Proceedings of the 3rd International Conference on Materials Chemistry and Environmental Engineering (CONF-MCEE 2023), Part II
DOI: 10.54254/2755-2721/7/20230388

New material: Metal-organic frameworks for natural gas storage

Jiale Tang[1,*]

[1]Strathallan School, Forgandenny, Perth, PH2 9EG, United Kingdom

[*]15JT020204@strathallan.co.uk

Abstract. As gasoline is a non-renewable source, scientists are continuing to find new sources which could replace the role of gasoline that are much cleaner and environmentally friendly. Natural gas is a good opinion as it reduces the amount of SO_x, CO_x, and NO_x being emitted and costs less compared to gasoline. The problems come as the volumetric energy density is much lower than expected. Scientists suggested three ways to overcome this challenge: CNG (Compressed natural gas), LNG (liquefied natural gas), and ANG (adsorbed natural gas). Metal-organic frameworks have been introduced for natural gas storage. The advantages and disadvantages of ANG using metal-organic frameworks (MOFs) have been discussed in detail. The quantification factors, such as gravimetric and volumetric uptake, adsorption conditions, thermal properties, and isosteric heat of adsorption usable methane capacity and morphology, are also mentioned for methane storage. Different metal-organic frameworks are compared to find the best material for methane storage. Considering all these quantification factors above between different MOFs, PCN-14 is the best MOF and has been widely used worldwide for methane storage. The paper hopes to provide state-of-the-art opinions regarding the application of MOFs in methane storage and facilitates the future of renewable energy usage.

Keywords: MOFs, Methane Storage.

1. Introduction

Nowadays, the globe is forced to deal with a worldwide energy crisis due to the uncontrolled usage of gasoline. Because gasoline consumption worsens air pollution, efforts are being made to find and develop "green" sources. Renewable and clean energy sources like wind, solar, and others are not reliable since they are so weather-dependent. As methane, which has the highest H to C ratio, makes up the majority of natural gas, it was brought to attention at that time. Thus, there will be reduced SO_x and NO_x emissions since less carbon dioxide, and carbon monoxide will be emitted. Emissions of C.O., CO_2, and NO_x will all decrease by 86%, 26%, and 77%, respectively [1]. Additionally, in many nations, the cost of natural gas is less than that of gasoline. Figure 1 below displays the cost of natural gas in various nations. In the U.K., the cost of natural gas is 0.105 dollars per kWh, which is more expensive than in other nations. For instance, natural gas costs 0.028 dollars per kWh in Ukraine, which is only a fourth of what it does in the U.K. [2]. For these reasons, natural gas is starting to partially take the place of gasoline and is becoming more and more significant globally.

DOI: 10.54254/2755-2721/7/20230388

Figure 1. Figure with short caption Natural gas price for households, December 2021 (kWh, U.S. Dollar).

To use natural gas, we also need to store natural gas. The problem is that natural gas has a volumetric energy density of only 0.04 MJ $L^{-1,}$ whereas gasoline has a volumetric energy density of 32.4 MJ L^{-1}, which is substantially higher than natural gas [1]. These issues can be resolved in several ways. There are two ways to improve the volumetric energy density of natural gas: compressed natural gas (CNG) and liquefied natural gas (LNG). Compression, however, is expensive and challenging to use. It needs large, heavy fuel tanks and multi-stage compressors. Furthermore, even though the combined pressure is 250 bars, the volumetric density is just 8.42 MJ L^{-1} [1]. Additionally, there aren't enough CNG filling stations, and building filling stations is expensive. Maintaining a low temperature is necessary to obtain 20.8 MJ L^{-1}, and the cooling system is expensive [1]. Therefore, CNG or LNG cannot be the optimal method for storing natural gas. However, LNG is still in use since it is more environmentally friendly, effective, and abundant than burning other fossil fuels directly. Table 1 demonstrates how the volumetric storage capacity of CNG grows with pressure. LNG needed less pressure than CNG to achieve a higher volumetric energy density at a significantly lower pressure. Because of this, LNG is preferred over CNG and is utilised more frequently globally.

Table 1. The volumetric storage capacity of CNG and LNG under different pressures[3].

