Metal–Organic Frameworks for Separation

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Dedicated to Prof. Susumu Kitagawa on the occasion of his 65th birthday

Separation is an important industrial step with critical roles in the chemical, petrochemical, pharmaceutical, and nuclear industries, as well as in many other fields. Although much progress has been made, the development of better separation technologies, especially through the discovery of high-performance separation materials, continues to attract increasing interest due to concerns over factors such as efficiency, health and environmental impacts, and the cost of existing methods. Metal–organic frameworks (MOFs), a rapidly expanding family of crystalline porous materials, have shown great promise to address various separation challenges due to their well-defined pore size and unprecedented tunability in both composition and pore geometry. In the past decade, extensive research is performed on applications of MOF materials, including separation and capture of many gases and vapors, and liquid-phase separation involving both liquid mixtures and solutions. MOFs also bring new opportunities in enantioselective separation and are amenable to morphological control such as fabrication of membranes for enhanced separation outcomes. Here, some of the latest progress in the applications of MOFs for several key separation issues, with emphasis on newly synthesized MOF materials and the impact of their compositional and structural features on separation properties, are reviewed and highlighted.

1. Introduction

Separation is one of the oldest techniques mastered by human beings. Even in ancient times, methods were already developed to extract dyes and medicines from plants or metals from ores. Today, separation remains one of the most essential technologies in the modern world, affecting the society in nearly every aspect. Separation processes are extensively used in applications such as petroleum refining, mining, paper manufacturing, chemical and pharmaceutical production, as well as in occasions varying from water treatment, enrichment of nuclear fuel, electronics, etc.[1] To address these vastly different separation needs, a variety of separation methods have been developed, including distillation, sublimation, adsorption, extraction, crystallization, chromatography, and electrophoresis. Despite much progress, there are still significant challenges in separation science and technology. For example, many separation processes are energy intensive. Distillation-based separation processes alone account for 10–15% of the world’s energy consumption.[2] It is therefore desirable to explore alternative methods that can allow separation with better economy and less adverse impacts. A central strategy to address many issues in separation is the development of advanced separation materials that can act as efficient separation media enabling and facilitating the separation processes.[3] Promising separation media include, but are not limited to, flexible or semirigid polymers,[4–56] molecular cages or capsules,[7–89] ionic liquids,[10,11] porous carbon materials,[12,13] and various crystalline porous materials such as zeolites,[14–19] coordination polymers (some of which are also called metal–organic frameworks (MOFs)),[20–23] covalent–organic frameworks,[24–26] and other porous oxides[27–29] or chalcogenides.[30]

Among these materials, MOFs or porous coordination polymers represent a unique yet enormous family of 3D crystalline solids that are constructed through the coordination bonds between inorganic nodes and organic linkers. During the past two decades, extensive research activities on MOFs have occurred.[31–50] Thanks to the versatility of MOFs, the research topics span from gas storage,[51–53] separation,[20–23,54–72] catalysis,[73–79] luminescence,[80,81] sensing,[82–84] to proton conduction,[82–84] electron conduction,[85,86] and even energy conversion.[87,88]

Among many application topics, separation has always remained in the mainstream, not only due to its significance and broadness, but also due to the fact that the intrinsic property of MOFs makes this class of materials especially suitable for this challenging task. One of the most important and superior properties of MOFs relevant to separation is their precisely
defined apertures that can be controlled in a large range to allow size and shape selectivity toward guest species. Other types of porous materials either have a limited range of pore size or suffer from a nonuniform pore size distribution. For example, zeolites are crystalline solids just like MOFs and have indeed been found in a number of separation applications. However, the pore size of zeolites is limited by the small size of inorganic crosslinking anions, making them useful to only a limited number of separation applications. In comparison, there is almost no such limitation for MOFs due to their modular synthesis and numerous choice of inorganic and organic building blocks. As a class of materials, the pore size of MOFs spans from a few angstroms to a few nanometers, covering a much wider range compared to zeolites. A more recent development on the control of pore size, called pore space partition method, further demonstrates the tremendous potential of MOFs for pore property engineering, which will offer even more opportunities for a broad range of separation applications.

Another superior property of MOFs is that they are amenable to the introduction of a variety of functional sites, either on the framework or within cavities and channels, to allow a high degree of control over host–guest interactions, sometimes in a cooperative and long-range manner. Exposed metal sites have been well documented and the original enthusiasm about them results from the possibility that they can provide relatively strong host–guest interactions whose strengths can be varied a great deal through the type of metal ions. Exposed metal sites are not unique to MOFs because they are well known in molecular metal complexes. MOFs offer a unique platform for open metal sites to work cooperatively for binding to one or more guest species. The sites of organic ligands can also provide various interactions with guest molecules. In some cases, multiple supramolecular interactions can work cooperatively when the pore geometry and the configuration of the guest molecules are coupled to form specific pockets or traps for a particular type of gas components, which can be exploited to facilitate the separation. Various methods have been developed to introduce functional binding sites into MOFs, including preembedded groups in the organic struts, postsynthetic ion- and ligand-exchange, and postsynthetic modification to the pore surface through attachment to either inorganic or organic struts. Finally, a rather peculiar feature of some MOFs is framework flexibility, which leads to new phenomena and properties that can be utilized to achieve efficient separation.

Studies on MOF separations cover a broad range of topics from gas or vapor separation, separation in the liquid phase, to chiral separation and separation with MOF membranes, classified according to the properties of analytes or adsorbents, or specific applications. These different topics can often be interleaved and various reviews have appeared about them. Here, we seek to give a survey on a range of separation applications that MOFs can make contributions to, and focus on recent developments in this area, particularly those involving new MOF materials.

2. Gas Phase Separation

Many important separation processes in petrochemical industry are gas or vapor phase separation, such as removing acetylene from ethylene, paraffin/olefin separation, fuel purification such as removal of H₂O, CO₂, or SO₂ from low-grade natural gas, and separation of hexane isomers or xylene mixtures. Recently, there is an increasing demand on capturing environmentally hazardous components from various mixtures of gases or vapors. Examples include CO₂ capture and sequestration, capture of toxic gaseous pollutants such as NH₃, H₂S, SOₓ, NOₓ, CO, and fluorocarbons, and even capture of chemical warfare agents. In addition, some gas-phase separations, such as H₂/D₂ separation, Xe/Kr separation, and capture of iodine vapor, are relevant to nuclear fuel purification and nuclear waste treatment.

During the past decade, intense research efforts were observed for MOFs on gas separation. Some specific topics of gas separations have been reviewed in the past, including CO₂ capture, hydrocarbon separation, noble gas separation, separation of hydrogen isotopes, and toxic gas removal. In this review, we focus on select topics to illustrate how different features of MOFs can be utilized to address these challenges.

2.1. CO₂ Capture and Sequestration

Carbon capture and sequestration have attracted much research attention during the past decade due to increasing concerns...
about global warming. Postcombustion flue gases at power plant, a major source of \( \text{CO}_2 \) emission, typically contain 15% \( \text{CO}_2 \) and 85% \( \text{N}_2 \). In general, MOF materials have very low \( \text{N}_2 \) uptake capacity under ambient condition and will preferentially adsorb \( \text{CO}_2 \) over \( \text{N}_2 \). Thus, the absolute \( \text{CO}_2/\text{N}_2 \) selectivity value becomes a less important consideration compared to other separation applications. Instead, the uptake capacity (especially the capacity at \( \approx 0.15 \, \text{atm} \) partial pressure), the working capacity, an appropriate working cycle, and the energy cost during regeneration together with the material stability (such as the survivability under moisture) are of greater practical impact.

One important trend in the latest research on \( \text{CO}_2 \) capture is that the real industrially used adsorption and regeneration processes (such as pressure swing adsorption or PSA, temperature swing adsorption or TSA, and vacuum swing adsorption or VSA) are often taken into consideration according to the specific feature of a MOF adsorbent. In 2011, Long and co-workers first reported a systematic assessment of MOFs on postcombustion carbon dioxide capture under a temperature swing setting, which is believed to be particularly promising for postcombustion \( \text{CO}_2 \) capture, owing to difficulties with compressing or applying a vacuum to such large volumes of a low-pressure gas stream, as well as to the potential availability of low-grade heat in a power plant as a source of energy for regeneration. Book reference or journal article citation.

Two distinct metal-organic framework materials (MOF-74(Mg) and MOF-177) were evaluated in comparison with zeolite NaX. It was found that with a high density of strong binding sites, MOF-74(Mg) exhibits significantly better performance than MOF-177 and zeolite NaX, in terms of selectivity and working capacity. Also, a dual-site adsorption behavior is clearly seen for MOF-74(Mg) and the contribution from the open metal site is almost in a stoichiometric manner as observed from the isosteric heat plot.

As stated earlier, creating open metal sites represents an important strategy to provide such strong binding. In addition, for certain guest molecules, the strength of binding with exposed metal sites varies with metal type, and the sequence of binding strength is dependent on the nature of metal-guest interaction. As early as 2008, Matzger and co-workers reported the dramatic tuning on \( \text{CO}_2 \) uptake by changing the metal type on MOF-74 platform. Book reference or journal article citation.

