Application of MOFs in The Field of Adsorption And Separation

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Abstract. Metal-organic frameworks (MOFs) materials are a new type of zeolite-like porous materials with high porosity, high adsorption capacity and good thermal stability, which have attractive application potential in gas adsorption separation, photoelectric performance, catalysis, sensors and other aspects. Computational chemistry can not only break through the limitations of traditional methods, but also provide theoretical basis for the design of the best adsorption materials and the determination of ideal operating circumstances, and realize the shift from the main experience to the quantitative and directional preparation, thus saving a lot of complicated experimental research. As a result, it is important to carry out theoretical research on methane adsorption in MOFs materials. In this research, the adsorption properties, gas separation, seawater desalination and chiral drug separation in MOFs materials were systematically studied by molecular simulation method. This research can provide a new design approach for the synthesis and structural design of MOFs materials, and expand their applications in other fields

Keywords: MOFs; gas adsorption separation; molecular simulation.

1. Introduction

Metal-organic frameworks (MOFs) belong to a type of porous materials. MOFs have played a vital role in diverse of various applications because of their high porosity, adaptable physical structure, and extensive chemical functionalities. Based on this, MOFs based functional materials have been widely used in various fields, such as battery construction, catalyst preparation, and adsorbent preparation. In addition, MOFs are frequently utilized for the field of absorption and separation as a result of their homogeneous pore size. The organic part of MOFs increases the strong interaction with the polymer matrix. MOFs surpass other inorganic materials such as zeolites in most applications because they require less energy through simple chemical synthesis and do not require structural directing agents and calcination steps. For example, MOFs offer a significant deal of potential for the separation of gas mixtures, which is due to their selective adsorption properties. Despite the fact that recent studies on kinetic separation, isotope separation, and membrane-based separation have demonstrated encouraging practical application potential, encouraging practical application potential, and there are few studies on the actual separation of gas mixtures by MOFs. It should be noted that at certain temperatures and pressures.

Due to molecular sieving phenomena, some MOFs materials show excellent adsorption selectivity for different targets [1, 2]. Under circumstances resembling the adsorption of a single component, these MOFs have the potential to separate gas mixtures containing multiple components. The next stage is to create a procedure for molecular sieve-based separation. Other MOFs materials, on the other hand, exhibit adsorption selectivity brought on by thermodynamic equilibrium or kinetic effects even while the pore location is adequate or large enough to hold a variety of gases. Thermodynamic equilibrium or kinetic effects even while the pore location is adequate or large enough to hold a variety of gases. In terms of gas adsorption separation, molecular simulation is effective to screen existing adsorbents for an assigned separation challenge. Owing to the predictability of the synthesis of certain materials, such as MOFs, simulations provide the possibility of testing hypothetical materials as well. Furthermore, at the molecular standard, theoretical simulations may be helpful for illustrating the macroscopic phenomena of adsorption and separation. This research method is not limited by sample preparation and testing techniques. Through powerful computer simulation, it helps people increase their understanding of the relationship between material microstructure and performance, fills the gap between most physical and engineering sciences, and also shows people

the difficult to observe microscopic principles. Guided by the theory of probability and statistics, repeated random sampling experiments are conducted to statistically analyze the results, calculate approximate solutions to the problem, and then analyze and organize the results to obtain the final simulation results. To this end, this research will analyze the applications of different types of MOFs materials in the field of adsorption and separation, including gas separation and drug separation. In addition, the application performance of MOFs in these fields will be systematically discussed, and it may look forward to providing a new approach for the development and new applications of MOFs materials.

2. Adsorption and separation analysis

2.1. Gas Adsorption

2.1.1 Carbon monoxide (CO) adsorption

CO is the most widely distributed and total amount of pollutants in the atmosphere. It is a class of colorless, odorless, tasteless gas and very easy to ignore and poisoning. Mainly from the incomplete combustion of various fuels, CO into the human body will cause hypoxia in the body tissues, and finally cause people to suffocate and die. As a result, the study of CO adsorption separation is of great significance. Owing to the enormous advantages demonstrated by MOFs in the field of adsorption and separation, MOFs is an ideal new material for CO adsorption.

At present, in the relevant technique of separating and purifying CO, adsorption is a choice with economic and environmental benefits. In the field of adsorption and separation, the used adsorbent is the most crucial factor that is can be used to enhance separation performance for different targets. Although different adsorbents have been developed and used in the separation field, they all exhibit their own shortcomings, such as low separation efficiency. For gas adsorption and separation, several MOFs were investigated for their CO adsorption properties, and the following were found to be effective. Saha et al. prepared a new MOFs material, where the prepared MOFs materials was used for CO adsorption [1]. The adsorption of CO on microporous MOFs-74 (Ni) has been studied and it is reported that sites on the three-dimensional cellular networks can strongly coordinate CO. Recently, Bloch et al. prepared a series of MOFs materials and used it to separate CO [3]. As shown in Fog. 1, the results show that the prepared material exhibits excellent adsorption performance for CO. Consequently, the moisture sensitive MOFs-6 could significantly hinder its industrial application. Although MOFs materials exhibit excellent separation capabilities in the field of CO separation, it is necessary to synthesize new MOFs materials and change the surface area of certain MOFs.