Pressure (MPa)	Volumetric uptake (v/v) at STP
CNG (15 MPa)	168
CNG (20 MPa)	222
CNG (21 MPa)	232
CNG (22 MPa)	241
CNG (25 MPa)	266
LNG (0.1 MPa)	600

2. Advantages and challenges of using MOFs for methane storage

Adsorbents have been used to store natural gas since the early 1970s. In comparison to CNG, it could operate at 35 bars with single-stage compressors and affordable onboard fuel tanks. Additionally, it permits convenient home fueling. The objective for storing CH_4 in absorbents in 2012 is 350 $cm_{STP}^3 cm_{adsorbent}^{-3}$ (v/v). The minimal volumetric energy density is 263 v/v due to the 25% drop in volumetric capacity. The highest volumetric energy density for activated carbon, however, is claimed to be between 100 and 170 v/v. The computer estimated that carbon would have a maximum volumetric energy density of 198 v/v, which is still less than projected [1]. MOFs were informed because they were able to achieve a higher volumetric energy density. For example, monolithic HKUST-1 meets the target of 263 v/v at 70 bars [4]. This promises MOFs to hold for methane storage.

However, although natural gas mainly consists of methane, there is still contains a specific number of impurities in natural gas. These contaminants will have an impact on an adsorbent's long-term stability. A guard bed is usually required to be placed before the storage tank to minimize the impurities, but there still will be impurities mixed with natural gas. Scientists are doing research and experiments to improve the lifetime of MOFs. Another challenge MOFs face as HKUST-1 is compacting. The structure will collapse, leading to the decrease in gravimetric and volumetric uptakes [5]. To solve this problem, scientists are finding ways to package the MOFs which could avoid serious damage. Thus, the MOFs will not be compacted under high pressure.

3. Quantification factors of methane storage

To store methane, a few quantification factors could be used as consideration criteria to compare different kinds of MOFs. Gravimetric and volumetric uptakes are two criteria that scientists value. The amount of methane that could be adsorbed per unit mass is shown by gravimetric uptakes. The amount of methane that could be adsorbed per unit volume is suggested by volumetric uptakes. For standard methane measurement, usually determined gravimetric uptake first, then converted the value into volumetric uptakes by multiplying by ideal crystallographic density. When doing the conversions, the type of density (crystallographic, tap, bulk, pellet) must be specified and reported. However, the value of volumetric uptakes usually being over-estimated. This is because the maximum volumetric uptakes were represented since the loss of density caused by compacting the particles in a fuel tank was disregarded. The ideal crystallographic density you utilised for your computation is 0.621 g cm^{-3}. However, in reality, MOF-5's bulk powder density is 0.13 g cm^{-3} [1]. This will not only make the actual volumetric uptakes lower but also leads the thermal conductivities to become lower.

Pore size and material surface area are key factors influencing the amount of methane stored. MOFs have larger pore size and greater surface area than other materials that could store methane, such as activated carbon. For example, the pore volume of an activation carbon (CP-AC) is 0.97 cm^3 g^{-1} [6]. In contrast, the pore volume of most MOFs is around 3.3 cm^3 g^{-1} [7]. For surface area, MOFs have a large range from 1000-10000 m^2/g [6] compared to the surface area of CP-AC is 1823 m^2/g [7]. This data shows the reason that MOFs are better materials for methane storage. The detailed parameters of the activated carbon and MOFs are shown in Table 2.

Table 2. Pore volume and surface area of CP-AC and MOFs.

	Pore volume /$cm^3\ g^{-1}$	Surface area /m^2/g
CP-AC	0.97	1823
MOFs	3.3	1000-10000

The isosteric heat of adsorption shows the heat released as the molecules are adsorbed from the bulk state to adsorbed state. As the value becomes more negative, more species will be adsorbed.

Not all the methane capacity can be used when delivering as it is required to overcome a minimum inlet pressure. Usually, the inlet pressure needed is 5-10 bars [1]. As the demand for natural gas cars increases, researchers are finding new ways to minimize the inlet pressure so that the usable methane capacity will increase. To increase methane capacity, binding enthalpy is required to be improved. The amount of usable methane capacity will decrease if they have extremely high binding enthalpies because too much methane will be held at low pressure. There will be insufficient methane adsorbed at high pressures if they have an inadequate bind enthalpy.

Thermal characteristics are also significant. As they are exothermic and endothermic, respectively, the heat of adsorption and desorption will have a significant impact on the useable methane capacity. Scientists are looking for a material with a high heat capacity. The temperature difference that occurs during adsorption and desorption is reduced by a large heat capacity. The usage of both internal and external temperature management systems is favored by a material's high thermal capacity, which enables the heat to dissipate fast.

MOFs also show diverse morphologies, such as cubes, octahedrons and etc. By controlling the morphology, the structures and functions of MOFs will change. Adsorption conditions of MOFs for methane storage are at 3.6 MPa and 25 degrees [8] which is lower than activated carbon which requires 4 MPa as the condition [9].