The sequence for \( \text{CO}_2 \) uptake at 298 K is Mg > Co > Ni > Zn, and the uptake for \( \text{CO}_2 \) by Mg/DOBDC at 1 atm and 298 K remains the highest to date. Besides MOF-74, MOFs built from trigonal prismatic metal-trimer clusters represent an even broader platform in terms of both inorganic and organic components. In 2016, Zhai et al. demonstrated the dramatic tuning on \( \text{CO}_2 \) uptake and \( \text{CO}_2/\text{N}_2 \) selectivity by systematically adjusting the metal components in CPM-200, a series of compounds constructed from metal trimers and planar tetracarboxylate ligand in the \( \text{scc} \) topology. Book reference or journal article citation. Instead of using a single-type trivalent metal ion as originally reported for CPM-200, systematic adjustment of the metal components in CPM-200 was emphasized that the pocket containing SMT was prede- signed by careful choice of the carboxylate linker. This is an excellent example demonstrating that the MOF materials offer researchers plenty of room in materials design. The obtained materials can preferentially absorb \( \text{CO}_2 \) over \( \text{N}_2 \) and \( \text{CH}_4 \), although the zero coverage isosteric heat and \( \text{CO}_2/\text{N}_2 \) selectivity is moderate, mainly due to the low percentage of SMT among the overall framework. Nevertheless, the single molecular trap still represents a valuable concept and enhanced separation performance can be expected if a high density of SMT can be incorporated.

Other than through open metal sites, single molecular trap can be also obtained by using other interactions. Zhou and co-workers reported a guest-responsive MOF constructed from copper paddlewheels and a bent di-isophthalate type linker, known as PCN-88. Book reference or journal article citation.

This compound contains a small pocket where the exposed Cu\(^{II} \) sites are aligned to point to each other, forming a unique “single molecule trap” (or SMT) that can perfectly trap a \( \text{CO}_2 \) molecule within it. It was emphasized that the pocket containing SMT was prede- signed by careful choice of the carboxylate linker. This is an excellent example demonstrating that the MOF materials offer researchers plenty of room in materials design. The obtained materials can preferentially absorb \( \text{CO}_2 \) over \( \text{N}_2 \) and \( \text{CH}_4 \), although the zero coverage isosteric heat and \( \text{CO}_2/\text{N}_2 \) selectivity is moderate, mainly due to the low percentage of SMT among the overall framework. Nevertheless, the single molecular trap still represents a valuable concept and enhanced separation performance can be expected if a high density of SMT can be incorporated.

Strong binding toward \( \text{CO}_2 \) can be also achieved through other methods, for example, by incorporating strongly polarized inorganic groups. Zaworotko and co-workers studied the \( \text{CO}_2 \) sorption upon a series of pillared square-grid type compounds, also known as SIFSIX MOFs. Book reference or journal article citation. These compounds contain square nets of divalent metal nodes and neutral bipyridine (or pyrazine) linkers, which are further pillared by SiF\(_6^{2-} \) anions. Thus a strong electrostatic field is present within the porous...
frameworks, mimicking that of zeolite (Figure 1a). In their work, the authors demonstrated the power of pore engineering on tuning the adsorption properties and separation performance. In this set of materials, the pore size varies, depending on the size of the linkers and interpenetration, which led to three representative materials. With a long bipyridine linker and without interpenetration, SIFSIX-Cu exhibits a nanometer-sized pore and a large surface area, yet its CO\textsubscript{2} uptake at 298 K and 1 bar is moderate. In comparison, the doubly interpenetrated SIFSIX-2-Cu-i exhibits much narrower pore of ≈5.1 Å and a lower surface area. The total CO\textsubscript{2} uptake capacity at 1 bar becomes 5.4 mmol g\textsuperscript{-1}, the highest among the three reported phases (Figure 1b). With a shorter pyrazine linker, SIFSIX-3-Zn has even narrower pore of ≈3.8 Å and the lowest surface area. The limited pore space leads to early saturation (≈0.3 atm) on CO\textsubscript{2} sorption and moderate total uptake at 1 bar (Figure 1c). Meanwhile, the narrower pore also provides stronger host–guest interaction, as can be seen from the higher and steady isosteric heat of −45 kJ mol\textsuperscript{-1}. As a result, its CO\textsubscript{2} uptake at 0.1 bar is even higher than that of SIFSIX-2-Cu-i, confirmed by single-component sorption curves, as well as by direct sorption measurement of 10/90 CO\textsubscript{2}/N\textsubscript{2} mixture at 1 bar and by column breakthrough experiment (Figure 1d). In this aspect, SIFSIX-3-Zn behaves more like a typical zeolite material, which is partially revealed through comparison with Zeolite 13X. The different CO\textsubscript{2} sorption features give these two materials advantages at different separation occasions. SIFSIX-2-Cu-i is more suitable for syngas separation due to its high selectivity (240) for CO\textsubscript{2} over H\textsubscript{2} in a CO\textsubscript{2}/H\textsubscript{2}:30/70 mixture, while SIFSIX-3-Zn is more suitable for postcombustion CO\textsubscript{2} capture.

It was further discovered by Eddaoudi et al. that pore size contraction could be observed by replacing Zn with Cu in SIFSIX-3-M. This is likely due to the Jahn-Teller distortion from Cu(II), resulting in a distorted octahedral coordination geometry with elongated Cu–F bonds and relatively shorter Cu–N bonds. As a result, the obtained SIFSIX-3-Cu showed even steeper adsorption curve for CO\textsubscript{2} at room temperature, indicating a stronger interaction supported by higher adsorption heat of −54 kJ mol\textsuperscript{-1}. This feature makes this material potentially useful for capture of trace amount of CO\textsubscript{2} from air. The CO\textsubscript{2} uptake value for SIFSIX-3-Cu at 0.4 mbar is 1.24 mmol g\textsuperscript{-1}, about 10 times that of SIFSIX-3-Zn, and

Figure 1. a) Crystal structures of SIFSIX-2-Cu, SIFSIX-2-Cu-i and SIFSIX-3-Zn. b,c) CO\textsubscript{2} sorption isotherms under different temperatures for SIFSIX-2-Cu-i and SIFSIX-3-Zn. d) Column breakthrough experiment for a CO\textsubscript{2}/N\textsubscript{2}:10/90 gas mixture at 298 K, 1 bar. Reproduced with permission.\textsuperscript{[117]} Copyright 2013 Macmillan Publishers Ltd.
20 times that of SIFSIX-2-Cu-i. In fact, by crystal engineering, the physisorption in this case becomes so strong that it is comparable to those materials possessing chemical adsorption sites. Similarly, the Ni version can also be made, which has pore size between SIFSIX-3-Zn and SIFSIX-3-Cu, making this family of materials suitable for CO2 capture in a variety of concentrations.[119] In addition, the tolerance to H2S impurity was tested for this Ni compound, which helps address one of the concerns in practical applications.

With a similar approach, Zhang and co-workers studied the CO2 capture on a square lattice type 2D coordination network named Qc-5-Cu-sql.[120] There are two forms of this compound, the solvated form (Qc-5-Cu-sql-α) with a pore size of ~3.8 Å and a desolvated one (Qc-5-Cu-sql-β) with pore size of ~3.3 Å. Given that the kinetic diameters of CO2, N2 and CH4 are 3.3, 3.64, and 3.8 Å, respectively, the small difference in their pore sizes resulted in significant difference in selectivity due to the molecular sieving effect from the narrower pore in Qc-5-Cu-sql-α, which can only allow the entrance of CO2 but exclude N2 and CH4. As a 2D compound, the absolute uptake value of Qc-5-Cu-sql-β is not high, however, the gating effect resulting from the perfect aperture size makes this material a top performing MOF in terms of CO2/N2 (IAST selectivity of 40 000 for 0.15 bar CO2/0.85 bar N2 mixture) and CO2/CH4 selectivity (IAST selectivity of 3300 for 0.5 bar CO2/0.5 bar CH4 mixture). In addition, this material is stable in moisture and its relatively high CO2/H2O selectivity helps maintain its CO2 capture performance under wet flue gas stream.

The coordinated water can sometimes facilitate the CO2 capture too, as shown by UTSA-16, a potassium cobalt citrate coordination compound with terminal water.[121] Distinct from regular practices in which the coordinated solvent molecules on metal sites are removed during activation, the coordinated water in UTSA-16 was retained after sample activation. It exhibits quite strong CO2 affinity with a steady Qst about ~32 kJ mol−1. Given a relatively high framework density around 1.6 g cm−3, its volumetric uptake capacity ranks the second highest at ambient condition, only slightly lower than MgMOF-74. Its CO2/N2 selectivity is even a little higher than that of MgMOF-74, though lower than mmen-CuBTri featuring chemical adsorption. The fixed bed breakthrough experiment with 15/85 CO2/N2 mixture showed that the performance of UTSA-16 is comparable to zeolite NaX, in terms of the breakthrough time, but slightly lower than MgMOF-74.

