A Review of the Application of Metal-Organic Frameworks in the Absorption, Storage and Release of Methane

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www.jrasb.com || Vol. 2 No. 6 (2023): December Issue

ABSTRACT

Natural gas, which mainly consists of methane, is a good fuel for vehicles. Metal-organic frameworks (MOF) have attracted much attention as a new group of adsorbent materials in natural gas storage. MOF structures form various networks by connecting secondary structural units composed of metal ions and organic binders. These regular materials have high porosity and have high design capabilities. This feature has made MOFs suitable for special applications in trapping and absorbing various materials. The investigation of these materials has focused on the absorption of pure methane, although natural gas contains a small amount of larger hydrocarbons such as ethane and propane, which have greater absorption than methane. This Manuscript presents an overview of the current state of the metal-organic framework for methane storage.

Keywords- metal-organic frameworks; storage; methane; Porosity.

I. INTRODUCTION

Crystalline solids with molecular-sized spaces have attracted the attention of chemists due to their unique surface adsorption, ion exchange, and catalytic properties. These solids can be divided into three categories according to the type of chemical bond that forms their skeleton: a- mineral zeolites (covalent bonds), b- layered compounds and ionic crystals (hydrogen bonds or ionic bonds) and c- frameworks. Metal-organic (MOF) and porous coordination polymers. Recently, a new class of porous coordination polymers, which are also called metal-organic frameworks, have been developed and have surpassed the previous fields of porous materials. The structure of MOFs is made of intermediate metal ions and organic ligand groups and is expanded by coordination bonds, π-π stacking and hydrogen bonds. Coordination bonds form a rigid skeletal structure, while π-π stacking

and hydrogen bonds give the structure a soft nature. Therefore, MOFs are divided into hard groups according to their constituent bonds. These materials are completely organized, have high porosity and have a completely designable structure. Its preparation in mild conditions and choosing a specific combination of individual molecular units creates networks of the desired findings[1]. Among the disadvantages of these materials, we can mention the difficult conditions of single crystal formation of their samples, which makes it difficult to identify these materials. Due to the high ability of structural engineering and very high specific surface area, MOFs are used in gas separation and storage [2], drug delivery systems[3], Separation of various ions or molecules[4], catalytic applications[5, 6], color removal and membrane-based processes[7] are highly used. Metal-organic frameworks are produced in various ways. Mechanical method and hydrothermal method are among

the most important of these methods. The spatial method refers to the ability to create metal-ligand chemical bonds by abrasion. Not using solvent in the mechanical method or reducing the amount of solvent is one of the advantages of this method. Therefore, this method is known as a green method for making covalent bonds. For example, the mechanical method allows the formation of crystals that are insoluble in most organic solvents. The difficulty of analyzing the product and the lack of obtaining a single crystal product are among the disadvantages of this method. Of course, these problems can be solved to some extent by the methods of solid state NMR analysis, molecular simulation and X-ray powder diffraction. In the hydrothermal method, metal salt and organic ligand are poured into the autoclave in specific proportions and factors such as concentration, reaction time, and speed of heating and cooling of the reaction medium are investigated in the formation of the desired product. Analytical analysis of the product and the lack of obtaining a single crystal product are among the disadvantages of this method. Of course, these problems can be solved to some extent by the methods of solid state NMR analysis, molecular simulations and X-ray powder diffraction. In the hydrothermal method, metal salt and organic ligand are poured into the autoclave in certain proportions and factors such as change, reaction time and speed of heating and cooling of the environment, the reaction in the formation of the desired product are investigated. The high probability of producing a single crystal product is one of the advantages of this method. In another method, the metal salt dissolved in the desired solvent and the organic ligand are reacted in specific proportions with reducing agents. The production of macrocrystalline product is one of the disadvantages of this method, which makes it difficult to identify the product. This problem can be solved by analysis methods such as X-ray powder diffraction. Common laboratory methods are used to check and prove the structure of metal-organic frameworks. As an example, the X-ray powder diffraction method is used to check the degree of crystallinity of the formed structures. By scanning electron microscope, the shape and size of formed nanoparticles are checked. Another method that has been known for several decades is to determine the specific surface area of porous particles by surface absorption of nitrogen gas near the temperature of liquid nitrogen. The physical absorption of a layer of nitrogen gas makes it possible to calculate the surface area by plotting the pressure graph in terms of the rising gas. In recent years, many advances have been made in the rapid determination of specific surface area, pore size distribution, pore volume, and overall greater ability to identify the shape of nanostructures. Methods such as infrared spectroscopy, elemental analysis and energy dissociation spectroscopy are also effective in identifying porous products as well as possible.[4, 5, 7].

