Application of Metal–Organic Frameworks-Based Functional Materials for Gas Separation

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Abstract: Energy scarcity is becoming the biggest problem of scientific research and industrial production in this century. And gas separation, as an essential part of production activities, naturally needs to be considered a more sustainable and environmentally friendly change. As an emerging porous material, metal–organic frameworks (MOFs) are one of the candidates to replace the traditional distillation process due to their special structural characteristics, such unique porous structure and adjustable surface properties. Therefore, MOFs-based functional materials have been widely used for a diverse of various fields, such as fuel cell construction, antibacterial agent development and gas separation. Due to each type of gas's chemical/physical properties, a variety of promising and practical separation functional materials based on MOFs are prepared by using the advanced laboratory techniques, like UTSA-68 for C_2H_2/CO_2 separation, r-FUM 67-MES 33-FCu-MOF for CH_4/N_2 and IRMOF-1 for Xe and Ar separation. Herein, this research will not only summarize the current importance and status of the application of functional materials in the field of gas separation, which include CH_4/N_2, C_2H_2/CO_2, Ar/Kr, Ar/Xe and Xe/Kr.

1 INTRODUCTION

A diverse of different functional materials have been used for gas separation over the past century, such as zeolite, which are now being utilized extensively in industrial development. In any event, developing new functional materials, such as metal-organic frameworks (MOFs), is currently making significant strides forward. Scientists began to realize the commercial potential of MOFs around the year 1990, which coincided with several significant technological advances. For instance, the high ductility, flexibility and efficient gas separation offered by MOFs contribute to the material's high industrial value. The chemical properties of various MOFs are different, and some changes typically influence these differences in temperature and pressure. As a result, this opens a wide variety of opportunities for gas separation. Recently, MOFs-based functional materials have been the subject of extensive exploration and research (Wang, 2022), and now their industrial potential is being realized. As more time passes, MOFs will be used in more official capacities in industrial applications.

Traditional thermal drive technology is based on distillation which is relatively energy-intensive by a continuous cycle of evaporation and condensation. The separation of similar volatile gas mixtures (e.g., hydrocarbons) are processed industrially to obtain the desired purity. To solve energy shortage and environmental pollution, more and more attention is paid to the energy consumption and sustainable development of the process. The traditional distillation separation process is bound to be replaced by a more environmentally friendly and efficient non-thermal process. Among these, porous materials are one of the focuses of future development.

MOFs are one of typical porous materials that involve single metal ions and coordination bonds connected by organic ligands. In gas separation applications, MOFs have plenty of benefits based on their special and unique structures and properties (Cui, 2021). The crucial characteristic of MOFs that enables the absorption of several guest gas species is high surface area, and an efficient procedure will be viable since less stuff is required. Moreover, MOFs can accept variable functional sites and highly adjust the interaction between host and guest species. These

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open metal sites can bind with guest species, forming interactions with ligands. MOFs are controlled easily due to their adjustable pore size and tunable porosity. In other words, scientists can regulate the functionalization of MOFs for specific applications such as capturing particular species. The controllable chemical properties of pores make various mixtures of this material, which means lots of different and advanced designs so that higher selectivity and efficiency of gas species can be achieved. Overall, MOFs will play a significant role in industrial progress in reducing energy consumption and improving industrial production efficiency.

This research will describe the research and development of MOFs-based functional materials for gas separation in recent years. MOFs and their composites have excellent application prospects in gas separation. MOFs and membrane separation technology are used in gas separation. These applications are easy to operate and reduce energy consumption by more than 30% compared with other methods, which meets the requirements of energy-saving society development. In the research process, it is also found that methane and nitrogen showed different pair interaction intensities in MOFs, resulting in a more significant pair surface diffusion rate. The combination of MOFs and membrane makes membrane have excellent separation performance, providing a new way for methane concentration and purification in natural gas and coalbed methane. The existing MOFs-based membrane materials are studied, and the selection of MOFs separation membranes and their synthesis process are discussed from the perspective of the surface diffusion rate of gas, as well as the application of MOFs-based functional materials in gas separation.

