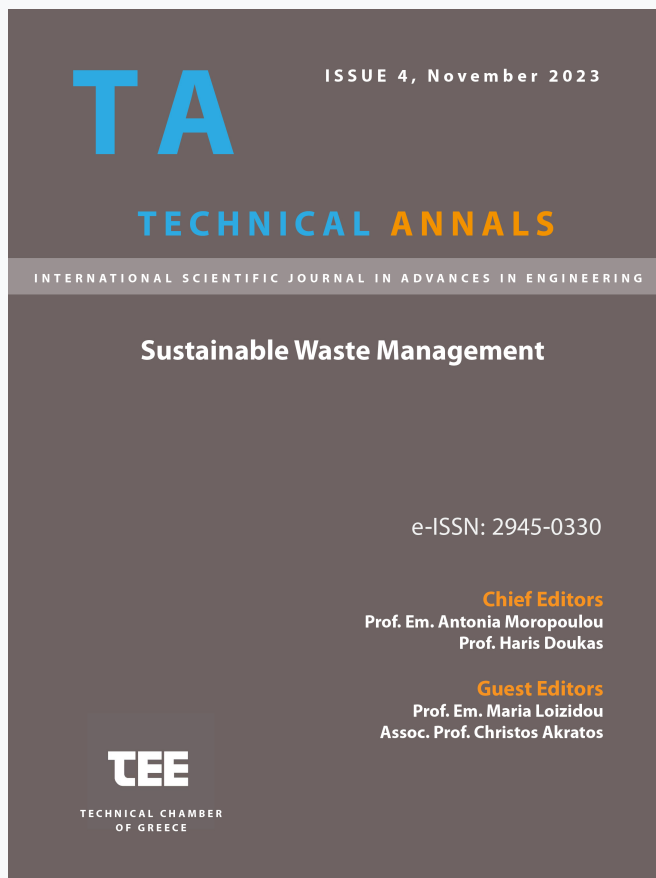


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Metal-organic frameworks (MOFs) as novel adsorbents for alternative fuel gas storage - A short review

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Metal-organic frameworks (MOFs) as novel adsorbents for alternative fuel gas storage - A short review

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Abstract. This comprehensive review examines recent research on key aspects of metal-organic frameworks (MOFs). Their chemistry, crystalline structure, ease of production, yield optimization, gas adsorption-delivery mechanisms, and performance are included. The potential for greater applicability in light of a wider utilization of MOFs as novel and effective adsorbents for storage of compressed natural gas and hydrogen is also considered. Using clean energy sources is essential for achieving zero net-carbon emissions to solve serious global warming and climate change problems. In this regard, natural gas and hydrogen are becoming well-known potential alternative car fuels. However, they should first be produced and then also stored till consumption, to accomplish sustainable transportation. Though, the volumetric energy density of hydrogen and natural gas (mostly methane) is significantly lower than that of gasoline. This presents a major obstacle to compressed gas storage in fuel cells for alternative vehicles. To overcome this hurdle and achieve a driving range comparable to that of conventional vehicles, an enhancement in the onboard gas storage capacity is required. One way to increase the energy density is storage of gas onto a solid surface via physical adsorption. For this purpose, MOFs stand out for their advantageous adsorption characteristics, particularly because of their high pore volume, specific surface and gas affinity adsorption sites, thus promoting future energy storage and cleaner energy solutions.

Keywords: Natural Gas, Hydrogen, Low-pressure Gas Storage, Metal Organic Frameworks (MOFs), Alternative Vehicle Fuels.

1 Introduction

Natural gas and hydrogen are increasingly obtaining traction as possible alternative vehicle fuels to cope with global warming and climate change, with extreme weather phenomena including rising sea levels, drought, and deforestation posing a threat to human health and survival [1,2]. Indeed, a zero-carbon future necessitates the utilization of clean energy sources, in accordance with current climate change mitigation policies that call for immediate, dramatic, and transformative adaptation activities, especially in terms of lowering greenhouse gas emissions for sustainable development [3,4].