4. Different MOFs in methane storage

M_2(dobdc) (M=Mg, Ni) has a high concentration of unsaturated metal cations, which are strong adsorption sites for methane molecules. HKUST-1 and PCN-14 are different from M_2(dobdc) (M=Mg, Ni) as their pore and pore windows have different sizes. MOF-5 and AX-21 both have a high Langmuir surface area as the Langmuir area of MOF-5 is 3995 m^2/g, and AX-21 is 4880 m^2/g [1]. However, MOF-5 does not contain any strong adsorption sites. This is the reason why AX-21 is more popular than MOF-5 and has been used in ANG storage.

Figure 2 (a) below shows that the material which has the highest gravimetric uptake at all pressures is AX-21. Of all MOFs, the highest gravimetric uptake from 0 to 35 bars is HKUST-1. MOF-5 is the highest gravimetric uptakes from 35 to 100 bars. At low pressure, the amount of methane of HKUST-1, PCN-14, and M2 (dobdc) adsorbed increases quickly. As the pressure increases, they become saturated and reach a maximum value of gravimetric uptakes.

Figure 2 (b) shows HKUST-1 and Ni2(dobdc) both have very high volumetric uptakes. This shows their ideal crystallographic density is higher than MOF-5 and AX-21. For methane storage, they both need to meet the 350 v/v targets for volumetric uptakes. The total volumetric capacity of Ni2(dobdc) is 172 v/v when one methane molecule is bound to each metal [1]. After the sites are fully occupied, there are only weaker secondary adsorption sites should be available. HKUST-1 can only contribute 98 v/v using all strong binding sites. However, it has additional strong adsorption sites of 65 v/v, which adds up to 163 v/v, which is similar to Ni2(dobdc) [1].

The detailed parameters of HKUST-1 and Ni2(dobdc) are shown as below in Table 3.

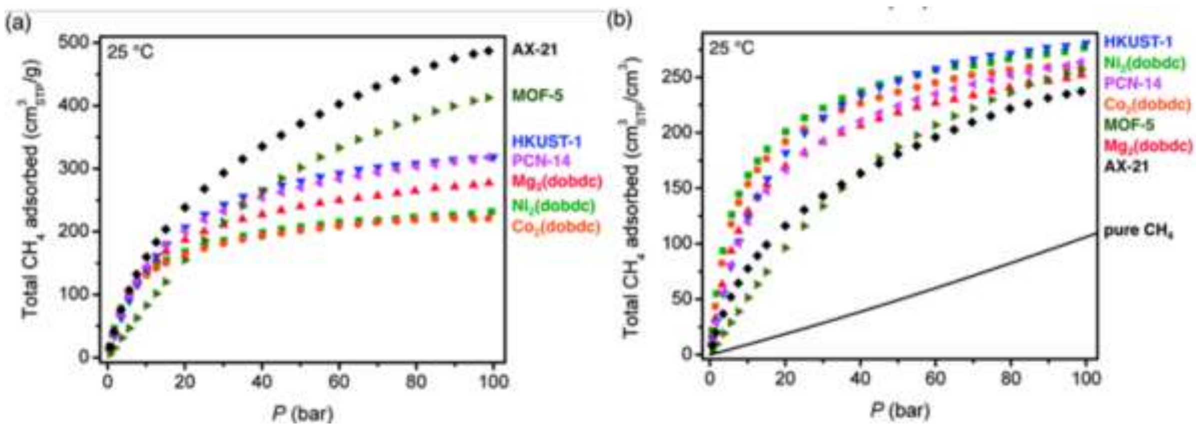

Figure 2. The Gravimetric and volumetric uptakes of different MOFs under different pressure.

Table 3. Total adsorption sites of Ni_2(dobdc) and HKUST-1.

	Ni_2(dobdc)	HKUST-1
Strong binding sites (v/v)	172	98
Additional adsorption sites (v/v)	0	65
Total (v/v)	172	163

Figure 3 below shows the isosteric heats of adsorption (Q_{st}) between six metal-organic frameworks and one activated carbon. M_2(dobdc) (M=Mg, Ni) has higher isosteric heat of adsorptions at low coverage; however, as the amount of methane adsorbed increases, the value of Q_{st} decreases sharply. PCN-14 and HKUST-1 have lower isosteric adsorption heat and almost remain at the constant value of -17 kJ/mol. Scientists suggest this might be the reason why PCN-14 has a high volumetric uptake, but any calculation or experiments have not proved this conjecture. AX-21 has a steep line showing that there are different sizes of pores in AX-21, and the smaller pores gave stronger interaction than the larger pores. The shallow line of MOF-5 shows its Q_{st} is low and constant.

