Metal-organic Frameworks for Natural Gas Storage

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Abstract. Methane, as the transitional fuel, still emits CO_2 during combustion but less than gasoline. Developing new adsorption materials can improve the efficiency of methane storage and then achieve the goal safely and economically. Metal-organic Frameworks (MOF) with the advantage of high porosity and adjustable pore surface area, are considered one of the promising materials for natural storage. Here, this article briefly introduces the preparation of MOF and mentions some details during this process such as the solvothermal technique, and electrochemical synthesis methods, covering some defects in the preparation process. Many kinds of materials have different volumetric adsorption rates and mass adsorption rates compared with DOE standards. In chronological order, this paper lists some typical materials and discusses specific structures inside MOFs corresponding to relative performance. Changing or adjusting organic ligands can improve capacities so that a series of MOFs are designed like MFM-132, MFM-112 and MFM-115. In addition, the factors influencing adsorption rate are also considered including internal factors, surface area, porosity, structure, adsorption isotherm and external factors, pressure, and temperature, respectively.

Keywords: metal-organic frameworks, natural gas, adsorption, synthesis, factors, types

1. Introduction

The amount of usage of natural gas is growing significantly. In the past few years, natural gas is widely used in tons of countries due to it is very clean and environmentally friendly. In the overall market, there's not as much demand for natural gas as there's for oil. The reason why for this phenomenon is because of its low energy content and in this case the price for transporting is quite difficult and expensive. The amount of natural gas used varies across industries. Natural gas emits less carbon dioxide than all other petroleum-derived fuels, making engines also beneficial in terms of greenhouse effects. However, storage and transportation of natural gas are closely linked to fires and explosions, which is why natural gas is not as widely used as fuel. Compressed natural gas (CNG) can solve the problem of natural gas transportation and storage, and also can be settled by liquefied natural gas (LNG). However, these two problems also have drawbacks. Most obviously, both CNG and LNG are very expensive, CNG can reduce the distance a car can travel, and the CNG method requires the use of refueling stations, which have not been widely used so far. LNG on the other hand requires low temperatures and protection against evaporation. Therefore, the situation is very harsh, which also leads to high costs. Therefore, only, can be used on trucks, so it has a small range.

Later, it was discovered that the absorbed natural gas (ANG) was stored by adsorption, which was found to be very efficient. One of the most promising and safe ways to store and transport natural gas must be adsorption technology, due to physical adsorption in microporous sorbents at moderate pressures, which can dramatically increase the density of methane to the characteristic values of a liquid. A series of MOFs were designed, such as MFM-112, MFM-115 and MFM-132 [1]. Between 5 and 80 bar, MFM-115 shows a particularly high ability to deliver CH_4 at room temperature, making its own outstanding performance of CH_4 storage. Strongly linked networks with a series of ultra-high porosity have been reported due to their extraordinary adsorption capacity[1]. Importantly,

desolubilized MFM-115 shows a particularly high deliverable CH_4 capacity from 5 to 80 bar at standard (room) temperature, for example, 208 cm^3/cm^3 (v/v), making MFM-115 become one the best-performing porous materials for CH_4 storage [1].

2. Preparation for MOFs for Natural Gas Storage

2.1 Aqueous (solution) Thermal Synthesis Method

Preparation of MOF is very important. The adsorption capacity and mechanical and thermal stability characteristics of MOFs all depend on the preparation of MOFs. In 1995, hydrothermal synthesis was completed for the first time, and $NO_3(H_2O)$ appeared. A standard procedure for preparing MOFs is to combine metal salts and organic ligands in solutions in water or organic solvents (DMF, ethanol, pyridine) are mixed. Subsequently, a slow diffusion process (MOF-2) was proposed, which can obtain MOF crystals that are very large but sustained for several weeks, therefore, it is considered inefficient. The hydrothermal synthesis of MOFs is feasible for the reaction system in which the organic linker is partially dissolved in water at high temperatures. The synthesized MOF-14 was synthesized by solubilizing the organic linker using an organic solvent to promote the synthesis of crystalline MOF materials [2].