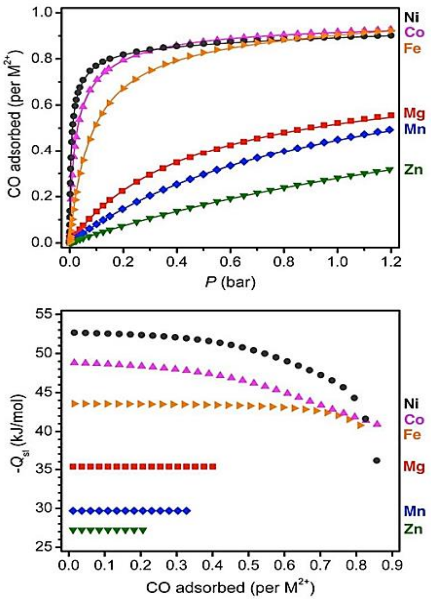


Fig 1. The CO isotherms and isosteric heats for CO adsorption [3, https://doi.org/10.1021/ja505318p].

2.1.2. Sulfur dioxide (SO2) adsorption

Once excessive SO_2 gas appears in the atmosphere, it can form acid rain after a series of actions under certain conditions. It is mainly derived from volcanic eruptions and the burning of some coal and oil, especially the smelting process of some fossil metals containing sulfur elements. SO_2 not only destroys the ecological environment, but also causes serious harm to the human body, so it is necessary to carry out some adsorption separation treatment for the removal of SO_2. Thanks to the adjustable physical and chemical properties of MOFs materials themselves, MOFs material can also be used as an ideal new adsorption material for SO_2. Liu et al. used MIL-160 and MFM-300 MOFs materials to separate SO_2 [4]. As shown in Fig. 2, the two MOFs materials prepared exhibit good adsorption capacity for both SO_2 and CO_2. Brandt et al. used the prepared MOFs materials to analyze their adsorption performance for SO_2 [5]. For the SO_2 absorption, the results show that MOFs-177 possesses the best performance, while MOFs-MIL-160 showed extremely high stability, making it a very promising class of materials.

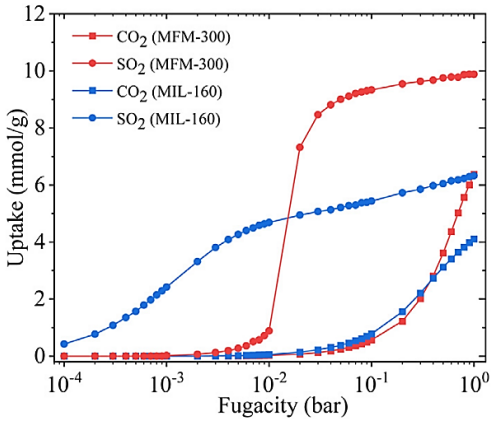


Fig 2. Comparison of CO_2 and SO_2 isotherms [4, https://doi.org/10.1016/j.fluid.2021.112963].

NO_2 is a brownish-red gas that comes mainly from fuel combustion and vehicle exhaust. And NO_2 has the ability to cause a range of environmental pollutants in a variety of ways, and it is also a significant contributor to the formation of photochemical smog and acid rain. When inhaled, NO_2 can damage the airways and cause lung disease. For this reason, solving the problem of NO_2 in the environment is also of great significance. There are some investments reported the use of MOFs material IOI-66-NH_2 to remove toxic gas NO_2 from the air at a very high level. The presence of amines helps to remove NO_2, with a NO_2 removal ability of up to 1.4g NO_2/g MOFs. Han et al. reported the adsorption performance of NO_2 in MFM-300(VIII) [6]. During the adsorption of NO_2, MFM-300 (VIII) was transformed into MFM-300(VI VI), NO_2 was transformed into NO, and water was produced. The results show that the MFM-300(VIVI) has excellent reversibility for the adsorption of NO_2, which provides a new method for the application of MOFs in the field of NO_2 separation.