II. THEORETICAL PART

2.1 Gas storage and principles of ANG storage

Safely stored and transported gases in these high pressure compression of desired gases (for example methane and hydrogen) at room temperature. This process consumes a lot of energy and is not safe for transportation. A solution for this issue is to use solid absorbents as carriers. Porous compounds such as zeolites and carbons are also active in this area, but each has its own. One of the most important limitations is the low gas absorption capacity. Porous coordination polymers, which have a large percentage of micropores of the same shape and can be designed, are introduced as the best candidates for gas absorbents. The gas storage potential is measured through adsorption isotherm studies, but the attraction in the development of single-crystal adsorbents leads to structural studies of gas-filled lattice compositions. Such structural studies are important for identifying suitable bonding positions for various gas molecules. When a gas molecule is transferred from the gaseous phase to a solid surface with surface cavities and sticks to the solid surface, gas surface absorption has occurred. This case is contrary to gas absorption in which gas molecules are transferred to the solid phase[8-10].

2.2 Gas storage mechanism in MOFs

There are two ways for a gas to interact with a solid. First, chemical absorption in which gas molecules form a chemical bond with the solid surface, and second, physical absorption in which gas molecules interact with the solid surface without forming a covalent bond. The process of chemical absorption allows the absorption of a very high volume of gas molecules in environmental conditions, but the release of this gas from the absorbed surface requires energy. On the other hand, since the interaction between gas and solid is weak in the adsorption process, the absorbed volume is usually small and occurs only at low temperatures. Therefore, each of these two processes has its own disadvantages, and as a result, to achieve optimal gas surface absorption in a solid adsorbent, porous compounds are needed, which show the interfacial strength of interactions. In the case of coordination polymers, porosity is one of the unique characteristics that has been widely studied. The lack of a clear definition of the term porosity has caused a large number of coordination polymers whose empty holes are filled by solvent or counterions to be reported as porous, although seeing the holes is not a proof of the composition's porosity and proves its porous property. does not Holes are defined as open spaces through which fluids or gases can pass [8, 11]. Therefore, in order for a substance to be called a porous compound, in addition to seeing a structure, its porosity must be proven through isothermal gas absorption-desorption studies. The holes that exist in porous compounds are divided based on the size of the hole [12]. Macroporous compounds have a hole diameter of more than 50 nm, mesoporous compounds have a diameter between 2 and 50 nm, and

microporous compounds have a diameter of less than 2 nm. Most of the porous coordination polymers are in the mesoporous and microporous pore size range. The adsorption of guest molecules on the solid surface plays an important role in determining the properties of porous compounds. This adsorption is controlled not only by the interactions of the guest molecules with the surfaces, but also by the shape and size of the pores. There is no fundamental difference between adsorption by micropores and adsorption by a single surface, and both are well expressed by the BET equation. There are six types of surface adsorption isotherms based on Abopaque's classification of isotherms for surface adsorption, which show the relationship between the structure of the porous composition and the type of adsorption