In water or organic solvents, mixing metal salt solutions and organic ligands are standard procedures for the preparation of MOF. Triethylamine is used to speed up the reaction under some circumstances. The building agent can use 101 kinds of water or organic solvents. Then, an external shock is applied to the reaction mixture to induce the self-assembly of MOFs. Then, an external shock is applied to the reaction mixture to induce the self-assembly of MOFs.

2.2 Sonochemistry

Compared with the conventional self-consistent synthesis method, the sonochemical method has uniform nucleation and shorter crystallization time. The production of MOF-5 by saturated acid and zinc nitrate solution was studied by sonochemistry by Son's Group. Based on the sonochemical synthesis of C_5H_9NO (NMP), the MOF-5 with 5-25 μm and high-quality, the produced materials' physicochemical properties can replace those conventional thermally synthesized crystals. Likewise, high capacity MOF-177, and Zn_4O-$(BTB)_2$, were also produced by the sonochemistry method with the NMP. The yield of the resulting MOF was as high as 95.6%, and the CO_2 adsorption capacity below 30 bar was higher than that of the self-synthesized MOF-177.

2.3 Microwave-assisted Solvothermal Synthesis

The microwave-assisted self-consistent synthesis method utilizes microwaves to generate nanoscale crystals, which means high-quality MOF crystals can be produced rapidly in one minute. By constructing three main MOFs, namely IRMOF-3, IRMOF-1 (MOF-5), and IRMOF-2. The application of microwave radiation in the conduction of MOF materials was studied. The resulting crystals of MOF exhibited the same cubic morphology with remarkably uniform particle size distribution in the micrometer to the nanometer range, thanks to the controllable nucleation process of this new synthesis method. Centrone's group also recently reported the method about use microwaves to assist the synthesis, which includes MIL-47 and other 6 types of MOFs with vanadium.

3. The Factors of MOFs for Natural Gas

Many factors influence the storage of NG, for example, include the MOF material itself conditions and other controllable environmental circumstances.

3.1 BET area

Compared with other porous materials, the BET area of MOFs is higher (experiment value is 7140 m^2/g, theoretic limit is 14600 m^2/g) [4], and the low surface area of zeolites is less than 1000 m^2/g

[5]. Same as H_2 storage, under certain conditions (for example, low temperature and high pressure), storage amount and the surface area of MOFs are proportional [6,7]. Otherwise, for instance, at the low pressure, which is less than 100 bar, despite the surface area of MOF-5 30% greater than Ni_2(dobdc), the volumetric adsorb is lower [5]. Therefore, the researchers gave up zeolites relatively with low surface area and paid more focus on MOFs study, because they need high capacities material to store CH_4 [5].

3.2 Porosity

Because of the weak interaction between the framework and adsorbed CH_4, therefore the strength of interaction might be regulated and controlled by the shape and pore size of MOFs, in addition, the interaction forces between adsorbed methane can also be strengthened [8]. According to the study, the places that have interaction of van der Waals between frameworks and natural gas (methane) molecules is the moderate site of methane interaction in MOFs [8]. On the other hand, there is the extensive porous structure of adsorbent materials, which leads to high capacity, high selective, gas separation, other stability and mechanical strength. But the porosity of MOF materials is also related to the diffusion rate of gas molecules in MOF pores, which decided the interaction between the pores' surface and the gas molecules [4]. For example, inside the ultramicroporosity (less than 0.7nm), there was a remarkable effect of the molecular sieve, as the gas kinetic diameter molecule increased, the rate of diffusion significantly decreased [9]. However, suitable porosity is a kind of essential factor in methane storage amount, high porosity determined the value and potential of MOFs. This shows the pore size of MOFs needs to be in a certain range, indeed, it was illustrated that with a 7.6 Å diameter, at 35 bar and 25 ℃, the methane can be accommodated in two layers [5].