2.2. Gas Separation

Using fossil fuels to burn generates the release of large amounts of gas into the atmosphere, which is a significant source of carbon dioxide gas leading to the greenhouse effect, so many studies have focused on using MOFs materials for gas capture. There are two main scenarios for the separation of CO_2. One is the flue gas, separating carbon dioxide from nitrogen. The second is natural gas, which separates carbon dioxide from methane. The introduction of Lewis base sites, such as unsaturated metal sites and amine groups, can improve the selective adsorption of CO_2 by MOFs materials. But these scenarios often require the presence of water vapor, so the water stability of MOFs materials is critical for capturing CO_2. The molecular simulation methods used in CO_2 capture research mainly include Monte Carlo molecular simulation, molecular dynamics simulation and high-throughput computational screening methods. Among them, Monte Carlo molecular simulation is based on statistical mechanics and only considers non-bond interaction, which provides theoretical support for

the calculation of adsorption capacity, selectivity, adsorption heat and other parameters of carbon capture materials. The simulation of molecular dynamics relies on the law of Newton's movement and considers bond interaction and non-bond interaction, which provides technical support for the calculation of parameters such as diffusion coefficient and number density of carbon capture materials. High-throughput computational screening combined with molecular simulation, data mining and machine learning can screen out high-performance carbon capture materials and obtain the relationship between structural characteristics and target properties, providing theoretical guidance for the development of high-performance materials.

Acetylene is not only an important chemical raw material, but also an important energy gas, which is produced primarily by the partial burning of methane and the cracking of petroleum hydrocarbons. CO_2 is often symbiotic with the production process of acetylene, so the separation of CO_2 from acetylene is of great significance for obtaining high purity acetylene. However, the physical and chemical properties of the two are very similar, such as molecular size and boiling point, which makes the separation of the two gases extremely difficult. The introduction of functional sites such as unsaturated metal sites enhances the affinity between the acetylene molecule and the MOFs skeleton, making most of the MOFs applied in this separation able to selectively adsorb acetylene.

Ethylene is an important raw material for petrochemical products. Traditional separation methods often use energy-intensive low temperature distillation to separate it from ethane. The separation of these two gases by MOFs materials can be divided into two categories. One is preferential selective adsorption of ethylene. The other is the preferential selective adsorption of ethane. The adsorption mechanism of the former is mainly based on the relatively strong interaction force between ethylene and MOFs material and the relatively small molecular size of ethylene. The separation of propylene and propane is an extremely important and demanding industrial process. By inserting unsaturated metal sites into the MOFs structure, the separation of propylene from propane can be facilitated by the strong interaction between them and olefins. Based on the principle of molecular sieve, the researchers designed an yttrium metal-organic framework with high hydrothermal stability, which can produce a purity of up to 99.5% propylene in the process of selective separation of propylene and propane, and is considered to be a real adsorbent for propylene/propane separation.

2.3. Seawater Desalination

The ordered pore structure and controllable crystal growth of MOFs make it have potential application value in reverse osmosis desalination field. The metal-organic skeleton composed of metal ions and bridged organic ligands has regular and highly adjustable characteristics, and the pore structure, organic ligands and topological structure are diverse, so their structural tunability is very superior. Zirconium organic frame material (Zr-MOFs) reverse osmosis membrane has great application prospect in the field of seawater desalination. Compared with the traditional membrane materials, the membrane of MOFs material will have better permeability and separation. To this end, MOFs-based functional materials have been prepared and used for seawater desalination. Although some report for MOFs membranes focuses on the gas adsorption and separation, there are also a lot of studies on the liquid's separation by using different MOFs materials. Taking advantage of the advantages offered by MOFs, the expansion of liquid separation can provide a broad platform to take full advantage of the unique capabilities of MOFs. In addition, the mixed matrix membrane prepared by MOFs compatible with polymer has excellent separation performance. Although some MOFs degrade under wet conditions, the MFS prepared by the high-valence metal clusters and the high acidity (low pKa) of the organic preparation system have excellent chemical stability. A typical example of such materials is Zr-MOFs composed of ZrO_4 $(OH)_4$) and COOH ligands. Zr-MOFs materials have excellent stability in water due to many coordination bonds, and have the potential of seawater desalination reverse osmosis membranes. In 2008, Lillerud et al reported the first case of Zr-MOFs UiO-66 composed of ZrO_4 $(OH)_4$ and 1, 4-dicarboxylate (BDC), in which each ZrO_4 $(OH)_4$ was connected to 12 BDCS [7]. Recently, researchers have successfully grown Zr-MOFs films on the surface of gold and silicon substrates by using steam assisted conversion. Zirconium organic

framework materials belong to the nanoscale, design the transport movement of water molecules and salt ions, in computer simulation technology belongs to the macro level and mesoscopic level, the use of molecular dynamics simulation can effectively explore the desalination performance of Zr-MOFs materials, but also save computing time and computing resources, to achieve the optimization of benefits. In addition, semi-empirical molecular orbital method is used to optimize the reverse osmosis membrane of Zr-MOFs, and the optimized model structure is better and the charge calculation is accurate. At present, the technology used is to optimize the zirconium organic framework material by semi-empirical molecular orbital method, and then to study the transport mechanism of seawater in the zirconium organic framework material by molecular dynamics simulation method, and analyze the influence of ligand configuration on the desalination performance of the material from the physical factors such as water molecular dynamics and water molecular spatial distribution.

