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# Natural Gas Storage using Metal Organic Frameworks (MOFs): A Review

Adeel Ahmad<sup>1</sup>, Srishti Mishra<sup>2</sup>, Rahul Takoria<sup>3</sup>, Naveen Kumar<sup>4</sup>

<sup>1,2,3,4</sup>Delhi Technological University, Delhi, India  
<sup>1</sup>adeel7ah@gmail.com

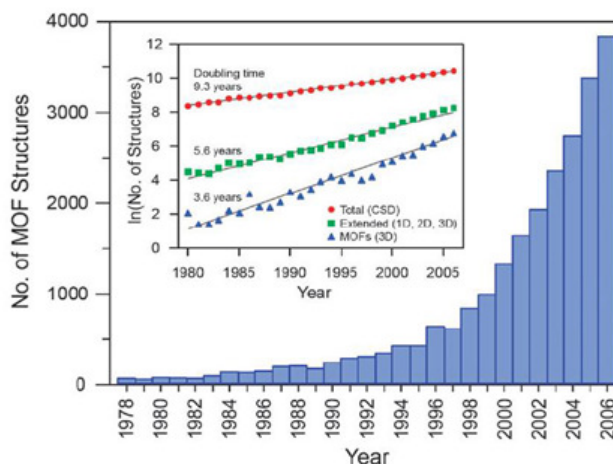
**Abstract:** Natural gas today has emerged as the leading alternative fuel for the commercial markets. While being widely used, it still is facing certain roadblocks to the full realization of its potential, primarily pertaining to its storage. Currently, the natural gas used today for transportation purposes is stored in high pressure tanks which do not offer any volumetric advantages. Taking a step forward in this direction, Metal Organic Frameworks (MOFs) are being researched upon for the storage of natural gas in commercial applications. Metal-organic framework (MOF) materials are an emerging class of crystalline materials consisting of metal ions or metal ion clusters and bridging organic linkers, with relatively well-defined pore structures and interesting properties. Gas and liquid separation applications with different MOF membranes are also included. Metal-organic frameworks have received significant attention as a new class of adsorbents for natural gas storage. Metal-organic frameworks (MOFs) are an emerging class of crystalline materials that have shown promise in the fields of gas capture, gas storage, separations, catalysis, magnetism, fluorescence, and sensing to name only a few. The use of these materials as self-sacrificing templates, via calcination or pyrolysis, for the design of green energy generation and storage devices is the focus of this review.

**Keywords:** Metal Organic Frameworks, Crystalline Ions, Organic linkers, Calcination, Pyrolysis

## 1. INTRODUCTION

Metal-organic frameworks (MOFs), also known as porous coordination polymers,<sup>1-4</sup> are a new class of zeolite-like hybrid solids. They are usually crystalline compounds built from organic multi-dentate organic ligands and metal ions or clusters. The two components are held together by covalent bonds to form extended 3-D infinite network structures. The chemistry of MOFs is developing at an extraordinary pace: in recent years, as shown by the increase in the number of published papers and reviews (Figure 1.1).<sup>5</sup> MOFs have exceptionally large surface areas and many have permanent porosity. MOFs have broad industrial applications because of two key attributes: their extremely large surface-areas and the flexibility with which their

structures can be varied. They are also very robust, with high mechanical and thermal stabilities. The highest surface areas reported to date are over 6,000 m<sup>2</sup>/g.<sup>6,7</sup> MOFs usually are crystalline solids, so that the exact positions of all atoms in the framework can often be identified and correlated with the measured properties.



**Fig. 1. Number of metal-organic framework (MOF) structures reported in the Cambridge Structural Database (CSD) from 1978 through 2006.5**

## 2. WHY NATURAL GAS?

Increasing population, global climate change, and dwindling fossil fuel reserves have led to a green energy revolution in the past few years, particularly in the fields of green energy generation and storage. While fuel cell, lithium-ion batteries, and super-capacitors are far from common slang in today's world, a good number of these devices is not yet displayed in the consumer market. So to overcome these problems the solution that we can imagine of and is feasible at the same time is the Natural gas. Natural gas has the potential to replace petroleum as the world's primary fuel for transportation. Consisting mainly of methane (CH<sub>4</sub>), natural gas has the highest H to C ratio of any fossil fuel, resulting in less CO and CO<sub>2</sub> released per unit of energy generated.<sup>8</sup> Lower sulfur and nitrogen contents also lead to lower SO<sub>x</sub> and NO<sub>x</sub> emissions, making natural gas a

significantly cleaner burning fuel than gasoline.<sup>2</sup> Indeed, initial field tests found up to 86% less CO, 26% less CO<sub>2</sub>, and 77% less NO<sub>x</sub> emissions after converting gasoline cars to run on natural gas.<sup>10</sup> Moreover, natural gas can be easily transported through pipelines and stored in tanks or cylinders.<sup>11</sup> In addition, recent engineering advances in horizontal drilling and hydraulic fracturing have led to a rapid increase in global natural gas reserves, driving the price of natural gas below that of gasoline in many countries.<sup>12</sup>