3.3 Metal ions

As known, the metal-organic frameworks are constructed by an inorganic metal center and linked frameworks. There was a special electrostatic interaction that happened at open metal sites (OMSs) in frameworks between methane and MOFs [8]. The significant uptakes of methane of M-MOF-74 (high densities of OMSs) are because of the powerful sites of interaction, which metals include Mg, Mn, Co, Ni, and Zn [8]. If the electrostatic interaction force becomes stronger, the MOF materials are more capable of adsorbing CH_4, which is the result of metal ions. For example, at 35 bar, 298 K, the Ni-MOF-74 adsorption loading is 230 cm^3/cm^3 [8], this is due to the Ni^{2+} ions having the strongest polarizing ability, which can get high electrostatic interaction compared to the others [8]. However, in a series of MOFs, different structures determined the unlike capacity and performance, and use to store natural gas must select a suitable MOF structure. For instance, when the pressure decreases to 5 bar, the electrostatic interaction between the metal ions and frameworks leads to a portion of natural gas still staying at the frameworks, which significantly limited the M-MOF-74 working capacity [8].

3.4 Pressure

The importance of pressure control in adsorption experiments is self-evident, different pressure will influence the accuracy of the experimental results. Based on the study, the data demonstrate a clear phenomenon is that the capacity of MOF to absorb natural gas will increase according to the continuous rise of pressure. As shown in a MOF, MIL-101(Cr) at 298 K, which can observe the capacities are proportional to the pressures, there are approximately at 5 bar is 30 $cm^3\ cm^{-3}$ [10], at 35 bar is 150 $cm^3\ cm^{-3}$ [10], at 65 bar is 215 $cm^3\ cm^{-3}$ [10]. However, as shown in figure 1, the isotherms of MOFs always shows this theory, the amount adsorbed always increased by relative pressure, although some of the isotherms tends to flat achieve a certain pressure (type I, IV, V), which is a kind of way can show the relationship between pressure and amount adsorbed by isotherms.

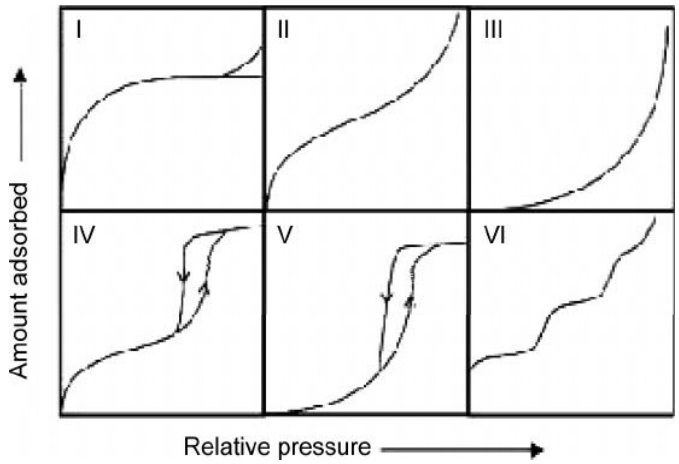

Fig. 1 The IUPAC classification of adsorption isotherms [11].

3.5 Temperature

The temperature of the experiment environment is also related to the whole process. According to the data, at standard pressure and temperature, the natural gas's density of volumetric energy is 0.04 MJ L^{-1}, which is very low in a gaseous state [5]. In fact, during the process must guarantee the independent variable and dependent variable are distinguished, controlling the different variables is an essential stage to get reliable information about the amount. However, temperature is an important element, such as one of the MOFs, HKUST-1, temperature is critically related the its final morphology of it, which decided the amount of adsorption [12]. On another hand, based on the same pressure, higher temperatures can increase the amount of natural gas adsorption, and different temperatures of measurement lead to diverse results. The temperature increase will lead to the amount of adsorbed growth [12]. Despite this conclusion, it is generally accepted that storing natural gas for industrial application is always done at suitable temperatures and pressure (298 K and 35 bar) [5,8,12].

4. MOFs for Natural Gas Storage

4.1 HKUST-1

HKUST-1, $C_{18}H_6Cu_3O_{12}$, is also called MOF-199 as a copper-based MOF. It has Cu^+ cation exposed as the strong binding site. Figure 2 provides the view of an additional binding site located in the four windows of the octahedral cage, filled by the Cu^+ cations simultaneously. Its BET-specific surface area is 1100-2200 m^2 [13].