Some reports have been published about the surface adsorption processes in zeolites and activated carbon with cylindrical holes[13]. On the other hand, the shape of the holes of porous coordination polymers is basically not cylindrical, because in terms of crystallography, they have shapes such as square, rectangular, They are triangles, hexagons, etc. New surface absorption isotherms for microporous coordination polymers have been obtained, which indicates their uniform microporous nature. If a large number of conformational transformations occur, a multistep surface adsorption isotherm will be observed. Structural flexibility along with structural transformations can also be done in porous inorganic compounds [14, 15].Structural change in inorganic networks is not as important as coordination polymers, because in inorganic porous compounds, the frameworks are very strong, which is obtained from the strong bonds between the metal ion and the ligand. The specific surface area is one of the most important factors for evaluating the cavity capacity and is related to the number of molecules that are in direct contact. The accessible specific surface area has increased from a few hundred square meters per gram, which is related to zeolites, to large values of 7000 m2/g in MOFs [16, 17]. Computer calculations show that a specific surface area of up to 14,000 m2/g is accessible in MOFs. These values are much larger than the ideal values related to carbon compounds (2630 m2/g). Basically, the narrowing of the cavity walls provides a higher surface area. In the case of mineral zeolites, the cavity walls are made of a large number of silicon, oxygen and aluminum atoms, while coordination polymers have a narrow wall with a diameter of one carbon atom. In general, nature tries to avoid any empty space. Any empty spaces or cavities created in the preparation of coordination polymers are usually filled by guest solvent molecules or counterions. The result is the formation of a network that is completely compact and in which there is no empty space. Sometimes there is also a network depression in which any empty space is filled. Porous composites can be obtained by carefully choosing network components to create different geometric shapes[18]. During the last ten years, metal-organic frameworks, which are also known as a subgroup of porous coordination polymers, have attracted wide attention[19]. This great attention and interest is not only due to the diversity and interesting geometric shapes of these compounds, but also their excellent properties and promising applications such as gas storage or separation, molecular separation from gas and liquid mixtures, catalytic processes, enantiomeric selectivity and sensing properties. They are the ones that have been taken into consideration[20]. They can also be designed as multifunctional materials with excellent physical properties such as magnetic, luminescence and optoelectronic properties[21], although most of these applications depend on the ability of MOFs to play the role of hosts for certain molecules. The structures of MOFs, which have been investigated so far as microporous materials with very high porosity, have openings of adjustable size and have fully defined sites for the absorption of guest molecules. The structure and characteristics of MOFs depend on two factors: raw materials and manufacturing process. In the case of raw materials, two metal ion agents or metal clusters on the one hand and organic binders on the other hand, which are called secondary structural units (SUB), are of interest. In coordination chemistry, the ligand acts as a programming species whose information is encoded and read by the metal ion. Depending on the metal atom and the organic composition, one, two, or three-dimensional structures may be created[22].

2.3 Examining excess, absolute and total absorption

In examining the adsorption of methane gas by porous materials, the first step is to measure and draw the adsorption isotherm. Two different methods that are used to measure the amount of absorption are the volume measurement that is done by using special devices and the other is the weight method that is done by using a micrometer scale. In the implemented reports, the terms excess absorption, absolute absorption and total absorption are used to describe absorption capacity[23]. Excess absorption is related to the amount of gas that interacts with the framework, while absolute absorption is both the amount of gas that is interacting with the framework and the amount of gas that is settled inside the framework without gas-framework interaction. includes. Total absorption also refers to the total amount of gas in the cavities. The amount of excess surface absorption is measured experimentally. Since the experimental methods used cannot determine the boundary between the absorbed and non-adsorbed gas phase, as a result, the absolute absorption capacity cannot be accurately determined. In the case of gas absorption and desorption, the amount of total absorption is one quantity higher than the excess absorption.[23, 24]

2.4 Weight and volume absorptions

Gas absorption capacity can be expressed both by weight and volume. Weight absorption capacity is the mass of gas absorbed per unit mass of absorbent, while volumetric absorption is expressed as the volume of gas

absorbed under standard conditions over the volume of absorbent. It seems that the volumetric absorption is the most suitable quantity to show the storage capacity of the adsorbent, especially in the application of ANG for the space industry. Measurement of gas absorption usually results as gravimetric absorption. In order to calculate volumetric absorption, various densities of absorbent material such as crystal density, accumulation density, and density obtained from mercury intrusion porosimetry method are necessary. The ideal crystal density of MOF frameworks is used to convert the weight absorption capacity to volume absorption, because their crystal density is easily available and shows the maximum volume capacity of MOF gas storage that it can have in practice. The crystal density of MOF is the upper limit of the bulk density and it cannot be obtained for MOF powder. Based on the low density of MOF accumulation, it reduces their volume storage capacity [25, 26]. Also, the use of mercury infiltration method in calculating the porosity can cause problems in the obtained measurement value due to the dependence of volume capacity on pressure. Permeant mercury is removed. In this method, the porosity of the target sample can be measured from the amount of mercury vapor absorbed by the porous adsorbent[27].