2 APPLICATION OF MOFs-BASED FUNCTIONAL MATERIALS FOR GAS SEPARATION

2.1 C_2H_2/CO_2 Separation

Acetylene (C_2H_2) and carbon dioxide (CO_2) separation is an essential process in the industry since C_2H_2 acts as a crucial raw material and has a broader application. C_2H_2 can be produced from the cracking process of hydrocarbon under high temperatures or the incomplete combustion of methane (Wang, 2022). According to public statistics, the global market value of acetylene is approximately 11.42 billion dollars, and it is expected to increase by 6% each year which displays the importance of this stock (Cui, 2021). As for the application of C_2H_2, it can be widely used in producing chemical substances such as acetic acid and benzene. It is also used for welding and cutting metals (Guo, 2017). These reactions need high purity of acetylene to be achieved, instead, carbon dioxide always exists as an impurity to affect

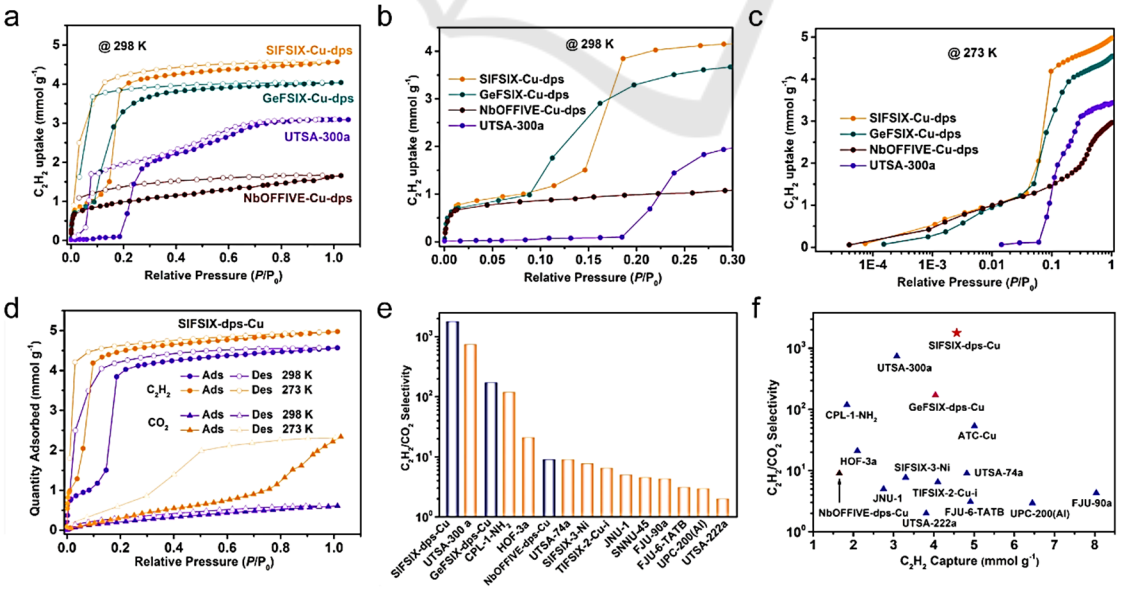

Figure 1: Application of MOFs for C_2H_2/CO_2 separation (Wang, 2022).

industrial manufacture, so it is necessary to separate CO_2 from C_2H_2. However, C_2H_2/CO_2 separation is difficult as they have similar molecular sizes and physical properties like the critical temperature. Overall, the appearance of MOFs-based functional materials will play a significant role on C_2H_2/CO_2 separation, which will benefit the industries, as shown in Fig. 1.

A previous study used molecular simulations to identify the adsorption power of magnesium format (Fischer, 2010). This light metal-organic framework is called magnesium formate, which combines with the most uncomplicated carboxylate formate. In comparing the single-component isotherms in the experiment, high absorption of 65.7 cm^3/g at 298 K and 1 bar of the pressure for acetylene is measured so that high selectivity of acetylene over carbon dioxide could be observed. Even though the theoretical acetylene absorption is smaller than the single-component isotherms, almost no carbon dioxide can be adsorbed. This result shows that magnesium formate's capacity to separate C_2H_2 and CO_2 molecules should be nearly constant at a suitable pressure range. To explore the ability of adsorption for magnesium formate, the calculated Henry constants ratio was used, which is shown in a line graph, and acetylene is highly adsorptive from carbon dioxide at room or even lower temperatures.