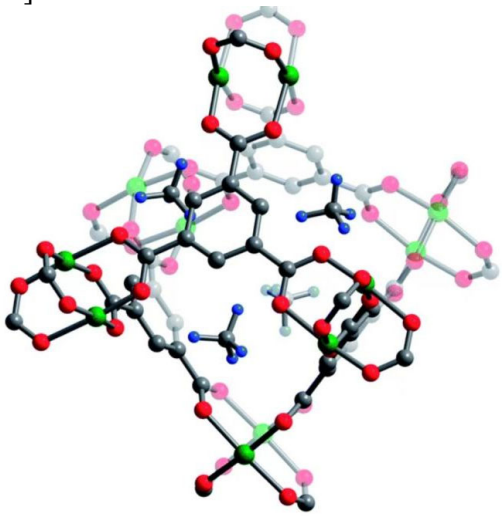

Fig. 2 The four windows of octahedral cage [13].

Briefly compared with nickel, HKUST-1 has a similar volumetric adsorption rate to nickel at 35 bar but due to close interaction between binding sites and CH_4 molecules, it has a higher gravimetric adsorption rate [13]. However, Figure 3 shows that HKUST-1 still did not reach the target set by DOE, the mass adsorption capacity of the material for methane gas reaches 0.5 g CH_4/g adsorbent, and reaching 263 cm^3CH_4/cm^3 adsorbent for volume adsorption capacity, the volume adsorption capacity 270cm^3/cm^3 met the requirements of a single index, but the mass adsorption capacity was only less than half of the targets [14].

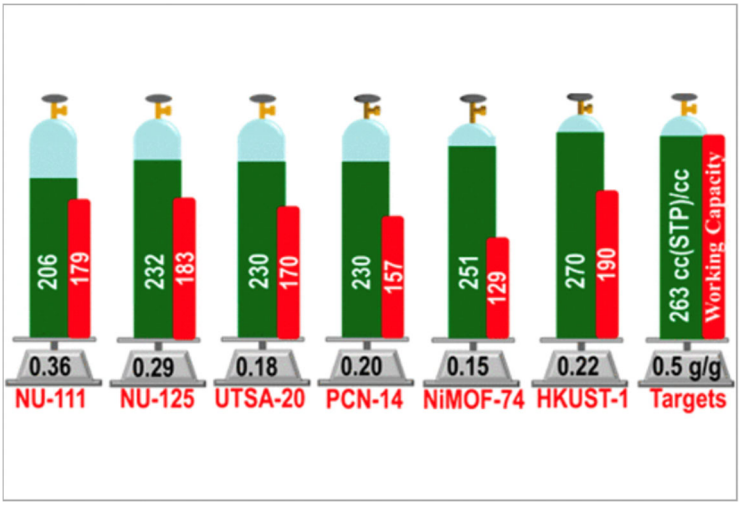

Fig. 3 The comparison with DOE targets [2].

4.2 NU-111 and NU-125

A hexa-carboxylic acid linker (LH_6) and Cu^{2+} salt produce the NU-125, which is corresponding to 86% of CNG. Its capacity of delivery is between ~5 to 8 bar and ~60 to 70 bar, which is very high. In addition, NU-125 is produced in high yield and vigorous enough to store or release natural gas repeatedly [15]. In 2013, Omar K. Farha's research group from Northwestern University found the linear ship between CH_4 adsorption and BET-specific surface area under the condition of 298 K 6.5 MPa through six types of MOFs. Compared with DOE targets, NU-111 and NU-125 had fair performance, which NU-111 has reached the 75% mass adsorption capacity and volume adsorption capacity target at 300k when the adsorption at 65 bar raises to 0.5 g g^{-1} and 284 cm (STP) per cm^3 [14].

4.3 MFM-115

MFM, the abbreviation of the multi-functional module, is also used in methane storage. MFM-115, with hexarboxylic acid as an organic ligand and binuclear copper ions as a structural unit, is cubic packing structural porous material. Due to its optimized pore structure, natural gas molecules can be packed tightly in their voids. 2017, MFM-115, has higher adsorption capacities than any known MOFs under the condition of pressure dropping from 85 atmospheres to 5 atmospheres. At room temperature, MFM-115 had shown outstanding methane uptake of 256 cm^3/cm^3 at 80 bar. What is more, between 5 atmospheres to 80 atmospheres, MFM-115 displays a high deliverable ability of 208 v/v at room temperature [16].