Conventional CO2 capture process involves chemisorption by alkylamine-containing liquids, which typically show strong affinity toward CO2. However, this process leads to high energy cost for regeneration, as well as corrosion problems. Inspired by this, Long and co-workers developed a strategy by grafting alkylamine onto porous solids through exposed metal sites to enhance the CO2 binding.[122] Specifically, on a sodalite-type triazole-bridged framework, CuBTri (H1BTri = 1,3,5-tris[1H-1,2,3-triazol-5-yl]benzene), ethylenediamine (en) was grafted onto the exposed Cu site to form en-CuBTri. The obtained material exhibits a high affinity for CO2 binding with an isosteric heat of ~78 kJ mol−1. This value can be even higher (~96 kJ mol−1) when the grafted amine is N,N′-dimethylethylene-diamine (mmen).[123] Compared to physisorption, such strong binding indicates a chemisorption nature of the host–guest interaction. Given the high binding strength, the gas cycling experiment monitored by TGA confirmed that the material can be well regenerated during a temperature swing process with moderate regeneration temperature (60 °C). However, the need for a pure N2 flow during regeneration may produce N2/CO2 mixture again.

This strategy was further employed by the same group on the M2(dobpdc) platform (M = Mg2+, Mn2+, Fe2+, Co2+, Ni2+, Zn2+), which is an expanded variant of M2(dobdc) (MOF-74) (Figure 2a).[124,125] Interestingly, a “phase change” behavior was observed for CO2 sorption with mmen-grafted M2(dobpdc), with unusual step-shaped CO2 adsorption isotherms. The spectroscopic, diffraction and computational studies indicate that the sharp adsorption step originates from an unprecedented cooperative CO2 insertions process (Figure 2b). The step-shaped isotherm usually exhibits dramatic capacity change around a certain threshold pressure, which can lead to high working capacity compared to regular-shaped adsorption isotherm (Figure 2c). Notably, the threshold pressure shifts markedly with temperature, the metal type, as well as the type of grafted diamine. As a result, large CO2 separation capacities can be achieved with small temperature swings and low regeneration energies (Figure 2d). This work points to a new route for designing highly efficient adsorbents for removing CO2 from various gas mixtures. Similar phenomenon was also studied by Hong et al.[126]

The chemisorption through Lewis base sites can also be achieved through inorganic species such as hydroxide ion instead of alkylamine. Zhang and co-workers reported a set of isostructural MOFs exhibiting MOF-74-like hexagonal-shaped 1D channels, with their formula as [M6(18Cl2(bbtja)] and [M16M3Cl2(bbtja)] (H2bbtja = 1H,5H-benzo[1,2-b:4,5-b]bis-triazole, MAF-X25 & MAF-X25ox, M = Mn; MAF-X27 & MAF-X27ox, M = Co).[127] When all the metals are in low valence form, the (MII) adopts the square-pyramidal coordination upon activation and acts as a Lewis acid site for CO2 binding, mimicking the case in MOF-74. Interestingly, the mixed valence form (M(II)/M(III) in 1:1 ratio statistically) can be obtained through in situ oxidation during material synthesis, the resulting extra positive charge is balanced by the monodentate hydroxide groups on the M(III) sites. The hydroxide in such monodentate manner is believed to bring strong binding toward CO2 to afford HCOO−, which can be converted back to OH− without too much energy cost. Indeed, the zero-coverage isosteric heat of MAF-X25ox is about three times the value for MAF-X25, which clearly revealed its chemisorption nature, and so is the case for the cobalt version (MAF-X27). The high CO2/N2 selectivity is further demonstrated by the single component adsorption and breakthrough experiments.

Introducing functional groups into pores of MOFs through ligand modification represents another approach for tuning CO2 adsorption and separation performance. In 2014, Li and co-workers reported two UiO-67 analogues named BUT-10 (with formula [Zr6O8(OH)4FDC4A] and BUT-11 (with formula [Zr6O8(OH)4(DTDAO)]). (H2FDC = 9-fluorenone-2,7-dicarboxylic acid; H2DTDAO = dibenzo[b,d]phiphene-3,7-dicarboxylic acid 5,5-dioxide).[128] FDC and DTDAO can be regarded as the modified version of biphenyl-4,4′-dicarboxylic acid, which was used in UiO-67. Without much change in the
length of ligand and with exactly the same structure, BUT-10 and BUT-11 showed great enhancement in CO$_2$ uptake capacity (from 22.9 to 50.6 and 53.5 cm$^3$ g$^{-1}$ at 298 K and 1 atm, in the order of UiO-67, BUT-10 and BUT-11) and CO$_2$/N$_2$ selectivity (from 9.4 to 15.6 and 31.5). The computational study indicates that through ligand modification, the sulfonate groups significantly enhance the affinity toward CO$_2$ molecules. In a follow-up study, by introducing a pair of nitro or sulfonate groups on Zr-NDC platform, a dramatic increase in the CO$_2$ uptake and CO$_2$/N$_2$ selectivity was again observed.\textsuperscript{[129]} For both working capacity and adsorption selectivity at 0.1 and 1.0 bar, these materials follow the following trend, Zr-NDC $<$ Zr-NDC-2NO$_2$ $<$ Zr-NDC-2NH$_2$ $<$ Zr-NDC-2SO$_3$H.

Most of the aforementioned studies focus on the design and synthetic strategy to develop new MOF materials with better CO$_2$ capture efficiency. For a practical CO$_2$ capture process from flue gas, other factors such as the impact from moisture or the energy efficiency have to be taken into consideration. For example, trace amount of moisture present in the flue gas can affect the CO$_2$ capture performance, sometimes significantly, either on the stability of adsorbent or its working capacity. In 2012, Thallapally and co-workers systematically studied selective CO$_2$ capture from flue gas with fixed bed sample of Ni-MOF-74, under dry and humid conditions, respectively.\textsuperscript{[130]} It was found that in the presence of trace amounts of water, both the CO$_2$ adsorption capacity and CO$_2$/N$_2$ selectivity decrease. Moreover, the CO$_2$ adsorption capacity could not be fully recovered after exposure to moisture. However, Ni-MOF-74 can retain a significant CO$_2$ capacity of 2.2 mol kg$^{-1}$ and a CO$_2$/N$_2$ selectivity of 22 at...
0.15 bar CO₂ with 3% RH water, which is still impressive. In addition, the material exhibits reasonable stability as well. Recently, Elsaidi et al. studied the selective removal of CO₂ from simulated flue gas with a series of ultra-microporous SIFSIX compounds, named SIFSIX-3-M (M = Ni, Co, Zn, and Cu).

Column breakthrough experiments were performed under both dry and wet (50% humidity) conditions. It was found that the Ni and Co variants of this platform are more robust under high humidity than their zinc counterpart, likely due to a phase change after contact with humid gas stream by the zinc phase.

A meaningful postcombustion CO₂ capture process has to be cost-effective, which requires a high energy efficiency. To evaluate the material performance in this regard, the concept of parasitic energy (or PE) has attracted increasing attention. It describes the energy required during the CO₂ capture process, which typically consists of two parts: the heat required to carry out the separation and the energy spent to compress the captured CO₂ up to 150 bar.[132] Huck et al. has systematically evaluated the energy efficiency of a number of benchmark MOF materials (e.g., Mg-MOF-74, PPN-6-CH2TETA, mmen-CuBTi). SIFSIX-3-Zn along with some zeolite adsorbents including NaX and MgX. In this study, the authors found that Mg-MOF-74 exhibits the lowest PE value (=727 kJ kgCO₂⁻¹), lower than that of the commercial zeolites. In addition, there are some interesting findings such as the trend of PE associated with metal type in MOF-74 series (Mg < Zn < Co < Ni) and the lowering of PE value by functionalization on PPN-6 platform. It is worth noting that the ideal two-component CO₂/N₂ mixture was used in this study. The result might differ once minor components in flue gas such as water, SOₓ and NOₓ are taken into account. Very recently, Nandi et al. reported a nickel isonicotinate MOF (coded as IISERP-MOF2) that exhibits a record-low parasitic energy of 655 kJ kgCO₂⁻¹.[133] Especially, this material shows excellent moisture stability and it only loses 7% of its maximum CO₂ capacity under 50% RH condition.

2.2. Removal of Acetylene from Ethylene

Both ethylene and acetylene are essential chemicals in chemical industry. Ethylene is massively used as the raw materials for production of polyethylene. Acetylene is widely used as a fuel as well as chemical building block. The worldwide production of ethylene exceeds 150 million tons annually, placing it the most produced organic compound. Ethylene is mainly produced by steam cracking in the petrochemical industry. During the process, acetylene usually appears as a side product, whose content is typically around 1% of the mixture. The presence of acetylene is harmful due to its explosive feature as well as its potential to poison Ziegler–Natta catalysts in polyethylene production. Thus, the removal of acetylene from ethylene stream represents an essential industrial challenge. Currently, the commercially used process relies on partial hydrogenation of acetylene into ethylene with a noble metal catalyst, which is a costly and energy intensive process. In comparison, adsorptive separation of acetylene from the C₂H₂/C₂H₄ mixture can be a promising alternative due to its much lower cost. However, the separation of these two molecules is extremely challenging due to their similar molecular size (3.32 × 3.34 × 5.70 Å for C₂H₂ vs 3.28 × 4.18 × 4.84 Å for C₂H₄), volatility and electronic structures based on unsaturated C=C bonds. The wide geometrical and compositional tunability of MOFs makes them promising candidates for this challenging task. Actually, C₂H₂/C₂H₄ separation has been one of the most vigorously studied separation processes using MOFs lately (Table 1).[166] Table 1 provides a summary of several benchmark MOF materials for C₂H₂/C₂H₄ separation, listing some important pore properties and separation performance.