Another method is to discuss the potential field of these two species. As for the C_2H_2, the interaction power ranges from -25 to over -40 KJ/Mol, whereas less than -30 KJ/Mol interaction is measured for CO_2. Due to the greater power of interacting with the framework for C_2H_2, the energetic areas will be taken up absolutely by acetylene molecules rather than carbon dioxide. These avoid the adsorption of carbon dioxide molecules effectively. In summary, magnesium formate should be efficient in C_2H_2/CO_2 separation. The UTSA-68 is an instance of an unpenetrated framework and can adsorb 70.1 cm^3/g amount of C_2H_2 due to the porosity at 296 K and 1 atm pressure (Chang, 2016). The C_2H_2 molecules can occupy inside the framework more frequently as the increasing porosity, and high selectivity is also possible for UTSA-68. The calculated range of selectivity, which is 5-3.4 based on the Ideal Adsorbed Solution Theory (IAST), is a comparatively high result. Above all this evidence, it is believed that UTSA-68 has beneficial properties such as a high ability of adsorption to be applied for C_2H_2/CO_2 separation.

In terms of MOFs with ultra-micropores, [Cu(hfipbb)(Hhfipbb0.5)] was studied by scientists (Cui, 2021). The pore size of this framework is suitable for acetylene and carbon dioxide molecules contributing to the sieving effect. First, the thermogravimetry analysis demonstrates that this MOFs can be maintained at about 350°. Compare the adsorption of guest molecules at 273 K and 298 K. Their powers are similar, while there is a significant difference (sevenfold) in the amount of acetylene and carbon dioxide adsorbed by MOFs. In other words, this microporous MOFs does have the potential to be applied. In addition, the IAST calculation investigates the adsorption capacity when the mixture contains the same mole of two gas species. Moreover, 696 selectivity is concluded, which is higher than most of the MOFs. The simulations suggest that CO_2 molecules can interact with the framework while the hydrogen repulsion prevents the interaction of C_2H_2. That is why the reverse separation of C_2H_2 and CO_2 is observed. After that, column breakthrough experiments are utilized to confirm the adsorption power. Since no CO_2 is indicated at the exit, it is possible to prove that a great ability of separation can be achieved to obtain pure C_2H_2 when using this type of MOFs under the kinetic circumstance.

2.2 CH4/N2 Separation

Methane (CH_4) is necessary for the world to reach zero emissions, yet it cannot separate from nitrogen (N_2). Due to the identical polarizability and kinetic dimensions of CH_4 and N_2, it is difficult to achieve CH_4/N_2 separation. Most common kinds of porous materials, including zeolite, do not sufficiently separate CH_4/N_2 in industrial applications. Also, it is crucial to separate CH_4 from N_2, which can reduce greenhouse gas emissions. The only technique employed directly to separate the gaseous mixture on a significant scale is cryogenic distillation. Although this method produces high purity products, it is expensive and energy-intensive.

According to the separation mechanism, there are two categories of adsorbents. Since CH_4 has stronger adsorption contacts and a greater capacity for adsorption than N_2, CH_4-selective adsorbents are primarily based on the equilibrium process. N_2-selective adsorbents based on kinetic or steric effects as N_2 can be adsorbed over CH_4. Because of their strong chemical stability and unique surface areas, porous organic frameworks contribute significantly in the separation of CH_4 and N_2. For example, when light metal ions are used to prepare functional materials, the affinity for the prepared functional materials can be greatly enhanced for adsorbing CH_4 as compared to the materials without added light metal ions, resulting in a high selectivity for CH_4/N_2

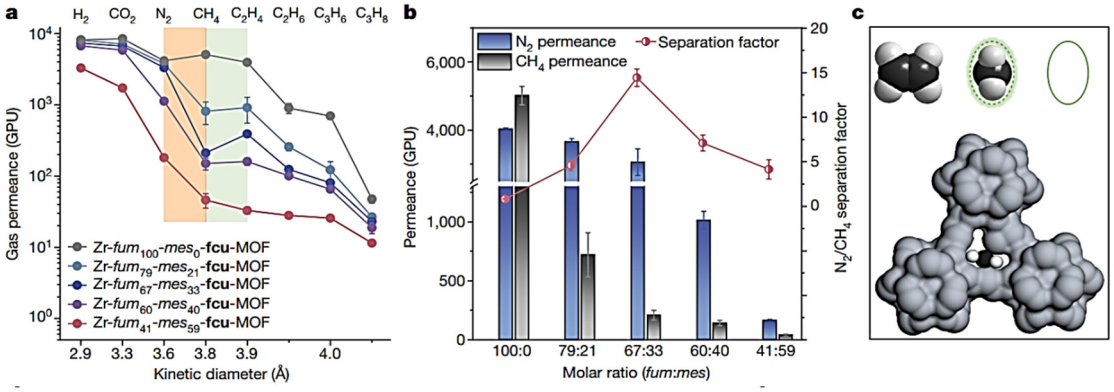

Figure 2: Performance of CH_4/N_2 separation by using the prepared MOFs-based functional materials (Zhou, 2022).