2.5 Storage and release capacity

Methane gas storage adsorbents should not only have the highest absorption capacity, but more importantly, they should also show high desorption capacity. Absorption capacity or efficiency capacity is defined as the amount of gas released when the pressure drops.It is clear that the desorption capacity is less than the absorption capacity. In other words, the absorption capacity depends on the conditions used to release the gas from the adsorbent. For example, the use of heat and vacuum in release conditions increases gas absorption. Also, the amount of absorption capacity is sensitive to the heat effects produced due to charging and discharging. If the absorption heat released by the storage system is not removed, the amount of absorbed methane gas will be low. If the heat of absorption is not supplied during discharge, the amount of gas remaining in the absorber will increase[28]. A possible proposed method to solve this problem involves inserting the absorbent bed inside a confined phase of substances that have a relatively high heat of fusion at ambient temperature. These materials will be able to absorb the absorption heat released during the charging process and supply it during the discharging process. Absorption volume capacity is very important for natural gas vehicle drivers. In the use of MOFs, the continuous desorption capacity is calculated, because when isothermal conditions are considered instead of experimental conditions, the amount of methane gas absorbed at high and low pressure of the working pressure range is different. Considering that it has been determined that a sufficient pressure difference must be provided for methane gas to flow with a suitable flow rate from the absorber to the engine, and that this pressure for natural

gas for use in engines designed with internal combustion is about 5 times obtained, the lowest size For the working pressure range, 5 bar pressure is considered[29]. The pressure of 35 or 65 bar can be considered as the lowest working pressure for methane injection in the porous framework, because this pressure can be provided by a single or two-stage compressor. It is clear that in order to maximize the adsorption capacity of the adsorbent, the amount of stored methane should reach the maximum at 65 bar, and at the same time, the amount of stored methane should reach its minimum value at 5 bar. In other words, it is better that the adsorption and desorption pressure of methane from the porous framework is 65 and 5 bar, respectively.[29, 30]

III. RESULTS AND DISCUSSION

Among other hydrocarbons, methane has the highest degree of hydrogen compared to carbon, and as a result, it has a higher octane number. Therefore, burning it emits the smallest amount of carbon dioxide per unit of heat released. Meanwhile, the relatively low volumetric energy density of methane has caused severe restrictions in its use. Therefore, it is necessary and necessary for large-scale use of safe measures and efficient technology to achieve the appropriate volumetric energy knowledge. So far, four different methods have been proposed for natural gas storage: liquefied natural gas (1) (LNG), compressed natural gas (2) (CNG), absorbed natural gas (ANG) and hydrous natural gas (NGH). CNG gas is stored as a supercritical liquid at room temperature and pressure of 200-300 bar inside steel cylinders. The main disadvantages of CNG storage are the need for high-pressure, expensive and heavy storage tanks, expensive and multi-stage compression facilities, as well as potential safety concerns. LNG gas is obtained by cooling method and is kept as a boiling liquid at a temperature of 112 K and a pressure of 100 kPa. Despite the fact that LNG has a high energy density, it requires special containers and low temperature storage. In addition, due to the increase in the pressure of the cooling fuel tank, the discharge of this gas must be done periodically. Also, the stored gas cannot be separated and released from water only by reducing the pressure. ANG technology is a more prosperous technology and requires relatively lower pressures than what is required for CNG storage. [29]This reduction in pressure has enabled the use of light, cheap, single-stage compressor tanks and has also simplified refueling at home. The development of efficient adsorbent materials is the key to the success of ANG technology. Many different porous materials with the ability to store methane gas have been widely investigated. Early studies were mainly focused on traditional porous materials such as zeolite and activated carbon. Despite the relatively high density of accumulation, the low amount of micropores and also the extreme hydrophilicity of zeolites have limited its use for methane gas storage. Similarly, in the case of activated carbon, the difficulty in adjusting the

shape and size of the pores causes limitations. The point that needs to be mentioned here is that MOF gas storage tanks have the advantage over other tanks such as CNG or LNG that there will be no explosion if the tank bursts due to an accident. . For this reason, these tanks have a high degree of safety[4, 31].