### Table 1. A summary of select state-of-the-art MOF materials for C₂H₂/C₂H₄ separation.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>BET surface area [m² g⁻¹]</th>
<th>Pore size [Å]</th>
<th>C₂H₂ uptake at 298 K [mmol g⁻¹]</th>
<th>C₂H₄ uptake at 298 K [mmol g⁻¹]</th>
<th>IAST selectivity for C₂H₂/C₂H₄ mixture</th>
<th>Qst [kJ mol⁻¹]</th>
<th>τbreak (s)</th>
<th>C₂H₂ adsorbed during 0–τbreak [mmol/L]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M'MOF-3a</td>
<td>110</td>
<td>3.4 × 4.8</td>
<td>0.279/1.9</td>
<td>0.021/0.4</td>
<td>24.03/34.17</td>
<td>25</td>
<td>58.45</td>
<td>68.67</td>
<td>134</td>
</tr>
<tr>
<td>UTSA-100a</td>
<td>970</td>
<td>4.3 × 4.3</td>
<td>0.761/4.27</td>
<td>0.2396/1.66</td>
<td>10.72/19.55</td>
<td>22</td>
<td>112.39</td>
<td>135.33</td>
<td>139</td>
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<td>NOTT-300a</td>
<td>1370</td>
<td>6.5 × 6.5</td>
<td>0.249/6.34</td>
<td>0.1636/4.28</td>
<td>2.17/2.3</td>
<td>32</td>
<td>56.28</td>
<td>68.33</td>
<td>138</td>
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<tr>
<td>FeMOF-74a</td>
<td>1350</td>
<td>11 × 11</td>
<td>1.257/6.8</td>
<td>0.9000/6.1</td>
<td>2.08/2.1</td>
<td>46</td>
<td>89.40</td>
<td>100.67</td>
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<td>MgMOF-74</td>
<td>927</td>
<td>11 × 11</td>
<td>2.475/8.37</td>
<td>1.689/7.45</td>
<td>2.18</td>
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a) C₂H₂ and C₂H₄ isotherms were obtained under 296 K; b) C₂H₂ and C₂H₄ isotherms were obtained under 293 K; c) C₂H₂ and C₂H₄ isotherms were obtained under 196 K; d) BET surface area calculated from CO₂ isotherms at 196 K; e) The highest Qst values at various surface coverage; f) τ_break is the dimensionless breakthrough time.
In 2011, Xiang et al. reported the earliest example of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} separation using MOFs, where a mixed-MOF approach was used to produce two compounds named M’MOF-2 and M’MOF-3.\[^{[134]}\] These two materials are isostructures assembled from presynthesized M-Salen metallogand and dicarboxylate to form a hexagonal primitive network, with the only difference being in their dicarboxylate building blocks (BDC in M’MOF-2 vs CDC in M’MOF-3, BDC = 1,4-benzenedicarboxylate, CDC = 1,4-cyclohexanedicarboxylate). As a result, M’MOF-3 exhibit slightly smaller pore aperture size than M’MOF-2. The narrower pore in M’MOF-3 can still allow the entrance of C\textsubscript{2}H\textsubscript{2} molecules into its pore while C\textsubscript{2}H\textsubscript{4} is blocked or experiences slow kinetics. The pore narrowing in M’MOF-3 eventually leads to significant enhancement on C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} selectivity (25.5 in M’MOF-3 vs 1.6 in M’MOF-2) at 195K. Note that the selectivity reported in this work was obtained by using Henry’s law, based on single component gas sorption data. The same group has further developed this method by replacing the M-Salen linker and the metal nodes.

M’MOF is such a modular structural platform that fine-tuning the pore properties can be simply achieved by modification of its metallogand. This was again demonstrated by the same group in a later work with the synthesis of four new derivatives (M’MOF-4 to M’MOF-7).\[^{[135]}\] In this work, in addition to single component gas sorption measurement, breakthrough experiment on packed bed adsorber was also used to evaluate the gas separation performance. The result shows that with a 1/99 C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} mixture at 296 K and 100 kPa, M’MOF-4a has the best separation performance, in terms of both its selectivity and capacity for C\textsubscript{2}H\textsubscript{2} capture.

In practical applications, the separation performance is not only dictated by the selectivity but also by the adsorption capacity and kinetics. For example, M’MOF-3a exhibits high thermodynamic selectivity, however, when its separation performance is compared with that of MgMOF-74, a material showing lower selectivity but higher capacity of C\textsubscript{2}H\textsubscript{2}, it is not straightforward to know which is better. In such case, breakthrough simulation and experiment become a powerful tool to examine and compare these materials. In 2012, He et al. did a systematic evaluation of hydrocarbon separation performance on a series of MOFs using breakthrough calculations.\[^{[136]}\] The calculation is based on the transient breakthrough of a C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} feed mixture containing 1% C\textsubscript{2}H\textsubscript{2} in an adsorbent bed packed with corresponding MOF material. A plot of the amount of C\textsubscript{2}H\textsubscript{2} produced, containing less than 40 ppm of C\textsubscript{2}H\textsubscript{4} per liter of the adsorbent during the time interval 0–\(\tau_{\text{break}}\) is plotted as a function of the breakthrough time, \(\tau_{\text{break}}\). The production capacities for the examined material is in a decreasing order of MgMOF-74 > CoMoF-74 > M’MOF-3a > M’MOF-4a. Long and co-workers also investigated the use of FeMOF-74 for removal of acetylene from mixtures with ethylene.\[^{[127]}\] Simulated breakthrough characteristics for a feed mixture containing 1 bar of ethylene and 0.01 bar of acetylene at 318 K indicate that final acetylene concentrations on the order of 10 ppm could be realized. The total amount of acetylene removed is also a little higher than that by MgMOF-74.

In 2012, Yang et al. reported the C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} separation on NOTT-300, an aluminum-based MOF in the formula of [Al\textsubscript{2}(OH)	extsubscript{2}(L)] (H\textsubscript{4}L = biphenyl-3,3’,5,5’-tetracarboxylic acid).\[^{[138]}\] This compound comprises inorganic chains of corner-sharing [AlO\textsubscript{4}(OH)\textsubscript{2}] octahedra linked via two mutually cis-H\textsubscript{2}-OH groups, which are further bridged by tetracarboxylate ligands to afford a porous structure with 1D channels. It is worth noting that this MOF can be easily obtained in large quantity and is water stable, which renders it a good candidate for practical use. Compared to FeMOF-74, NOTT-300 exhibits slightly lower C\textsubscript{2}H\textsubscript{2} capacity but higher selectivity (2.30 vs 1.87 for equimolar mixture) according to IAST calculation. Though NOTT-300 exhibits no open metal sites, its hydroxyl group, together with the compact pore channel, provides moderate isosteric heat for C\textsubscript{2}H\textsubscript{2} of −32 kJ mol\(^{-1}\), between the value of FeMOF-74 (−47 kJ mol\(^{-1}\)) and M’MOF-3a (−27.1 kJ mol\(^{-1}\)). The combined inelastic neutron scattering (INS) and DFT study showed that the M-OH groups, aromatic −CH groups and phenyl rings in NOTT-300 all participate in weak additive, supramolecular interactions with C\textsubscript{2}H\textsubscript{2}. These are supplemented by cooperative intermolecular dipole interactions between adsorbed C\textsubscript{2}H\textsubscript{2}. In contrast, the initial isosteric heat for C\textsubscript{2}H\textsubscript{2} is much lower (16 kJ mol\(^{-1}\)) than that of C\textsubscript{2}H\textsubscript{2}, which is due to the lack of strong interaction between ethylene and the host. However, this value gradually increases to 28 kJ mol\(^{-1}\) with increased loading since the C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} π−π interaction becomes more dominant. Compared to the situations in both FeMOF-74 and M’MOF-3a, where C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} exhibit similar adsorption heat, the difference between adsorption heat for C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} in NOTT-300 is more pronounced. This indicates a completely different mechanism of selectivity by NOTT-300, which comes from its unique cavity that is particular favorable for C\textsubscript{2}H\textsubscript{2} binding. Also, different from the strong binding in the presence of open metal sites, the relatively weaker interaction from the cooperative supramolecular binding with a moderate isosteric heat can minimize the potential energy penalty during the regeneration process. The breakthrough experiment on equimolar mixture can lead to the production of ethylene with 99.5% purity.