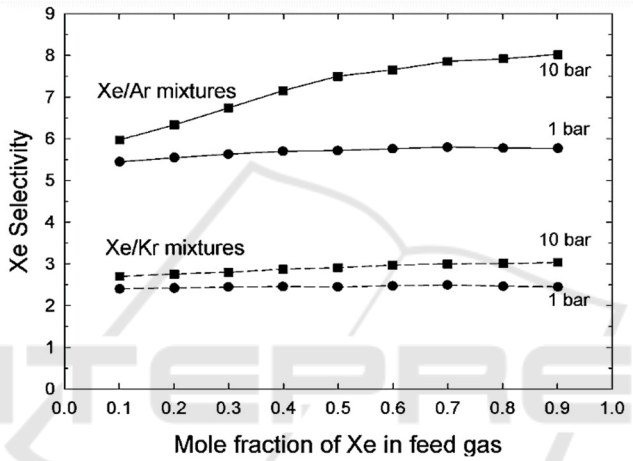

Figure 3: Influence of mole fraction of Xe in feed gas on Xe selectivity (Greathouse, 2009).

separation. Gas separation may be able to filter natural gas effectively using membranes (Wu, 2021). One component of the gas mixture can enter these membranes' holes only when desired. However, even the most sophisticated membranes offer poor selectivity because CH_4 and N_2 share many physical and chemical characteristics. Zhou et al. designed a new MOFs-based membrane material for CH_4/N_2 separation (Zhou, 2022), as shown in Fig. 2. In this work, they have fine-tuned the pore structure characteristics of the prepared membrane materials, making them exhibit good selectivity for CH_4/N_2 separation. In addition, the prepared membrane material still exhibits high CH_4/N_2 selectivity and N_2 permeability at practical pressures up to 50 bar.

Scientists employ water as a solvent for the electrochemical synthesis of MOFs membranes for membrane manufacturing, in which an external current is used to apply deprotonation. All the films had an excellent symbiotic layer, a similar crystal shape, and an ultra-thin thickness of roughly 30 nm when the conditions were optimized, and the ratios of the various components were changed (Zhou, 2022). Additionally, as a demonstration of concept for reducing the price of membranes, the authors demonstrate that the same synthetic MOFs film displays comparable layer thickness and intactness on low-cost support made of stainless-steel nets modified with carbon nanotubes. Of course, the literature has also reported other efficient MOFs-based functional materials for CH_4/N_2 separation, such as zeolites-based MOFs (Wu, 2019).

2.3 Noble Gas Separation

Noble gases have very low conductivity and reactivity and are therefore favoured in human industry. Among other things, inert gases can be used in light bulbs and protective gases. For example, Krypton can be used in lasers and Xenon can be used in cosmic rays. A new type of material, MOFs, is currently valued by scientists because of its high efficiency, tunable void size, and industrial potential.

Greathouse et al. prepared IRMOF-1 that can

selectively absorb Xe atoms in Xe/Kr and Xe/Ar mixtures (Greathouse, 2009), as shown in Fig. 3. In both their models and their tests, they discovered a correlation between an increase in the polarizability of the linker and an improvement in adsorbate interaction, as well as an improvement in adsorption selectivity for the Xe/Kr separation. With a specific cavity width, the IRMOF-1 has a pore capacity that is equivalent to 74% of its overall volume. Because the system has a significant amount of empty space, the adsorbates act as if there were just a single component present. For instance, slow Xe atoms do not considerably diffusion of Kr atoms that have relatively short, which suggests the correlation relationship influence among the various adsorbates are relatively minimal, which ultimately results in KP accuracy that is very high. This comparison demonstrates that the KP correlation adequately predicts Xe/Kr mixes' self-diffusivities under various situations. The preceding reasoning also applies to combinations of Xe and Ar in IRMOF-1 (Greathouse, 2009). And the performance of the MOFs in adsorbing noble gases is also optimized. (Meek, 2012; Gurdal, 2012; Gurdal, 2013).

2.4 Oxygen Separation

Oxygen accounts for approximately 20.9% of the total composition of air and is one of the main components for maintaining human metabolism. Moreover, it is an indispensable substance in various industries and processes. In the petroleum purification industry, oxygen has already been employed for air-in-furnace enrichment, which provides the convenience of reduced fuel consumption, increased capacity and better temperature control. It is used in water treatment for water purification, as an oxidizer, and in oxyfuel technology using acetylene for oxyfuel welding and cutting. However, those low-efficiency methods such as cryogenic distillation, membrane or zeolite separation dominate the modern O_2 supply. While most of these technologies yield high purity and large-scale finished products, the complexity, high cost and energy intensity behind them cannot be ignored. To balance the economics and efficiency of separation processes, metal-organic frameworks are naturally one of the promising processes for the future owing to their porosity and adjustable host/guest interactions.