Natural gas, in particular, can be viewed as the fuel that can aid in the transition of the energy mix to one fully dominated by hydrogen-based, carbon-neutral clean energy. However, these alternative vehicle energy sources must not only be produced, but also stored before being utilized to achieve entirely sustainable transportation, as they exist in the gaseous phase with high entropy at usual atmospheric conditions.

Despite the promising future of hydrogen as an energy source, some technological challenges must first be resolved. Although hydrogen technologies using renewable energy sources have been developed to achieve a sustainable energy cycle, a major barrier to the adoption of hydrogen technology is the storage process.

Actually, both hydrogen (H₂) and natural gas (mostly CH₄) have lower volumetric energy densities than gasoline, posing a substantial issue in terms of storing compressed gas in alternative vehicle fuel cells. To overcome this obstacle and achieve a driving range comparable to that of traditional automobiles, more onboard gas storage capacity is required. Storage of gases onto a surface via physisorption via intermolecular weak van der Waals interactions is one essential strategy for enhancing energy density. Then, gas desorption can be easily conducted by employing appropriate pressure or heat [5,6].

So far, numerous materials with high chemical and thermal, structural stability, tailorable porosity, lightweight, efficient reversibility, and ease of manufacture have been considered as promising adsorbents for the storage of different gases, like hydrogen and natural gas. Carbon-based nanostructures, including multi-walled carbon nanotubes, peat, coconut shell-based molded active carbons, activated carbon fibers, as well as titanium-decorated polycrystalline graphene sheets, and even metal-decorated beryllium carbide have been reported as low-cost, environmentally benign, and high-performing storage options for both processes, adsorption and desorption [7-12]. Moreover, nanocluster synthesis from nanoparticle sources was reported for applications in hydrogen fuel cells and also metal addition in inorganic nanoclusters to improve gas adsorption capacity, such as in the design of novel gallium nitride nanoclusters via encapsulation with alkali metals [13]. For reversible hydrogen gas storage, materials based on decorated all-boron B₃₈ nanocluster, anionic LaH₈⁻, C₂₀, C₁₅M₅, and H₂@C₁₅M₅ (M = Al, Si, Ga, Ge), and PtPd nanoclusters have been reported [14-17].

MOFs in particular, represent a new category of inorganic-organic solid hybrid materials studied for that purpose in recent years due to their excellent adsorption capabilities. Especially: i. their versatile chemical composition that can be tweaked during and after synthesis for increased adsorption performance, and ii. their microstructure with a high pore volume, specific surface and adsorption sites with gas affinity are being taken into consideration in order to assess their use for improved hydrogen and methane (natural gas) adsorption and storage in specially designed tanks at temperatures closer to ambient ones and at relatively low pressures in comparison with those obtainable in liquefied storage applications.

2 MOFs as novel gas adsorbents

For the first time, the term "metal-organic framework" was mentioned in 1994 [18]. Since then, numerous MOFs have been reported in the literature, each consisting of a

network of metal cations connected by organic linkers: Cu-BTC, a highly porous metal coordination open-framework polymer made up of Cu-based clusters and benzene tricarboxylate ligands, was first created [19]. Also, the MOF-5 structure was developed, consisting of Zn-based cations/clusters and benzene dicarboxylate ligands [20]. MOFs are now made from components like triethylamine, terephthalic acid, zinc acetate dihydrate, chloroform, and dimethylformamide, among others. Usually, the organic linkers are molecules with a negative charge, such as ditopic or polytopic organic carboxylates, bound to metal cations forming nodes, thus creating strong MOF crystalline architectural microstructures [21-23].

In comparison to commonly utilized microporous inorganic materials like zeolites, MOFs exhibit significantly greater specific surface areas and pore volumes, with highly tailorable pores ranging from 0-3 nm up to 10 nm, which can bridge the space between microporous zeolites and mesoporous silicas.