Hu et al. studied the removal of acetylene from acetylene/ethylene mixtures on UTSA-100a, another high-performance MOF for C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} separation.\[^{[139]}\] UTSA-100 is a copper-based compound with its formula as [Cu(ATBDC)] (H\textsubscript{2}ATBDC = 5-(5-amino-1H-tetrazol-1-yl)-1,3-benzenedicarboxylic acid). It has 3D framework with rhombic open zigzag nanochannels with amino- and tetrazole- functionalized wall running in the c-direction (Figure 3a). Similar to M’MOF-3a, UTSA-100a exhibits relatively low isosteric heat for C\textsubscript{2}H\textsubscript{2} and high C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} selectivity, compared to other state-of-the-art materials for this task including FeMOF-74 and NOTT-300. However, its uptake capacity for C\textsubscript{2}H\textsubscript{2} is dramatically higher than that of M’MOF-300 (Figure 3c). The combined high capacity and selectivity make it superior than the previous materials in breakthrough performance, regarding the amount of C\textsubscript{2}H\textsubscript{2} captured before breakthrough with a C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} mixture containing 1% C\textsubscript{2}H\textsubscript{2} at room temperature (Figure 3d). The binding site was identified through pore structure analysis and first-principle calculations (Figure 3b). It was believed that besides the high sieving effect brought by the suitable pore opening and windows, the weak acid–base interactions between −NH\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} molecules also play important roles for the preferential binding of UTSA-100a with C\textsubscript{2}H\textsubscript{2} over C\textsubscript{2}H\textsubscript{4}.\[^{[139]}\]
Recently, Cui et al. studied the C$_2$H$_2$/C$_2$H$_4$ separation upon four SIFSIX materials, which were previously well known for their superior CO$_2$ sorption properties.\[140\] SIFSIX compounds are coordination compounds featuring 2D nets of divalent metal nodes and bipyridine linkers, which are further pillared by SiF$_6^{2-}$ anions to form primitive cubic topology, whose pore walls are lined by inorganic anions. The frameworks vary with each other by the metal nodes, framework interpenetration and channel size resulted from bipyridine linkers with different lengths (Figure 4a,b). The different pore size renders them quite different adsorption behavior for C$_2$H$_2$. SIFSIX-1-Cu exhibits exceptionally high C$_2$H$_2$ uptake (\(\approx 8.5\) mmol g$^{-1}$) at 298 K and 1 bar. In contrast, though with a lower total uptake at 1 bar, SIFSIX-2-Cu-i rapidly adsorbs C$_2$H$_2$ at very low pressure (2.1 mmol g$^{-1}$ at 298 K and 0.025 bar). Such features make both of them good candidates for C$_2$H$_2$/C$_2$H$_4$ separation, for different occasions. Record-high C$_2$H$_2$/C$_2$H$_4$ selectivity was found in SIFSIX-2-Cu-i at any molar fraction of C$_2$H$_2$ and at varying total pressure (1/99 mixture) by IAST calculations. Breakthrough experiment showed that SIFSIX-2-Cu-i is far superior to all the previously studied materials regarding the amount of C$_2$H$_2$ captured before breakthrough time for 1/99 C$_2$H$_2$/C$_2$H$_4$ mixture (Figure 4c,e). While for equimolar mixture, SIFSIX-1-Cu exhibits the best performance due to its overall high capacity (Figure 4d,f). The binding sites of C$_2$H$_2$ in these four compounds were studied using first principle DFT-D calculations, which was partially confirmed by structural analysis using high-resolution neutron powder diffraction. Strong C–H···F hydrogen bonding between the weakly acidic C$_2$H$_2$ molecules and weakly basic SiF$_6^{2-}$ sites was found in these compounds. The binding energy in SIFSIX-2-Cu-i is especially high, which partially explains the rapid adsorption of C$_2$H$_2$ at very low pressure. In addition, the stronger acidity of C$_2$H$_2$ over C$_2$H$_4$ and the special geometry of SIFSIX materials make it more suitable for C$_2$H$_2$ binding than for C$_2$H$_4$.

In 2017, Li et al. further studied a novel SIFSIX material UTSA-200a with record-breaking selectivity and acetylene uptake in 1/99 C$_2$H$_2$/C$_2$H$_4$ mixture.\[141\] Compared to 4,4′-dipyridylacetylene in SIFSIX-2-Cu-i, a shorter ligand 4,4′-azopyridine (azpy) was utilized in UTSA-200a ([Cu(azpy)$_2$(SiF$_6$)]$_n$) to reduce the aperture size to 3.4 Å. Smaller pore size in UTSA-200a leads to lower C$_2$H$_4$ and higher C$_2$H$_2$ uptake capacities. Especially, under 0.01 bar and 298 K, the C$_2$H$_2$ uptake (58 cm$^3$ cm$^{-3}$) of UTSA-200a surpasses all other materials to date. The IAST

![Figure 3. a) The pore structure showing the zigzag channels along the c axis and the cage with a diameter of about 4.0 Å in the pore wall with window openings of 3.3 Å. b) The acetylene sits right at the small cage connecting two adjacent channel pores. c) Acetylene (red) and ethylene (blue) sorption at 296 K. d) Experimental column breakthrough curve for C$_2$H$_2$/C$_2$H$_4$ mixed gas containing 1% C$_2$H$_2$ over UTSA-100a. Reproduced with permission. Copyright 2015 Macmillan Publishers Ltd.](image-url)
selectivity of over 6000 for 1/99 C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} mixture also exceeds other materials at 1 bar and 298 K. During the breakthrough process, the C\textsubscript{2}H\textsubscript{4} production from the outlet effluent and the C\textsubscript{2}H\textsubscript{2}-captured amount for a given cycle were analyzed to be record high of 85.7 and 1.18 mmol g\textsuperscript{-1}, respectively. There is no obvious decline of column breakthrough performance in 12 cycles of recyclability test. UTSA-200a avoids the trade-off between selectivity and uptake capacities and shows promising application in acetylene capture for ethylene purification.

2.3. Separation of Alkenes from Alkanes

Alkenes (including ethene, propene, butadiene, and butene isomers) are essential raw materials for manufacturing plastics such as polythene and polypropene. Global production of ethene and propene reaches over 200 million tons each year. Alkene is conventionally recovered from alkene/alane mixtures from hydrocarbon cracking through cryogenic distillation, which is energy intensive. As a promising alternative route, separation by porous sorbents represent a more energy efficient process.
Yoon et al. reported one of the earliest paraffin/olefin separation using MOFs.\cite{142} In this work, through controlled reduction by heating under helium flux followed by further activation under vacuum, MIL-100(Fe) with partially reduced Fe sites was obtained. Especially, the appearance of Fe$^{II}$ was found to enhance the interaction between the framework and propylene, likely due to the π-back donation. As a result, the adsorption heat with propylene at low coverage dramatically increase from $-30 \text{ kJ mol}^{-1}$ (with only Fe$^{III}$) to $-70 \text{ kJ mol}^{-1}$ (in the presence of Fe$^{II}$), while the value for propane remain unchanged. Preferential adsorption of propylene over propane was observed through breakthrough experiment upon equimolar mixture of C$_3$H$_6$/C$_3$H$_8$. The separation factor for propylene over propane was estimated to be 28.9 calculated from the breakthrough curve, which far exceed the value for [Cu$_3$(btc)$_2$] reported earlier.\cite{143,144}

In 2011, Bao et al. studied the adsorption of paraffins and olefins on Mg-MOF-74.\cite{145} A dual site Sips model was used to fit the adsorption equilibrium data. It was found that the isosteric heat of adsorption for propylene is much higher than that of propane and the same trend holds for ethylene over ethane. The high zero-coverage adsorption heats and Henry’s constants of olefin suggested strong interactions with the open sites of MOF framework by the π-complexation. Also an ethylene/ethane selectivity of 15.3 and a propylene/propane selectivity of 18.7 were estimated at 298 K. Soon after that, Bae et al. also reported a combined experimental and computational study on propylene/propane separation with MOF-74 (Co, Mn, Mg).\cite{146} With all three compounds, propylene was preferentially adsorbed to the material. The IAST-derived selectivity shows that Co-MOF-74 ($\approx 46$) and Mn-MOF-74 ($\approx 24$) exhibit substantially higher selectivity than Mg-MOF-74 ($\approx 4.5$). The most remarkable finding is that Co-MOF-74 shows excellent selectivity (46) even at 1 bar. Noticeably, a calculation on binding energy shows that while there is not much difference on binding energy between propane and M-MOF-74, there is a clear increasing trend on binding energy between propene and M-MOF-74 in the order of Mg < Mn < Co, which can partially explain their trend in selectivity.

