent porosity for hydrogen storage. Microporous and mesoporous materials 153 (2012) 88 - 93.

[7] Varsha, M. V., and Gomathi Nageswaran. Direct Electrochemical Synthesis of Metal Organic Frameworks. Journal of The Electrochemical Society 167, 15 (2020) 155527.

[8] Beamish-Cook, Jethro, Kenneth Shankland, Claire A. Murray, and Paz Vaqueiro. Insights into the Mechanochemical Synthesis of MOF-74. Crystal Growth & Design 21, 5 (2021) 3047 - 3055.

[9] Ren, Jianwei, Tshiamo Segakweng, Henrietta W. Langmi, Nicholas M. Musyoka, Brian C. North, Mkhulu Mathe, and Dmitri Bessarabov. Microwave-assisted modulated synthesis of zirconium-based metal–organic framework (Zr-MOF) for hydrogen storage applications. International journal of materials research 105, (2014) 516 - 519.

[10] Ilknur Erucar, Thomas A. Manz & Seda Keskin. Effects of electrostatic interactions on gas adsorption and permeability of MOF membranes, Molecular Simulation.Taylor & Francis 40. (2014) 557 - 570.

[11] Sebastian Zuluaga1, Pieremanuele Canepa, Kui Tan, Yves J Chabal and Timo Thonhauser. Study of van der Waals bonding and interactions in metal organic framework materials. J. Phys. 26 (2014) 1 - 11.

[12] R. Balderas-XicohtØncatl, Maurice Schlichtenmayer, Michael Hirscher. Volumetric Hydrogen Storage Capacity in Metal-Organic Frameworks, Energy Technology, 6 (3) (2018) 578 - 582.

[13] Dipendu Saha, Shuguang Deng, Hydrogen Adsorption on Metal-Organic Framework MOF-177 tsinghua Science and Technology 15 (4) (2010) 363 - 376.

[14] Jacob Goldsmith, Antek G. Wong-Foy, Michael J Cafarella, and Donald J. Siegel, Theoretical Limits of Hydrogen Storage in Metal-Organic Frameworks: Opportunities and Trade-Offs, Chem. Mater, 25 (16) (2013) 3373 - 3382.

[15] Myunghyun Paik Suh, Hye Jeong Park, Thazhe Kootteri Prasad, and Dae-Woon Lim Hydrogen Storage in MetalOrganic Frameworks, Chem. Rev. 56 (10) (2012) 809 - 812.

[16] Rafael Balderas-Xicohténcatl, Phillip Schmieder, Dmytro Denysenko, Dirk Volkmer, and Michael Hirscher High volumetric hydrogen storage capacity by interpenetrated metal-organic frameworks, Energy Technol. 6 (3). (2018) 441 - 441.

[17] Weigang Lu, Zhangwen Wei, Zhi-Yuan Gu, Tian-Fu Liu, Jinhee Park, Jihye Park, Jian Tian, Muwei Zhang, Qiang Zhang, T. Gentle, Mathieu Bosch, Hong-Cai Zhou. Tuning the structure and function of metal-organic frameworks via linker design, Chem Society Review, 43 (16), (2014) 5561 - 5593.

[18] Yubiao Sun, Li Wang, Wael A. Amer, Haojie Yu, Jing Ji, Liang Huang, Jie Shan, Rongbai Tong, Hydrogen storage in Metal-organic Framework, J Inorg Organomet Polym .23 (2013) 276.

[19] Hao Li, Kecheng Wang, Yujia Sun, Christina T. Lollar, Jialuo Li, Hong-Cai Zhou, Recent advances in gas storage and separation using metal-organic, Materials Today. 21 (2017) 112.

[20] Wenxiu Cao, Yingwei Li, Liming Wang, Shijun Liao, Effects of Metal Ions and Ligand Functionalization on Hydrogen Storage in Metal Organic Frameworks by Spillover, J. Phys. Chem. C, 115 (2011) 13830 - 13832.