In fact, due to their huge specific surface area (usually between 1000 and 10,000 m²/g), molecular dimensions, diversified microstructures, and adaptable functionalities, MOFs have significant advantages for gas separation and selectivity [24,25]. Indeed, an extraordinary porosity with a pore volume in the range of 0.04-4.40 cm³/g has been reported [26,27]. Different approaches, such as metal ion exchange, can improve the chemistry of their pores. The possibility to control the structure and properties of MOFs is achieved by modifying their chemical nature and pore size without altering their basic topology or chemical functionality. The isoreticular (same network topology) principle arose from the capability to change the performance of MOF microstructures by employing an extended form of the organic linker initially used, without modifying their intrinsic topology. The application of this principle facilitated the development of MOFs with lower densities (0.13 g/cm³) due to larger pore apertures [20]. Such organic linkers, when properly functionalized, can also aid in improving target molecule selectivity [28-30]. Moreover, because they have lower heats of adsorption and heat capacities, these materials are able to conduct physical or weak chemical adsorption, demanding less regeneration energy.

MOFs are manufactured using various densification methods that influence their final stability and textural properties: initially, the interaction of hydrated metal salts with combined organic ligands in relatively expensive organic solvents at 100-150°C was used in solvothermal synthesis procedures [31-33]. Different processing routes have been explored in recent years, not only to increase adsorption properties but also to take material/system costs and environmental impacts into consideration. Indeed, the cost of adsorbents is a significant obstacle to their practical application in gas storage beyond thermal management requirements for the system [34]. For instance, opportunities to cut MOF costs by shortening the required time for synthesis and significantly reducing the solvent amounts have been reported using mechanochemistry methods, including grinding assisted by liquids or ions, aimed at achieving improved molecular mobility via the introduction of stoichiometric liquid phase quantities to a solid-state reaction, also assisted by catalytic effects [35-37]. Aqueous synthesis methods, which substitute water for the far more expensive and environmentally harmful traditional use of organic solvents, were also recently established and represent yet another alternative to conventional synthesis [38-40]. Furthermore, by using a chemical reduction approach,

synthesized MOFs can be intercalated with carbon black, Pd/activated carbon, and carbon nanomaterials to improve hydrogen adsorption capabilities [41].

3 Hydrogen / Natural gas storage in onboard low-pressure MOF-based fuel tanks

Among several adsorbent materials, MOFs are increasingly being studied for enhancing hydrogen/natural gas solid-state storage capabilities in onboard low-pressure adsorbent-based fuel tanks. Indicatively, the increasing attention related to hydrogen storage into MOFs is illustrated by the notable number of publications, especially over the last 5 years, as illustrated in Fig. 1.

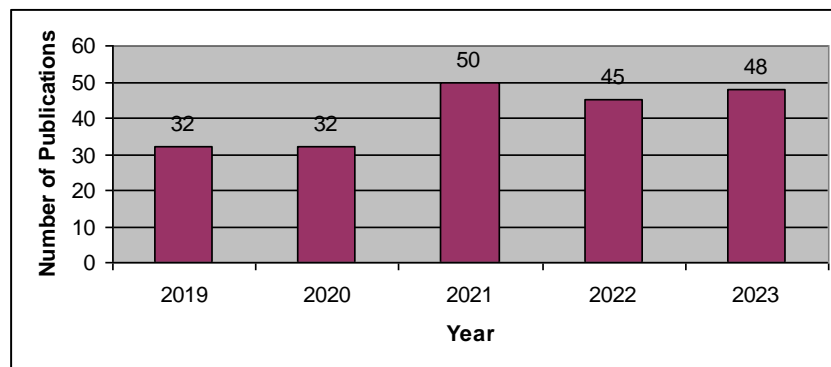


Fig. 1. Journal article results from the last five years using the keywords “hydrogen AND storage AND MOFs” via Scopus.