At about the same time, Bloch et al. studied the hydrocarbon separation on the redox-active Fe$_2$(dobdc) (also known as

![Figure 5](image_url)

**Figure 5.** a) Crystal structure of Fe$_2$(dobdc)·2C$_2$D$_4$ determined from neutron powder diffraction data; orange, red, gray, and blue spheres represent Fe, O, C, and D atoms (left). Right: First coordination spheres for the iron centers upon dosing Fe$_2$(dobdc) with acetylene, ethylene, ethane, propylene, and propane. b) Gas adsorption isotherms for methane, ethane, ethylene, and acetylene. c) Experimental breakthrough curves for the adsorption of equimolar ethane/ethylene mixture flowing through a packed bed of Fe$_2$(dobdc) at 318 K. Reproduced with permission.\cite{137} Copyright 2012, AAAS.
Fe-MOF-74 or CPO-27-Fe platform.[137] With a compact tetraanionic bridging ligand, the structure features an extremely high surface density of 2.9 FeII coordination sites available per 100 Å² on its surface (Figure 5a). The heat of adsorption for ethylene and propylene at zero loading is ~45 kJ mol⁻¹ and ~44 kJ mol⁻¹, respectively, much higher than that of ethane (~25 kJ mol⁻¹) and propane (~33 kJ mol⁻¹). For an equimolar mixture of ethylene and ethane at 318 K, the adsorption selectivities obtained for Fe2(dobdc) of 13–18 are significantly greater than those calculated for either zeolite NaX or the isostructural MOF Mg2(dobdc), which display selectivities of 9–14 and 4–7, respectively (Figure 5b). The better performance is believed to come from the softer character of FeII²⁺ relative to Mg²⁺, leading to a stronger interaction with the π electron cloud of the olefin. Also, it has a superior propane/proplylene selectivity (13–15) to other porous materials such as zeolite ITQ-12. It was found that greater than 99% pure propylene can be realized during the desorption step of the breakthrough experiment. In a similar manner, breakthrough experiments showed that Fe2(dobdc) can separate an equimolar mixture of ethylene and ethane into the pure component gases of 99% to 99.5% purity (Figure 5c).

Cu(I) and Ag(I) ions can form π-complexation with the C–C double bonds of olefin molecules, which was employed for adsorptive separations of olefins from paraffins.[147] Inspired by this, Li et al. used a sulfonate-functionalized porous aromatic framework to immobilize Ag(I) ions into the pore channels, named PAF-1-SO₃Ag.[148] This method leads to a very high isosteric heat with ethylene, around 106 kJ mol⁻¹ at zero loading. In comparison, the isosteric heat of the frameworks before functionalization (PAF-1) and before loading of silver (PAF-1-SO₃H) is only 14 kJ mol⁻¹ and 23 kJ mol⁻¹, respectively. Due to the lack of strong interaction, PAF-1-SO₃Ag shows a significantly lower Qₑst for ethane with a value of 27 kJ mol⁻¹. As a result, the IAST selectivity of PAF-1-SO₃Ag reaches 26.9 at 100 kPa for equimolar mixture of ethylene and ethane, much higher than that from the pristine framework. A similar approach was reported by Chang et al. by immobilizing Ag⁺ onto (Cr)-MIL-101-SO₃H.[149] Compared to PAF-1-SO₃Ag, this material shows lower C₂H₆/C₃H₆ selectivity of ~16 at 100 kPa but much higher selectivity under low pressure (1 kPa at 296 K). A high C₂H₆/C₃H₆ selectivity of 32 at 1 kPa was also observed.

Another material with excellent ethylene/ethane selectivity is NOTT-300, which was discussed earlier for C₂H₂/C₂H₄ separation.[118] This compound exhibits a much higher C₂H₆/C₃H₆ uptake ratio (~5.03) than previously reported materials such as Fe2(dobdc) (1.22) and PAF-1-SO₃Ag (1.82). Also, the calculated IAST selectivity of 48.7, is higher than that of Fe2(dobdc) (13.6) and PAF-1-SO₃Ag (26.9). The combined inelastic neutron scattering (INS) spectra and DFT calculation indicate clear overlap between π electrons of C₂H₆ and the hydroxyl groups from the framework, while the C₂H₆ is located at a very long distance to the -OH group due to the lack of π electron density. In addition, the π–π stacking between C₂H₆ molecules also accounts for the selective adsorption of C₂H₆ over C₂H₄.

Different from regular MOFs for C₂H₆/C₃H₆ separation, with which preferential adsorption of ethylene is usually observed, Güçüyener et al. reported the first example of preferential adsorption of paraffins over olefins on ZIF-7.[150,151] The adsorption isotherm was found to fall into three different regions, indicating a gate-opening effect. It is believed that the adsorption process is strongly affected by the interaction between the adsorbate and the benzimidazole linker. The threshold pressure of gate opening for ethane uptake is lower than that of ethylene. It is speculated that because of the three-fold symmetry of the methyl groups, ethane molecules fit best in the largest opening of the ZIF-7 cage, a three-lobe structure formed by three benzene rings, and thus can penetrate at lower pressures than ethylene. Similar selectivity trend was also observed for propane over propylene.

Another material that can selectively trap ethane over ethylene was MAF-49, recently reported by Liao et al.[152] MAF-49 is a zinc azolate framework in the formula of [Zn(batz)]·0.5H₂O (H₂batz = bis(5-amino-1H-1,2,4-triazol-3-yl)methane). The isosteric heat obtained from adsorption isotherms turns out to be ~60 kJ mol⁻¹ for C₂H₆, ~48 kJ mol⁻¹ for C₂H₄, ~30 kJ mol⁻¹ for CO₂ and ~25 kJ mol⁻¹ for CH₄, which indicates strong binding between the C₂H₆ and the porous host. The grand canonical Monte Carlo simulation has revealed that the key to the high C₂H₆ selectivity is a combination of multiple hydrogen-bonding acceptors and dipole repulsion groups located at appropriate positions on the pore surface of a very narrow channel, which not only allows multiple attractive interactions for C₂H₆ but also restricts C₂H₄ to adopt a position that can only form fewer and weaker attractive interactions. Breakthrough experiment with equimolar four-component gas mixture of CH₄/CO₂/C₂H₆/C₂H₄ was performed on MAF-49 at 313 K and 1 bar, in comparison with five other MOFs (i.e., CPO-27-Mg, CPO-27-Co, MAF-4, UiO-66 and HKUST-1). MAF-49 is the only material that shows clear separation on the gas mixture in the breakthrough sequence of CH₄, CO₂, C₂H₄ and C₂H₆. One advantage brought by the ethane trapping material is that it can be particularly valuable for direct production of high-purity C₂H₆ from C₂H₆/C₃H₆ mixtures.

Eddouadi and co-workers reported the superior C₂H₆/C₃H₆ separation performance from a pillared square grid structured MOF, named NbOFFIVE-1-Ni (also known as KAUST-7).[153] This MOF is isostructural with previously reported SIFSIX compounds, which were found to be excellent separation medium for CO₂ capture and C₂H₆/C₂H₄ separation. Especially, this compound is closely related to the SIFSIX-3-Ni in crystal structure, except that the pillaring inorganic building block (SiF₆)²⁻ is replaced by (NbOF₆)³⁻ (Figure 6a). This change resulted in a longer metal–fluorine distance (1.95 Å) and a subsequent tilting of pyrazine molecules, which leads to significant narrowing of the pore opening. The final pore aperture is so small that it only allows the transport of the smaller propylene molecule, while shows total exclusion of propane, known as the molecular sieving effect (Figure 6b,c).[154] Actually NbOFFIVE-1-Ni exhibits quite strong affinity and high capacity toward propylene adsorption, and thus almost infinite C₂H₆/C₂H₄ selectivity can be reached, given the complete sieving of C₂H₆ from C₂H₄. This high selectivity allows simplified separation process based on a concentration swing recycling mode (CSR) or a vacuum swing recycling mode (VSR), in which the ideal working C₂H₆ capacity can be accomplished by performing a desorption step with an inert gas (such as He or N₂) purge.
C4 hydrocarbons containing butanes, butylenes and butadiene mixtures (primarily consisting 30–60% C4H6, 10–20% 1-butene (n-C4H8), 10–30% isobutene (i-C4H8), and 3–10% butane (C4H10)) are also an important product stream from the steam cracker, where 1,3-butadiene is usually the desired component as an important raw material for rubber manufacturing. Thus there is a large demand to separate C4H6 from the mixture. However, compared to C2 and C3 hydrocarbons, the separation of C4 hydrocarbon is even more challenging, due to the existence of multiple structural and cis/trans isomers. Conventional materials for separating C4 hydrocarbons usually preferentially adsorb C4H6 over butylenes and butanes, however, the selectivity is usually not high enough and the separation needs multiple purification cycles and subsequent desorbing of C4H6, which will cause high energy consumption and polymerization problems. Recently, Zhang and co-workers developed a strategy that leads to low C4H6 affinity and thus changes the breakthrough sequence (Figure 7a). As the desired product, C4H6 can break through the column ahead of other C4 hydrocarbons with high purity. In this contribution, ten MOF compounds with distinguished properties were chosen as candidate adsorbent, including four compounds with open metal sites, two with hydrophobic pore surface and four with hydrophilic pore surfaces. The breakthrough experiments showed that all

Figure 6. a) Structure description of NbOFFIVE-1-Ni highlighting the building blocks arrangement and its comparison with the parent SIFSIX-3-Ni. b) The pure C3H8 (pink), pure C3H6 (purple), and equimolar mixture of C3H6/C3H8 50/50 (orange) isotherms of NbOFFIVE-1-Ni at 298 K, demonstrating the full propylene from propane sieving ability. c) Calorimetric measurements of C3H8 and C3H6 adsorption on NbOFFIVE-1-Ni were performed so as to quantify the heat of adsorption of propylene and to reaffirm the exclusion/no adsorption of propane. Reproduced with permission. Copyright 2016, AAAS.
MOFs with OMS or hydrophobic surfaces did not lead to good separation of the C4 mixtures. The pore features of four hydrophilic MOFs can be further identified as large continuous pore (Zr-BDC), narrow continuous pore (Cu-SiF₆), discrete pore (Zn-BTA), and quasi-discrete pore (Zn-BTM). It turns out that Zn-BTM exhibits the best separation performance for C₄H₆ following the sequence as C₄H₆ < C₄H₁₀ < n-C₄H₈ < i-C₄H₈ (Figure 7b,c). It has been rationalized that isolated cavities with suitable sizes, shapes, and surface functionalities are useful for controlling guest conformation and achieving desirable adsorption selectivity (Figure 7d), but continuous channels are necessary for guest diffusion. Thus, MOFs like Zn-BTM with quasi-discrete pores can be particularly advantageous.