Gas absorption capacity can be expressed both by weight and volume. The weight absorption capacity is the mass of absorbed gas per unit mass of the absorber, while the volumetric absorption is expressed as the volume of gas absorbed under standard conditions over the volume of the absorber (cm^3 (STP) cm^{-3}). Adsorbents for storing methane gas should not only have the highest absorption capacity, but more importantly, it should also show a high desorption capacity. Absorption capacity or efficiency capacity is defined as the amount of gas released when the pressure drops. In many ANG studies, measuring the amount of stored gas from methane gas has been used. However, in real systems, natural gas, which is a complex mixture of various gases, has methane gas as a storage fuel. The US Energy Agency (DOE) calculates the amount of energy stored in a CNG capsule at a temperature of 298 K and a pressure of 250 bar as 350 cm3 (STP) cm^{-3}, or (0.5g[CH4]/g), and the energy obtained from a capsule CNG has been considered equal to 9 MJ/L (megajoules per liter). Typically, methane adsorption in zeolites is less than 100 cm3/cm3 (standard temperature and average pressure, in terms of volume of methane to adsorbent volume, (STP: T = 273.15 K, P = 101.325 Pa), while many carbon adsorbents absorb about cm3/cm3 They show 50-160 [26]. [The maximum methane adsorption capacity reported in MOFs, (cm3 (STP) cm-3270), at a temperature of 298 K and a pressure of 65 bar, is much lower than the final target set by DOE, cm3 (STP) cm-3350. However, MOFs are very promising porous adsorbents for methane gas storage. In addition, it seems very difficult to achieve the DOE targets for volume capacity cm^3 (STP) of 350 cm^{-3} and weight capacity of 0.5 g[CH4]/g) at the same time with a metal-organic framework. It has been well proven that the weight storage capacity of methane (cm^3/g) is dependent on the volume of the cavity or the surface area of the framework [31].

A hypothetical framework with a BET surface area of 7500 m^2/g and a pore volume of 2.3 cm^3/g and a structural density of 0.28 g/cm^3 can be the new DOE mass target for absorbing 0.5 g of methane per gram of adsorbent.[32]

The results showed that the volumetric absorption of HKUST-1, UTSA-76, NOTT-102 and also NU-111 significantly increased from 267, 257, 237 and 206 at 298 K to 301, 301, 280 and cm^3 (STP) cm^{-3}, respectively. reaches 284 at 270 Kelvin. The capacity of cm3 (STP) cm-3301 is very close to the target of cm3 (STP) cm-3350 set by DOE. In addition, NU-111 shows a weight absorption above 0.5 g/g at 270 K and 65 bar, which shows good promise to achieve the new goal of weight absorption. It shows an impressive high work

capacity of 239 cm-3 (STP) at 270 K, which is 34% higher than 179 cm-3 (STP) cm-3. These exciting results show that lowering the storage temperature to 270 K may be an effective way to bring the methane gas storage capacity by MOF closer to the DOE targets.

These results give us more motivation to systematically evaluate and compare their methane storage capacity between 270 and 298 K in order to achieve a comprehensive understanding of methane storage by MOF materials. The structures of MOFs NU-111 and SOC-MOF-1-Al, which have a BET higher than 4900 m^2/g, a weight storage capacity of 0.5 and g(CH_4)/0.51, show that they have actually reached the new goal of DOE. Additionally, we found that the total gravimetric absorption of MOF materials below 65 bar and 270 K is essentially proportional to the BET surface area or pore volume. This means that the importance of larger porosity will be equal to higher weight absorption[29, 32].

MOF structures with Lewis base nitrogen sites (UTSA-75-79) have higher volumetric absorption (301-289) than (298cm3 (STP) cm-3) NOTT-101 It shows. These results show that optimal cavities and functional groups are still useful for achieving high volumetric absorption at 270 K. Among the studied MOFs, HKUST-1 and UTSA-76 showed the highest overall methane absorption capacity with a value of 301 cm^3 (STP)cm-3. The cavity space is optimized and the introduction of functional groups inside MOFs can still be used to achieve volume storage of methane at 270 K. In the case of bulk adsorption, porosity is still the main factor and a MOF with a BET surface area above 4900 m^2/g can achieve a weighted adsorption target of 0.5 g[CH_4]/g at 65 bar and 270 K. The more important point is that the working capacity of the frameworks (the most important factor for the application of methane absorption) at 270 K is purposefully increased by increasing the pore volume, which has led researchers to obtain MOFs with working capacity and volume and weight capacity that are It is necessary to store methane.For example, the high pore volume NU-111 and MOF-177 frameworks have work capacities above 239 cm3 (STP) and 230 cm-3 It also shows a very high weight absorption capacity, 0.5 and 0.43/g[CH_4], respectively. This work capacity is much higher than the maximum value reported at 298 K cm3 (STP) cm-3 (197). If the final release temperature of methane is 298 K, due to heating during the transfer time at 5 bar, the working capacity of NU-111 and MOF-177 can be increased to 257 cm3 and 236 cm3 (STP), respectively. It is worth mentioning that these values are based on 25% empty MOF tank volume. Therefore, the given values compared to the target value of DOE, only include a tank with 75% MOF. Although initially it is useful to check the performance of various adsorbents at 35 or 65 bar pressure for methane gas storage, but in the release stage in an all-storage methane gas engine is not used because a minimum inlet pressure is required to drive the methane gas stream from the absorber to the