Such systems, with their amenability to scale-up, have the potential to lower the cost of onboard tanks as well as to reduce the technical complexity of high-pressure compressors at the station. They also facilitate the development of a fuel delivery infrastructure, which is key to making transportation greener [42,43]. Given the increasing use of natural gas (methane) and hydrogen, and in view of their ample deployment, the US Department of Energy has introduced specific technical goals to compete with traditional fuels such as gasoline, specifically in onboard adsorption-based vehicle tank storage applications. Selected technical performance targets for hydrogen are summarized in the following Table 1.

Table 1. Technical performance targets: hydrogen adsorption-based onboard storage for light-duty fuel cell vehicles [44].

| Storage Parameter | 2020 | 2025 | Ultimate |
|--|--------------|--------------|-----------------|
| Gravimetric capacity (usable specific energy from H ₂) (kg H ₂ /kg) | 0.045 | 0.055 | 0.065 |
| Volumetric capacity (usable specific energy from H ₂) (kg H ₂ /L) | 0.030 | 0.040 | 0.050 |
| Ambient temperature (°C) of operation | -40/60 (sun) | -40/60 (sun) | -40/60 (sun) |
| Min/max delivery temperature (°C) for H ₂ | -40/85 | -40/85 | -40/85 |
| Min/max delivery pressure (bar) from storage system | 5/12 | 5/12 | 5/12 |
| Onboard efficiency (%) | 90 | 90 | 90 |
| System fill time (min) | 3-5 | 3-5 | 3-5 |

Balancing between a pore volume containing gas adsorption sites and a large specific surface area with high affinity for physisorption, MOFs can improve gravimetric and volumetric density. Therefore, they can hold and store significant volumes of hydrogen and natural gas at moderately low pressures in order to meet the above-mentioned DOE's target specifications.

In fact, the outstanding properties of MOFs have led to their considerable investigation in several research works, as advanced porous adsorbents for hydrogen and natural gas (methane) storage. In the beginning, efforts were made to identify MOFs with optimal spacing between pore surfaces for high gas uptake. Although this method is an established strategy for identifying adsorbents with high gas capacities, several materials studied based on this criterion did not necessarily exhibit high gas uptake. Therefore, for discovering stable and effective storage media, some specific MOF structures have been proposed. Specifically:

For hydrogen solid-state storage, some materials are good candidates, depending on their structure and chemistry. Relevant data reported in literature are summarized in Table 2.

Table 2. Data for Hydrogen Storage into MOFs [45-48].

| MOF Type | Temperature | Pressure | Gas |
|----------|-------------|----------|-------------|
| MOF-5 | 77 K | 0,8 bar | 4.5 wt% |
| | | > 10 bar | 1.6 wt% |
| | | 20 bar | 4.5 wt% |
| | | > 80 bar | 5.1 wt% |
| | | 170 bar | 11.5 wt% |
| HKUST-1 | 77 K | 20 bar | 1 wt% |
| | | 67 bar | 0.2 wt% |
| HKUST-1 | 77 K | 1 bar | 1.25 wt% |
| | | 1 bar | 1.6 wt% |
| | | 1 bar | 2.5 wt% |
| | | 298 K | 0.35 wt% |
| | | 303 K | 0.47 wt% |
| ZIF-8 | 77 K | 353 K | 0.34 wt% |
| | | 860 mmHg | 6.92 mmol/g |
| ZIF-8 | 77 K | 55 bar | 3 wt% |
| | | 298 K | 0.1 wt% |
| MOF-177 | 77 K | 55 bar | 0.1 wt% |
| | | 0.9 bar | 1 wt% |
| | | 1 bar | 1.5 wt% |
| | | 90 bar | 7.5 wt% |
| | 87 K | 100 bar | 19.6 wt% |
| | | 1 bar | 0.75 wt% |
| | | 46 bar | 0.37 wt% |
| 298 K | 40 bar | 0.35 wt% | |
| | | 100 bar | 0.62 wt% |