2.4. Separation of Noble Gases

Noble gases have many important industrial applications. Xenon is widely used in lighting, lasers, and medical devices. Krypton is also used in fluorescent lamps. Separation of noble gases is a longstanding topic. Of special interest is the capture and separation of Xe and Kr from the off-gas stream in nuclear plants[62]. Radioactive ⁸¹Kr is produced by the fission of uranium and plutonium and has a half-life of 10.76 years. Radioactive Xe isotopes are also produced during the nuclear fission, yet exhibit much shorter half-lives. They will quickly decay into nonradioactive isotopes by the time the used nuclear fuel (UNF) is reprocessed, resulting in a mixture containing

![Figure 7. a) Controlling the guest conformations by variation of the pore size, shape, and dimensionality. b) Mixture breakthrough curves for C4 hydrocarbons on Zn-BTM for b) 1:1:1:1 and c) 5:2:2:1 C₄H₆/n-C₄H₈/i-C₄H₈/C₄H₁₀ mixtures. d) Single-crystal X-ray host–guest structures. From left to right: C₄H₆, n-C₄H₈, i-C₄H₈, and C₄H₁₀. Reproduced with permission.[155] Copyright 2017, AAAS.](image-url)
nonradioactive Xe and radioactive Krypton in 10:1 molar ratio. Therefore, the separation of Xe/Kr has great significance since it can not only minimize the volume of radioactive noble gas waste to be stored, but can also recover Xe for further commercial use. Currently, cryogenic distillation method is commercially used to isolate Xe and Kr from air, which is an energy-intensive and costly process. Alternative adsorption and separation methods using porous solids at ambient temperature and pressure are desired.

In 2006, Mueller et al. first demonstrated the possibility of using MOFs for separation of rare gases mixture based on pressure swing adsorption. In this work, a mixture of Kr (≈94% mol) and Xe (≈6% mol) was fed continuously to an isothermal tubular reactor filled with HKUST-1 at 55 °C and 40 bar. It was observed that Xe was preferentially adsorbed by the packed bed of HKUST-1 and only 50 ppm level of Xe was detected in the leaving stream before breakthrough, while most of the Kr can pass through. The calculated capacity of HKUST-1 for Xe is more than 60 wt% of the adsorbent, almost twice as much as a high-surface-area activated carbon under identical condition. Later in 2012, Liu et al. performed the dynamic breakthrough column measurement with HKUST-1. Under 1 bar and room temperature, the results showed that the capacity for Xe and the Xe/Kr selectivity of HKUST-1 (at three different gas compositions, i.e., Xe/Kr 20:80, 50:50, 80:20) are lower than those for activated carbon.

Noble gases vary with each other mainly in dynamic diameter and polarizability, therefore the two parameters that can be adjusted for separation are the pore size and interactions between porous host and noble gases. MOF-74 is a platform with high density of open metal sites, which is a very powerful MOF for capture of CO₂ and a number of other gases. In 2012, Thallapally et al. did a comparative study of NiMOF-74 versus charcoal for xenon capture. It was found that NiMOF-74 has slightly higher Xe uptake than charcoal in the range of 0.25–1 bar and room temperature. Its selectivity of Xe over Kr is superior than charcoal as well. Perry et al. later carried out a combined experimental-computational study on the influence of metal types in MOF-74 on Xe/Kr selectivity. By systematical tuning the metal type in MOF-74, the Xe/Kr selectivity (based on the comparison on Henry’s constant for single component Xe and Kr sorption) showed a decreasing order of Co > Ni > Mg > Zn experimentally, though the calculated trend is different.

In most cases, however, the interaction between noble gases and the porous host is relatively weak and does not show much difference between Xe and Kr, even when open metal site is present. Therefore, the pore size is a more critical parameter in determining the Xe/Kr selectivity. Snurr and co-workers used Grand Canonical Monte Carlo (GCMC) simulations to predict Xe/Kr separation on a number of existing MOFs and a large pool of hypothetical MOF structures with different topologies and pore sizes. The computational study shows that the MOF material should have uniform pores that are slightly bigger than the kinetic diameter of Xe to achieve the highest thermodynamic selectivity.

Figure 8. a) Distribution of simulated selectivities for experimentally synthesized (green) and hypothetical (yellow) MOF structures out of ~125 000 MOF compounds; vertical, dashed line is SBMOF-1. b) Histogram showing relationship between selectivity and pore size, with the largest included sphere diameter as a metric. c) Crystal structure of SBMOF-1. d) Calculated potential energy contours of an Xe atom adsorbed in the pore (blue surface, −32 kJ mol⁻¹; white surface, 15 kJ mol⁻¹). Reproduced with permission. Copyright 2016 Macmillan Publishers Ltd.
Recently, Banerjee et al. also performed a high-throughput computational screening on ~5000 existing MOF structures and ~120 000 hypothetical MOFs to predict their Xe/Kr selectivity (Figure 8a,b). According to their calculation, SBMOF-1 exhibits the highest thermodynamic selectivity of ~70.6 among all existing MOFs. Note that the above selectivity was calculated using the ratio of Henry’s coefficient, which is feasible at dilute conditions relevant to UNF reprocessing off-gas. SBMOF-1 (also known as CaSDB, SDB = 4,4-sulfonyldibenzoate) is a calcium-based MOF originally synthesized for CO2/N2 separation (Figure 8c,d). The separation performance of SBMOF-1 was tested through both single component equilibrium and kinetic adsorption experiment and column breakthrough experiment. The pure component adsorption of Xe and Kr revealed that SBMOF-1 exhibits much higher Xe Henry coefficient than all top performing MOF materials prior to this work, which is actually a factor of two higher than CC3, a previously reported material with the second highest Xe Henry coefficient. Its thermodynamic Xe/Kr selectivity (~16) also tops all MOFs to date, though it is much lower than the predicted value. The authors further used a gas mixture that mimics the composition of UNF reprocessing off-gas (40 ppm Xe, 40 ppm Kr, 78.1% N2, 20.95 O2, 0.03% CO2, and 0.9% Ar) to conduct a single column breakthrough experiment. The result showed that Xe was retained in the column for more than an hour while all other gases broke through within minutes. The capacity of adsorbed Xe (13.2 mmol Xe per kg) is superior to that of benchmark materials such as Ni-MOF-74 (4.8 mmol Xe per kg) and CC3 (11 mmol Xe per kg). Similar capacity can be obtained even in the presence of moisture. SBMOF-1 has a pore size of ~4.2 Å, slightly larger than an Xe atom, ~4.1 Å. It was found that such a pore diameter is a prerequisite for a highly Xe-selective material, as the pore size controls the proximity and degree of overlap from multiple framework atoms contributing van der Waals interactions from multiple directions to achieve a highly favorable host-Xe interaction. A pore of optimal size for Xe is suboptimal for Kr so this forms a pore that is highly discriminatory for Xe over Kr.

Most reported MOFs for Xe and Kr separation preferentially adsorb Xe over Kr. MOF materials in this category typically possess larger pore size than the size of Xe. The preferential adsorption of Xe occurs due to stronger van der Waals interaction between host and Xe resulting from the more optimal pores or stronger polarizability of Xe. Alternatively, when the pore size of the MOF falls in between the kinetic diameters of Xe and Kr, it is possible to selectively adsorb Kr over Xe (“reverse selectivity”) through the molecular sieving effect. Fernandez et al. reported the first example of Kr/Xe separation by using partially fluorinated Cu based MOF (FMOFCu). This material exhibits tubular cavities (~0.51 nm × 0.51 nm) with bottleneck windows having estimated dimensions of 0.35 nm × 0.35 nm. Accordingly, under appropriate conditions, it is possible for only Kr (~0.36 nm) to enter the pore window while Xe (~0.39 nm) is blocked out. Interestingly, the adsorption behavior is temperature dependent. The preferential adsorption toward Kr was only observed under 0 °C, and the trend became opposite when it is above 0 °C. This phenomenon can be understood as the pore window shrinks at lower temperature to block Xe while it will expand at higher temperature to allow Xe to diffuse into the pore.

A two-column adsorption module was proposed for UNF off-gas treatment. Specifically, the first bed is filled with NiDOBDC, which has high Xe adsorption capacity. Most Xe is captured by this column, leaving out a mixture stream that has very low content of Xe but much higher percentage of Kr than the original mixture. The leftover gas stream was then flowed over a second bed filled with FMOFCu, which has reverse selectivity and can preferentially capture Kr from the mixture.