2.4. Chiral Drug Separation Membrane

The separation of chiral drugs is particularly important. Compared with other separation methods, membrane separation technology, as a new chiral separation technology, has advantages that other separation methods cannot compare (low energy consumption, continuous operation, etc.), so it has broad application prospects. For membrane separation technology, compared with ordinary separation membranes, chiral separation membranes have higher requirements, which should not only provide a large permeability, but also provide chiral recognition function, so as to separate the two enantiomers of chiral compounds. However, most existing polymer membranes do not have chiral recognition function, and MOFs materials have variable chemical/structural flexibility, and can be modified by appropriate methods (such as post-modification synthesis) to make MOFs materials have chiral recognition function, so MOFs materials are good precursors for synthesis of chiral separation membranes. Although many studies have demonstrated the possibility of this method, the selection of suitable MOFs materials as candidates for chiral separation remains a challenge. Because it is impractical to select suitable materials for subsequent chiral modification based on the principle of group master-guest interaction on so many kinds of MOFs materials experimentally. However, molecular simulation technology can better solve this problem, thus greatly reducing the number of experiments, and can provide theoretical support for related experiments at the molecular level, and can better predict its application. Compared with small molecules such as gases, ibuprofen is a large molecule, and the selection of molecular simulation techniques for ibuprofen in drug adsorption studies will be limited. Liu et al. studied the adsorption of ibuprofen in bio-MOFs-1, -11, -100 and UMCM-1, and found that ibuprofen molecules were mainly adsorbed around metal clusters of MOFs [8]. The results show that the adsorption OF ibuprofen by bioMOF-100 can reach ~2030 mg IBU/g MOFs at 1 bar and 298 K. Bernini et al. studied the adsorption capacity of biocompatible MOFs materials for ibuprofen, and found that bioMOFs-100 had a high adsorption capacity for ibuprofen (1975 mg IBU/g MOFs) due to its high pore volume (2.9 cm^3/g), and CD-MOFs-1 was also found [9]. Both bioMOF-100 and Mg-MOF 74 have great potential for drug storage. The study of Erucar et al. is currently aimed at the adsorption of ibuprofen by MOFs materials of the largest number of purposes [10]. The research results show that the data obtained in this study are in good agreement with previous data and experimental results. In addition, MOFs-74 series materials, bio-MOFs-100-102 and other materials show great advantages in ibuprofen adsorption capacity due to their large pore volume, among which RAVXIX in MOFs-74 series materials is the material with the largest adsorption capacity for ibuprofen in the current simulation study. The adsorption capacity of ibuprofen can reach 2559 mg IBU/g MOFs at 1 bar and 310 K. The above research is mainly to screen suitable MOFs material candidates for drug carriers through molecular simulation, so it is necessary to ensure that drugs can be released slowly in the human body, so as to improve the effect of drugs in the treatment of diseases. Structured bias Monte Carlo (CBMC) simulation and molecular dynamics (MD) simulation can be able to calculate the adsorption capacity, radial distribution function (RDF), diffusion coefficient and other properties of ibuprofen molecules in MOFs materials. Adsorption capacity is the key to evaluate whether a MOFs material has good properties, and the diffusion

coefficient determines the speed of ibuprofen passing through the pores of MOFs materials. For the application of the membrane, this is closely related to the performance of the membrane (such as permeability flux).

3. Conclusion

This research discusses the applications of different types of MOFs materials in the field of adsorption and separation. The specific performance of these MOFs materials in separating different target substances was systematically analyzed. The research and development of various types of MOFs materials can carry out scientific adsorption and separation of a large number of air pollutants in the air in a targeted manner, and can effectively deal with polluting gases in the air. The research of MOFs can further promote the research of chemical technology for health and environmental protection. Molecular simulation technology, as a new type of computer simulation technology, is not limited by sample preparation and testing technology. Through the simulation of powerful computer computing power, people can increase their understanding of the microstructure and properties of materials. The research and utilization of molecular simulation technology has opened up new fields of research. It shows the most basic principle of gas adsorption separation by intuitive theory. By combining MOFs research with molecular simulation research, scientists have greatly promoted the process of studying gas separation and adsorption, so that scientists can more intuitively study the theory and application of it.

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