The MOFs-based functional materials are reported to have different selectivity for mixtures of oxygen and nitrogen at characteristic temperatures and pressures, as shown in Fig. 4. At low

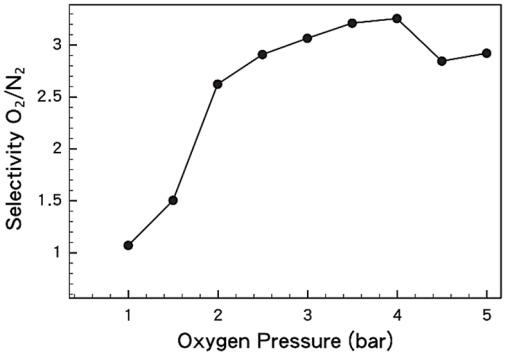

Figure 4: The selectively for O_2/N_2 with the used functional materials (Wang, 2017).

temperatures, oxygen can be adsorbed more selectively compared to nitrogen. This thermodynamic and kinetic selectivity was confirmed in experiments and structural probes. At typical temperature regions, the internal energy of oxygen adsorption amount is one half more than that of nitrogen, an unprecedented increment in materials with oxygen selectivity. The opening door process can be used to explain the positive proportional change in the coverage and the internal energy of adsorption of the two gases. One of them is due to the increasing number of gas molecules during the opening of the door, or it is because the energy in the subsequent steps reduces the amount of escape in the expansion of the process (Wang, 2017).

UIO-66 containing fluorine was found to have superior oxygen adsorption capacity. In the experimentally obtained adsorption isotherm results, highest flourine concentration UiO-66-F100 showed the remarkable absorptional ability to adsorb more and more oxygen with increasing pressure. At 40 bar, each gram of MOFs can even store an astonishing amount of oxygen-72mg. However, the steric hindrance of the functional group causes the decrease of the average available volume of material which does not affect the superiority of the total adsorption capacity of this MOFs (compared to the conventional UIO-66). It is the oxygen/fluorine interaction makes its exceptional ability, which is different from the usual functional group/guest adsorption (Piscopo, 2016).

The newly-discovered MOFs "Fe-BTTri" is decorated with an iron (II) center bound in a hemoglobin-like environment. Its unique framework could adjust to iron centers of different spin-height which made it suitable for studying the various electronic transitions. The experiment demonstrates that Fe-BTTri can undergo electronic changes like those occurring when hemoglobin and oxygen bind,

thereby allowing for a much higher O_2/N_2 selectivity than other iron-based adsorbents. The oxygen adsorption result of the MOFs is characterized by a progressive decrease in its relative adsorption capacity for oxygen as the pressure increases. However, the performance is average at high pressures, in the region of 210 mbar. The adsorption capacity of the used functional materials can be up to 3.3 mM/g, or about 10 wt% of O_2, suggesting that the prepared MOFs-based functional material can be used as a promising material for O_2 separation (Reed, 2020).

3 CONCLUSION

In conclusion, MOFs-based functional materials have the potential to be applied in gas separation due to their unique properties and structure. Through the research in the previous study, the application of a diverse of different MOFs-based functional materials to four different types of gas separations is analyzed. As for the C_2H_2/CO_2 separation, three categories of MOFs, including light, unpenetrated and ultramicroporous MOFs, are studied through experiments such as molecular simulation. Owing to the data, they can all separate C_2H_2 and CO_2 molecules effectively. MOFs-based membrane with fumarate and mesaconate linkers can be utilized in CH_4/N_2 separation, which shows an excellent selectivity on specific gases and is also so energy-efficient that it can substitute cryogenic distillation. Another MOFs called IRMOF-1 plays a role in adsorbing Xe atoms from Kr or Ar mixtures based on the data of experiments and simulation. Regarding O_2 separation, MOFs-based functional materials like UIO-66 containing fluorine, Fe-BTTri, and RPM3-Zn are all practical for oxygen adsorption according to their unique structural characteristics. Only several kinds of gas separation are focused on in this report, but it would be better if more research on MOFs application could be done so that utility of MOFs can be achieved to the maximum extent in the industry and benefit humans.

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