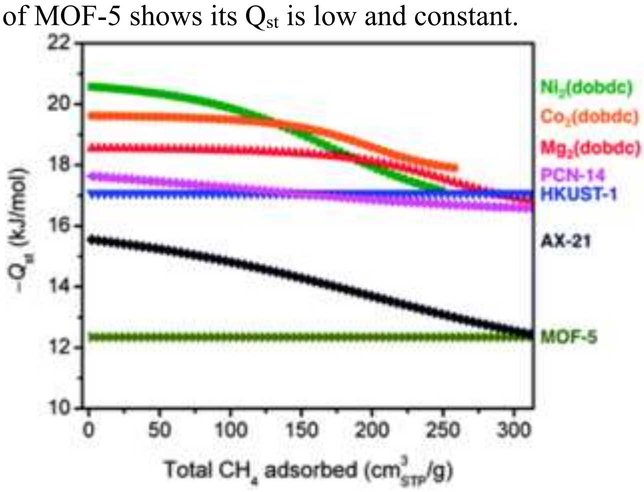

Figure 3. The relationship between isosteric heats of adsorption and total methane adsorbed.

Figure 4 below shows the usable methane capacity of MOFs during adsorption and desorption. The condition for adsorption is at 35 bars and 25 degrees, and the condition for desorption is at 5 bars and from 25 to 145 degrees [1]. The graph shows that HKUST-1 has the highest usable methane capacity of all other MOFs. As the temperature increases, the usable methane capacity increases slowly as a shallow curve. At 25 degrees, the usable methane capacity of Ni_2 (dobdc) is only 117 v/v. It increases quickly as the usable methane capacity goes up to 210 v/v at 145 degrees. The usable methane capacities of MOF-5 and AX-21 remain at a low value at 120 v/v.

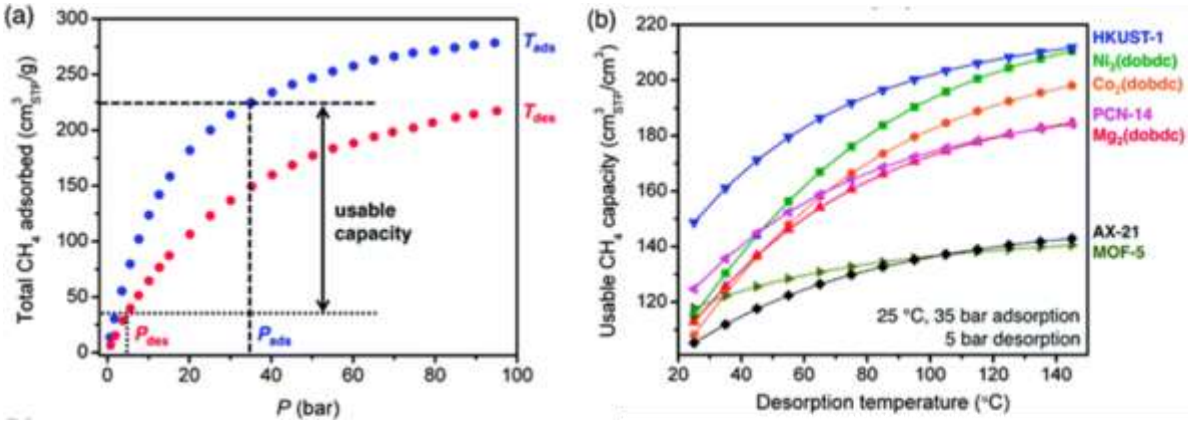

Figure 4. The usable methane capacity of MOFs during adsorption and desorption.

The correlation between temperature and specific heat capacity is depicted in Figure 5 below. The temperature increases in direct proportion to the specific heat capacities of MOF-5 and MIL-53. As the line for MOF-177 passes through the origin, the temperature and specific heat capacity are directly related. All MOFs on the graph have an increasing specific heat capacity as the temperature rises. This demonstrates that there are no temperature-induced phase transitions present.

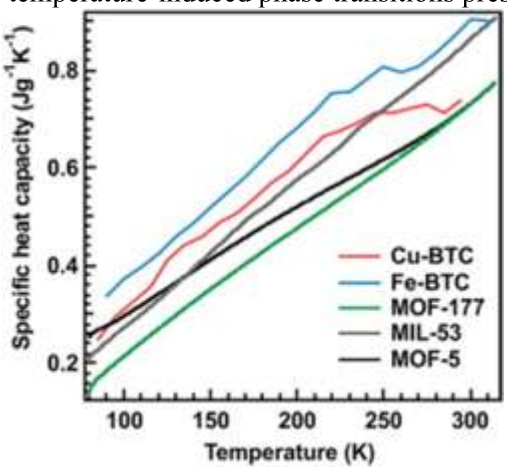

Figure 5. The relationship between temperature and specific heat capacity.