Particularly efficient MOFs appear to be those that include open metal sites, lighter and extra metal cations into the framework (which positively influence hydrogen-framework interactions), ultra-high void fraction and specific surface area in the framework, optimized pore size (small pores seem more appropriate for hydrogen molecule uptake), and also diversified topologies (for instance, the 'she' topology in the isoreticular she-MOF-x series for hydrogen adsorption at cryogenic conditions) [49-56]. One promising method recently reported for quick, safe, and reversible hydrogen storage is cryoadsorption on the inner surface of zeolitic imidazolate frameworks (e.g. ZIF-8), a family of very porous MOFs exhibiting exceptional mechanical, chemical and thermal stability [57,58].

On the other hand, for effective methane storage, such adsorbents include isorecticular MOFs based on Zn₄O, M₂(bdc)₂(dabco) (M= Ni, Co, Zn) frameworks, copper carboxylates groups, MIL (Materials of Institute Lavoisier) series, and water stable Zr-based MOFs. For example, MOF-177, a structure comprising a complex called [Zn₄O₆]⁶⁺ and ligand molecules known as 1,3,5-benzene-tribenzoic (BTB) ligands, has exhibited hydrogen adsorption capacity beyond the amount expected under certain conditions. The framework consists of Zn₄O clusters located at the corners, bound to organic ligand molecules, specifically benzotriazoate (BTB) in the case of this typical MOF-177 framework. An interpenetrating framework structure is generally preferred, as it preserves the adsorption sites without blocking them although it may reduce the pore volume and create a complex pore structure [59-66]. Furthermore, hydrogen/methane mixtures adsorption onto different MOFs was also reported [67-69]. Relevant data are summarized in Table 3.

Table 3. Data for Natural Gas Storage into MOFs [70-75].

| MOF Type | Temperature | Pressure | Gas |
|----------|-------------|------------------------|---|
| MOF-5 | 273 K | 0.015 P/P ₀ | 2.3 mmol/g |
| | | 0.025 P/P ₀ | 3.4 mmol/g |
| | 298 K | 40 bar | 550 g/L |
| HKUST-1 | 298 K | 1 atm | 0.67 mmol/g |
| | | 1 atm | 1.55 mmol/g |
| | | 5.8 - 65 bar | 190 cm ³ /cm ³ (STP) ³ |
| | 303 K | 35 bar | 160 cm ³ /cm ³ (STP) ³ |
| | | 35 bar | 227 cm ³ /cm ³ (STP) ³ |
| | | 35 bar | 255 cm ³ /cm ³ (STP) ³ |
| NU-125 | 220 K | - | 94 v/v |
| | 298 K | 5.8-65 bar | 32 mmol/g |
| | | 58 bar | 174 cm ³ /cm ³ (STP) ³ |
| MIL-53 | 303 K | 35 bar | 228 cm ³ /cm ³ (STP) ³ |
| | | 35 bar | 155 cm ³ /cm ³ (STP) ³ |
| | | 35 bar | 165 cm ³ /cm ³ (STP) ³ |

4 Concluding

The research papers that were examined and discussed highlight the intrinsic chemistry of MOFs, porous microstructure design, technical simplicity, and optimization of the production process, as well as gas adsorption-desorption mechanisms and

performance as significant factors in view of increased applicability and broader implementation of this category of materials. These factors are crucial for the development of potentially efficient novel adsorbents for natural gas and hydrogen storage in onboard low-pressure MOF-based fuel tanks.

With the potential to address the challenges of gas storage, MOFs offer promising solutions for achieving efficient and safe storage of hydrogen and natural gas, which is vital for their widespread adoption as a source of clean energy and reducing dependence on fossil fuels. By continuing research and development efforts in the area, we can pave the way towards an environmentally friendly and economically sustainable economy. The use of MOFs represents an important step in shaping the future of energy storage and promoting sustainable and greener energy solutions.

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