### 3. CHALLENGES ON THE WAY

In spite of all the benefits of natural gas, several challenges have prevented the widespread use of natural gas in vehicles. Most importantly, the volumetric energy density of natural gas at ambient temperature and pressure is only 0.04 MJ L<sup>-1</sup>, compared to 32.4 MJ L<sup>-1</sup> for gasoline.<sup>13</sup> The volumetric energy density can be increased by compression or liquefaction, but both of these solutions are costly and poorly suited for light-duty passenger vehicles. For instance, compressed natural gas (CNG) requires expensive multi-stage compressors that consume energy, as well as heavy, bulky fuel tanks that reduce passenger and cargo space. Even with compression to 250 bar, the energy density of CNG (near 9 MJ L<sup>-1</sup>) is only 26% that of gasoline,<sup>2a</sup> leading to a significant reduction in the driving range of a vehicle. Moreover, CNG refueling stations are not yet common enough for convenient refueling and are costly to build.<sup>14</sup>

Moreover, due to the low critical temperature of CH<sub>4</sub> (190.6 K, Table 1), natural gas cannot be liquefied by compression alone, and cryogenic cooling is necessary to store liquefied natural gas (LNG). While the volumetric energy density of LNG can reach 20.8 MJ L<sup>-1</sup> (64% of gasoline),<sup>13</sup> the overall system energy density is reduced due to the insulation required to maintain a low temperature and prevent boil-off. Additionally, the high cost of cooling systems and complications of handling a cryogenic fuel make LNG unlikely to find much application in the transportation sector beyond commercial trucking and public transportation.<sup>15</sup>

TABLE 1: Relevant physical properties of pure CH<sub>4</sub>

Critical temperature <sup>8a</sup>	190.6 K	190.6 K
Boiling point <sup>8a</sup>	111.7 K	111.7 K
Kinetic diameter <sup>9</sup>	3.80 Å	3.80 Å
Polarizability <sup>9</sup>	2.6 Å <sup>3</sup>	2.6 Å <sup>3</sup>
Volumetric density (1 bar, 25 °C) <sup>8</sup>	0.9v/v	0.9 v/v
Volumetric density (250 bar, 25 °C) <sup>8</sup>	263v/v	263 v/v
Volumetric density (1 bar, -162 °C) <sup>8</sup>	591v/v	591 v/v

Even with CNG, the challenges that are faced during the storage of the gas will always be an issue for its economic feasibility and the convenience to use it as a common fuel. These problems will persist until alternative storage

methods are devised for the storage natural gas. The conventional compressed natural gas tanks today can store up to 10 liters of CNG which is almost one fifth as compared to the conventional gasoline tanks.

### 4. METAL-ORGANIC FRAMEWORKS AS THE SOLUTION

As an alternative to CNG and LNG, using adsorbents to store natural gas at higher densities at ambient temperature and moderate pressures has been an active area of research since the early 1970s. Significantly, adsorbents that operate at relatively low pressures should allow the use of inexpensive on-board fuel tanks and single-stage compressors. Additionally, adsorbed natural gas (ANG) systems would permit the use of lightweight, conformable fuel tanks that can be more optimally integrated into the limited space available within a small car.

While early efforts in adsorbed natural gas (ANG) storage focused primarily on zeolites, their relatively low surface areas of less than 1000 m<sup>2</sup> g<sup>-1</sup> resulted in insufficient CH<sub>4</sub> capacities. With considerably higher surface areas, activated carbons have been the most studied class of materials for ANG over the last several decades. A large portion of research has involved investigating the effects of surface area, pore size, and pore shape on the CH<sub>4</sub> adsorption properties of different carbons. Indeed, it was demonstrated that slit-shaped pores with a diameter of 7.6 Å, which can accommodate two layers of CH<sub>4</sub>, are ideal for maximizing the volumetric density of CH<sub>4</sub> stored at 35 bar and 25 °C. Note that 35 bar has been widely used as a standard pressure for evaluating adsorbents for ANG storage, as this has represented the maximum pressure achievable by most inexpensive single-stage compressors. Additionally, strategies for compacting and shaping activated carbons to optimize packing inside a storage tank have been explored in depth, and prototype activated carbon ANG systems have been demonstrated and tested.