engine. In this case, the concept of desorption (delivery) capacity, which is also called work capacity, is defined as the desorption amount of methane gas, which is released by reducing the absorption pressure to the minimum inlet pressure. In practical applications, the working capacity is more important than the storage capacity, because it determines the driving range in gas vehicles. Selection of high absorption pressure and low working pressure are two key factors in determining working capacity. In general, two types of pressure (35 and 65 bar) are considered as absorption pressure, because they are the maximum pressure values that can be provided by cheap single-stage and two-stage compressors, respectively[33, 34]. In addition, two higher pressures of 80 and 100 bar have been considered by several research groups as the upper limit of absorption pressure. On the other hand, taking into account the fact that an inlet pressure of 5 to 10 bar is required to drive a sufficient flow of methane from the fog absorber side to the engine in the gas burner itself, the maximum pressure referred to as the minimum absorption pressure is 5 or 5.8 times.[34]

Heavy hydrocarbons are preferentially absorbed as soon as they are charged, and as a result, the methane storage capacity decreases. On the other hand, as soon as these components are absorbed, they are not completely discharged. Therefore, to store natural gas in a porous absorber, a protective device such as a guard bed must be placed at the entrance of the tank. The protective bed removes these components as well as other destructive impurities from the natural gas flow that is flowing as fuel, and then returns them to the primary fuel flow by means of internal vapors. Usually, with a simple but necessary industrial process, MOFs are compressed in the form of powder inside a tablet or monolith under external pressure to increase its density. This is while the properties of networks and even their crystal structure may be affected by this process. Compression at a pressure less than 1.1 gigapascal cannot significantly affect the absorption kinetics and crystal structure. The obtained MOF tablet shows the same weight capacity of methane absorption as the first synthesized MOF powder.

Although methane is the main component (96%), commercial natural gas is a mixture that includes many other impurities such as ethane (3.3%), propane (0.7%), and carbon dioxide (0.5%) [31]. These impurities will definitely have harmful effects on the absorbent storage capacity . For example, despite partial fractures in natural gas, heavier hydrocarbons and carbon dioxide can be absorbed by the adsorbent[35]. This will reduce the capacity of the tank in subsequent charges. The results show that the molar fraction of methane in the NU-125 frame decreases from about 88% to about 50% in 5.8 bar in the first to 200th discharge of the frame cylinder [33]. In addition, very small amounts of other impurities such as S2H, H2O, O2, and 4C hydrocarbons may gradually contaminate the methane absorption sites or destroy the framework over a long period of time. To minimize the effects of these impurities, a protective bed is placed at

the entrance of the ANG tank to purify the natural gas and allow only methane to pass into the tank as much as possible In addition, improving the thermal and chemical stability is also very important to make the adsorbent resistant to the negative effects of existing impurities and as a result increase the storage capacity and service life of the adsorbent[36, 37].

IV. CONCLUSION

From the presented information, it can be concluded that the storage of methane gas in porous solid materials, including MOFs, is very important. High biocompatibility, the ability to obtain nano-cavities of various sizes, the ability to absorb and de-absorb various gases, drugs and chemicals, and the ability to change the nano-cavity sizes of various MOFs have made these porous materials very important. Today, extensive studies are being conducted on the absorption and desorption of methane in these materials. The United States Energy Agency estimates the amount of energy stored in a CNG capsule at a temperature of 298 Kelvin and a pressure of 250 bar equal to (STP) cm-3 350 cm3, or (0.5g[CH4]/g) and the energy obtained from a CNG capsule equals 9 MJ/L is considered. Metal-organic frameworks absorb methane gas in the first charge of the tank at a temperature of 298 K and a pressure of 65 bar, that is, a pressure of about a quarter of CNG tanks, close to 86% of a CNG gas tank. Meanwhile, only 75% of the tank is filled with MOF and 25% of the tank is empty. Therefore, the use of MOFs as methane gas storage is of great importance.

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