In 2007, PCN-14 was reported which have the highest methane uptake value over the current record of MOFs. The total volumetric uptake of PCN-14 could reach 230 v/v at 17 degrees and 35 bars [10]. PCN-14 also contains exposed metal cation, different-sized pores, and pore windows, which is different from M_2(dobdc) [M= Ni, Mg]. The pore capacity of 0.87 cm^3/g, which is greater than many MOFs, and the huge BET area of 1753 m^2/g are further features [11]. Due to its effectiveness in storing methane, PCN-14 is now the most extensively utilised MOF.

5. Conclusion

A big success in the ANG process by using MOFs for methane storage has been achieved. High porosity and tuneable pore surfaces seem to be their most impressive properties. They are cheaper, much easier to progress, and more environmentally friendly compared to CNG or using 'old fashion' gasoline. However, there are still several challenges that need to be solved, such as how to purify natural gas to get pure methane. The lifetime of ANG will increase by decreasing the number of impurities the natural gas consists of. Although a guard bed has been placed to minimize the impurities, it is not enough. Is that possible to reduce the impurity to a very little number that we can ignore? Another challenge is how to avoid collapsing MOFs when compacting under high pressure. The cost of ANG in the U.K. is higher than gasoline which is unusual compared to many countries. It is a worthy study to think about how to compress the cost of MOFs. Some scientists also questioned that MOFs have just been discovered for almost 30 years and have not experienced enough tests and research. To be widely used instead of gasoline, there is a long way to go. Scientists should consider the possibility of combining different MOFs to make a new MOF that has the best properties for methane storage. To explore more information about MOFs, scientists need to do more experiments to validate the feasibility of this new material and improve its properties. The technique and assay of MOFs are well-established to a large extent. Nevertheless, there are challenges still to be faced and refinements still to be made. MOFs are likely to be used in the industry field to provide an alternative assay for methane storage.

References

[1] Mason J A, Veenstra M, Long J R. Evaluating metal–organic frameworks for natural gas storage[J]. Chemical Science, 2014, 5(1): 32-51.
[2] United Kingdom natural gas prices, December 2021, Global Petrol Prices
[3] Kumar K V, Preuss K, Titirici M M, Rodriguez-Reinoso F. Nanoporous materials for the onboard storage of natural gas[J]. Chemical reviews, 2017, 117(3): 1796-1825.
[4] Mahmoud E, Ali L, El Sayah A, Awni Alkhatib S, Abdulsalam H, Juma M, AL-Muhtaseb A H. Implementing metal-organic frameworks for natural gas storage[J]. Crystals, 2019, 9(8): 406
[5] Peng Y, Krungleviciute V, Eryazici I, T. Hupp J, K.Farha O, Yildirim T. Methane storage in metal–organic frameworks: current records, surprise findings, and challenges[J]. Journal of the American Chemical Society, 2013, 135(32): 11887-11894.
[6] Li L, Sun F, Gao J, Wang L, Pi X, Zhao G. Broadening the pore size of coal-based activated carbon via a washing-free chem-physical activation method for high-capacity dye adsorption[J]. RSC advances, 2018, 8(26): 14488-14499.
[7] Zhang X, Lin R B, Wang J, Wang B, Liang B Yildirim T, Zhang J Zhou W, Chen B. Optimization of the pore structures of MOFs for record high hydrogen volumetric working capacity[J]. Advanced Materials, 2020, 32(17): 1907995.
[8] Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter, O'Keeffe M, M.Yaghi O. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage[J]. Science, 2002, 295(5554): 469-472.
[9] Alcaniz-Monge J, De La Casa-Lillo M A, Cazorla-Amorós D, Linares-Solano A. Methane storage in activated carbon fibres[J]. Carbon, 1997, 35(2): 291-297.
[10] Kloutse F A, Zacharia R, Cossement D, Chanhine R. Specific heat capacities of MOF-5, Cu-BTC, Fe-BTC, MOF-177 and MIL-53 (Al) over wide temperature ranges: Measurements and application of empirical group contribution method[J]. Microporous and Mesoporous Materials, 2015, 217: 1-5.
[11] Ma S, Sun D, Simmons J M, D.Collier C, Yuan D, Zhou H C. Metal-organic framework from an anthracene derivative containing nanoscopic cages exhibiting high methane uptake[J]. Journal of the American Chemical Society, 2008, 130(3): 1012-1016.