Accordingly, a next generation of adsorbents is required to meet these storage targets without moving to higher adsorption pressures or lower temperatures, both of which would add significant complexity and cost to an ANG vehicle.

Research shows that owing to their high porosity and tunable pore surfaces, metal-organic frameworks have received significant attention as a new class of adsorbents. While early research on these materials for gas storage applications was mostly related to H<sub>2</sub>, a growing number of frameworks have been evaluated for CH<sub>4</sub> storage. Significantly, several metal-organic frameworks have reported CH<sub>4</sub> capacities comparable to or exceeding those of the best activated carbons. Also, most porous materials that are used as the adsorbents exhibit classical Langmuir-type isotherm adsorption, where the amount of methane adsorbed increases continuously but with a decreasing slope as the pressure is raised so that, upon discharging the methane

down to the minimum delivery pressure, much of it remains in the tank. With MOFs, the adsorption process is stepped because the gas must force its way into the MOF crystal structure, opening and expanding the pores. This means the amount of methane that can be delivered to the engine, i.e., the usable capacity, is higher than for traditional, non-flexible adsorbents.

A variety of factors influence the methane uptake capacities of porous MOFs, namely, surface areas, pore sizes, ligand functionalization, and heats of adsorption (with contributions from both framework topology and chemical functionality).

Some of the MOFs devised for the storage of natural gas are as follows:

1. A material called PCN-14, which contains copper (II) ions and 5, 5'- (9, 10-anthracene-diyl) di-isophthalate units, has the highest methane-adsorption capacity reported to date: 230 v/v at 290 K and 35 bar.
2. "Cobalt-bdp" or Co(bdp) for cobalt (benzenedipyrzolate)- In its most open form, cobalt-bdp features square-shaped pores that can flex shut like an accordion when the pores are evacuated. Combined gas adsorption and in situ powder X-ray diffraction experiments performed under various pressures of methane at 25°C (77°F) showed that there is minimal adsorption of methane by the cobalt-bdp MOF at low pressures, then a sharp step upwards at 16 bar, signifying a transition from a collapsed, non-porous structure to an expanded, porous structure. This transition to an expanded phase was reversible. When the methane pressure decreased to between 10 bar and 5 bar, the framework fully converted back to the collapsed phase, pushing out all of the adsorbed methane gas.

## 5. MOFS ARE ALSO CURRENTLY UNDER RESEARCH FOR THE STORAGE OF HYDROGEN

Zn<sub>4</sub>O (BDC)<sub>3</sub> (BDC = 1, 4-benzenedicarboxylate), also called IRMOF-1 or MOF-5, was one of the first MOFs investigated for hydrogen storage due to its high porosity, high surface area (4400 m<sup>2</sup>/g), and stable structure in the absence of guest molecules.<sup>25</sup> The measured sorption isotherm for H<sub>2</sub> at 78 K reveals type I behavior, in which saturation is reached at low pressures followed by a pseudoplateau at higher pressures (Figure 1.4a). At 78 K and 1 bar, the H<sub>2</sub> uptake of IRMOF-1 is 4.5 weight percent, which corresponds to 17.2 H<sub>2</sub> per Zn<sub>4</sub>O (BDC)<sub>3</sub> formula unit. At room temperature, the uptake of H<sub>2</sub> by IRMOF-1 increases linearly with pressure, and reaches 1.0 weight % at 20 bars (Figure 1.4b). Later research found that the H<sub>2</sub>

uptake capacity of IRMOF-1 varies somewhat according to the method used to prepare and activate it.<sup>25-35</sup>

## 6. CONCLUSIONS

In this paper, in-depth literature study of natural gas and its advantages over other fuels has been done and the need to address the issue of searching a better fuel and the fuel storage has been highlighted. But the problem of natural gas storage still forbids the driving range of vehicles equivalent to that of gasoline. The use of MOFs (metal-organic frameworks) has been addressed as a method to increase the storage capacity of the conventional storage tanks somewhat similar to the storage of hydrogen in the cryogenic storage tanks with the phenomenon of adsorption. With some of the highest volumetric and gravimetric CH<sub>4</sub> capacities ever reported, metal-organic frameworks have shown significant potential as adsorbents for natural gas storage. However there are still some difficulties that are yet to overcome before they are likely to find widespread usage in the Natural gas vehicles.

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