MFM-132 has different linker backbones from MFM-112, MFM-115 but in the same family. Compared with the other two compounds, MFM-112 and MFM-132, the benzene rotation ring of MFM-115 was found that the rotation rate of the benzene ring structure in MFM-115 was slower than that in MFM-112 but faster than that in MFM-132, which was almost stationary. So that is the reason why it had a higher adsorption capacity than the other two materials.

4.4 NU-1500

NU-1500 is chromium-based with terephthalic acid as the ligand. NU-1500 is chosen as the starting point because this material has several attractive characteristics. First of all, with high porosity, it also has a specific surface area, and the relatively small diameter of the pore is worth mentioning. Then it has a rigid triangular prism connection and metal mesh construction for easy design and improvement. Thirdly, good stability of humidity makes it convenient to process. Chemical stability is important for any application. Having a MOF with large porosity and high stability is always difficult. In addition, this material is rich in trivalent metal ions such as Al and Fe. Omar K. Farha and Taner Yildirim found that adding a benzene ring could improve the capacity of MOFs so they upgraded the organic ligands, In 2020, NU-1501-M, which M represents aluminum and iron, was designed and it was the first material that satisfied the standard of DOE. Figure 4 illustrates the structure of NU-1501.

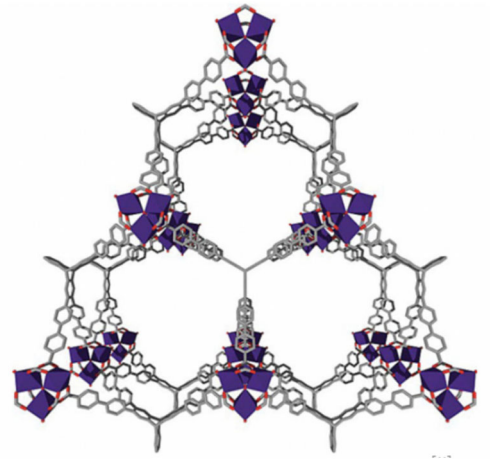

Fig.4 The structure of NU-1501 [17].

NU-1501-Al has a mass and volume-specific surface area of about 7310 $m^2 g^{-1}$ and 2060 m^2/cm^3, the volume of the pore is 2.91 $cm^3 g^{-1}$ and the pore size is 1.5~2.5 nm. NU-1501-Fe also has a large specific surface area of about 7140 $m^2 g^{-1}$ and 2.90 $cm^3 g^{-1}$ pore volume. These data may seem abstract, in Omar K. Farha's own words, one gram of sample would have a surface area spread over 1.3 football fields [18]. Overall, researchers designed a series of microporous NU-1501 materials with narrow mesopores and pore sizes less than 2.5 nm. The advantage is that synthesized material can balance the region between the weight and volume of BET, enabling them to store methane with prominent performance. Especially, Nu-1501-Al exceeds DOE standard, 0.5 g/g, to 0.66 g/g [18].

5. Summary

The MOFs with high adsorbability of natural gas are being tried as an alternative to traditional gasoline, which will achieve the target set by DOE. This article involves the preparation of synthesis, the factors affecting the adsorption capacity and different types of MOF materials for natural gas storage. The synthesis methods include hydro (solve) thermal synthesis, microwave method, and the acoustic chemical method. The different processes have special stages which will lead to the production of different types of MOF. On the other hand, the factors of natural gas storage of MOFs must be noticed, these show the ability of MOFs to adsorb NG on different variables. Based on the same conditions, which makes the performance compare more sense that showing the capabilities of the different types of MOF. The BET area and pressure always have positive effects on the amount adsorbed. The porosity and temperature need to be in the right range, the former must be in a suitable pore size that can ensure the capacity and later always applicate at ambient temperature. The last factor is determined by MOF, which is influenced by the metal ions, different types of metal will result in different interactions and affect the amount of adsorption. The use of MOFs to store NG is a crucial step in the field, as it plays a fundamental role in industrial applications, and further research

will be carried out step by step based on the current findings. In a word, the continuous progress and development of the whole process not only shows the improvement of technology but also lays the foundation for the future. The huge development and unexplored potential of this field are reflected.

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