2.5. Separation of Hydrogen Isotopes

Deuterium is a potential energy source for next generation nuclear fusion reactors, and it is also widely used in many applications such as neutron moderators for heavy-water nuclear reactors, for nonradioactive isotopic tracing and in neutron scattering techniques. However the natural abundance of deuterium is extremely low, which is only up to 0.0184% of all hydrogen on earth and ~156.25 ppm in the ocean. So the enrichment from isotope mixtures is needed for applications. Unfortunately, D2/H2 separation is an extremely difficult task because their size, shape, and thermodynamic properties almost mirror each other. Current industrial production of deuterium mainly relies on cryogenic distillation or electrolysis of heavy water produced by the Girdler sulfide process, both of which are time consuming and energy intensive.

Instead, porous solids, especially MOFs can be used to assist the H2/D2 separation, which can be a promising alternative method by addressing the above cost and efficiency concerns. Due to the difficulty, the study on H2/D2 separation using MOF is not as extensive as other types of gas separations. In general, the separation was also achieved through either size confinement or chemical affinity; however, due to the unique property of hydrogen molecules, quantum effect has been taken into consideration (Figure 9a). According to the separation mechanism, the reported works can be roughly classified into two categories: kinetic quantum sieving (KQS) and chemical affinity quantum sieving (CAQS).

The kinetic quantum sieving concept for isotope separation was first introduced in 1995 by Beenakker et al. They proposed that isotope separation in nanopores can be possible when the difference between pore size (σ) and molecular size (σ) becomes comparable to the de Broglie wavelength of the molecules (λ) when the molecules are restricted in their transverse motion in a given space. Since D2 has a shorter de Broglie wavelength than H2, the effective particle size of D2 is therefore also slightly smaller than that of H2. By exploiting this small difference between H2 and D2 with the aid of a sufficiently small opening, a higher mobility of D2 into the porous medium with small apertures can be observed. This faster diffusion of D2 than of H2 leads to isotope separation.

Since 2006 when hydrogen storage on MOFs became a hot topic, D2 sorption was studied by some research groups and the difference between H2 and D2 sorption was first found with [Cu2(L)(H2O)2] (H4L = Terphenyl-3,3′,5,5′-(tetra carboxylic acid) and HKUST-1, respectively. However, the observed D2/H2 ratio was typically below 1.20 at 78 K, which is just comparable to porous carbon and zeolite NaA. In 2008, Chen et al. carried out the first systematic experimental study on
quantum sieving by using a mixed MOF material M’MOF-1. M’MOF-1 has a curved pore of 5.6 × 12 Å in the c axis direction. Through virial analysis of the H₂ and D₂ isotherm data, it was found that D₂-surface interaction is slightly greater than H₂–surface interactions while D₂–D₂ interactions were lower than H₂–H₂ interactions. The former is attributed to differences in the quantum statistical mass effect on the vibrational energy levels normal to the surface and the dispersion energy, while the latter is attributed to the higher zero-point energy of H₂.

At the same time, Noguchi et al. studied the D₂/H₂ separation on an ionic MOF called CuBOTf. This MOF features a cationic framework with triflate counter anion located in the pore channels. Its 1D channels have entrance sizes as 0.87 × 0.87 and 0.20 × 0.20 nm², respectively. Both experimental and IAST calculation were performed for the D₂/H₂ selectivity at 40 and 77 K. The selectivity at 40 K was found to be much higher than carbon nanotubes at 77 K. However, the temperature range for improved selectivity is too low, which is not suitable for real applications.

To investigate the correlation between effective quantum sieving and pore size, Oh et al. performed an experimental study on four microporous materials with different pore sizes, including two MOFs, ZIF-7 (3.0 Å) and ZIF-8 (3.4 Å), and two covalent-organic frameworks, COF-1 (9.0 Å) and COF-102 (12.0 Å). The results have shown that ZIF-8 exhibits quite high selectivity (≈11) at extremely low pressure and 20 K, while ZIF-7 did not show significant H₂ uptake. It is predicted that an optimal pore aperture for quantum cryo-sieving should lie between 3 Å and 3.4 Å.

In 2013, Teufel et al. studied the H₂/D₂ separation on MFU-4, a Zn-based MOF featuring exceptionally high thermal and hydrolytic stability. This structure has two differently sized pores alternatively arranged next to each other, mimicking the structure of MOF-5 (Figure 9b). Their cavity sizes are 3.88 and 11.94 Å in diameter, which are connected by a square shaped small aperture of 2.52 Å gated by Cl atoms. Usually, the adsorption isotherms indicate decreasing gas uptake with rising adsorption temperature. However, in this study, increasing uptake of hydrogen isotopes was observed with increasing temperature (Figure 9c). This abnormal trend was believed to be attributed to the temperature-triggered opening of the aperture that reduces the kinetic barrier and therefore facilitates the gas uptake. In other words, below the gate opening temperature, the intact crystal lattice with large diffusion barrier due to the Pauli repulsion between the Cl atoms and H₂ blocked...
the penetration of hydrogen; however, at higher temperature, the increased lattice vibration and higher energy of the gas molecule make the diffusion possible. This reminded us the “reverse Kr/Xe selectivity” due to the molecular sieving effect in the previous section. Similar phenomenon is likely to occur when the dimension of gas molecule and the pore aperture are very close to each other.

Due to similar property and very small molecular weight, the detection of individual hydrogen isotopes from their mixture is extremely difficult. Prior to this work, the D$_2$/H$_2$ selectivity is ubiquitously obtained through calculation upon single component adsorption isotherms. In this work, Teufel et al. has for the first time measured the selectivity (with a 1:1 D$_2$/H$_2$ mixture) directly by applying a customized cryogenic thermal desorption spectroscopy (TDS) apparatus. By using this technique, temperature and time-dependent selectivity was studied and a maximum selectivity of up to 7.5 was observed at 60 K and 10 mbar for short exposure times of $\approx 15$ min (Figure 9d).

Different from the above examples, in which the pore size control is the primary driving force for separation, chemical affinity quantum sieving represents a different mechanism, which mainly relies on strong interactions between gas molecules and the pore surface, provided by features such as open metal sites. It has been known that, due to the high density of exposed metal sites, MOF-74 exhibits some of the highest enthalpy for hydrogen adsorption. In 2013, Fitz-Gerald et al. for the first time studied MOF-74-M (M = Fe, Co, and Ni) for quantum sieving. They have measured the D$_2$ and H$_2$ sorption in a large temperature range from 77 to 150 K. It was found D$_2$ shows a significantly larger initial heat of adsorption than H$_2$, with the largest difference being 1.4 kJ mol$^{-1}$ (Ni-MOF-74). IAST calculation indicates the D$_2$/H$_2$ selectivity can reach as high as 5.0 at 77 K, which was much higher than previously reported MOFs. Interestingly, strong correlation between selectivity and the center-of-mass translational frequencies of the adsorbed molecule was identified through infrared spectroscopy study, which suggested that the selectivity primarily comes from the difference in the zero-point energies of the adsorbed isotopes at these strongly binding sites.

In another study on CPO-27(Co) (MOF-74-Co), outstanding hydrogen isotope separation at open metal sites was directly observed by Oh et al. through TDS study. The efficiency of separation of an equimolar D$_2$/H$_2$ mixture at 60 K and 30 mbar showed a selectivity of 11.8. The selectivity still exhibited a fairly high value of 6.3 at even higher temperature of 80 K. Due to the high selectivity of CPO-27(Co), a three-cycle temperature swing deuterium enrichment process was further developed by the authors. Starting from an isotope mixture of low deuterium content (5% D$_2$ + 95% H$_2$), a final mixture of largely enriched D$_2$ content (95% D$_2$ + 5% H$_2$) can be obtained after only three temperature swing cycles at operating temperature between 80 K to 110 K. The high efficiency and relatively high operating temperature makes it a quite promising method for real industrial applications.

Very recently, Weinrauch et al. studied the isotope separation on MFU-4l, an elongated version of MFU-4 mentioned above, with the using of a linear ditriazolate type ligand named bis[1H-1,2,3-triazolo{-[4,5-b],[4,5-i]}dibenzo[1,4]dioxin(H$_2$-BTDD)]. By partially replacing the terminal Zn-Cl sites with Cu(I) metal sites, Cu(I)-MFU-4l was obtained, which shows remarkably strong hydrogen adsorption enthalpies with pronounced isotope effects, even at temperatures well above 100 K. The thermal desorption spectroscopy (TDS) study at different loading temperatures and the inelastic neutron scattering study (INS) reveal a strong isotope exchange mechanism that allows the enrichment of heavy isotopologues from low-concentration phases. An experimental D$_2$/H$_2$ selectivity (for 1:1 mixture) of 11.1 was obtained at 100 K and even higher selectivity can be predicted for thermodynamic equilibrium conditions based on first principles calculations. The high selectivity of Cu(I)-MFU-4l makes it a very promising material to produce high-purity deuterium, and for capturing tritium from low-concentration hydrogen gas mixtures, which could significantly enhance the ability to treat radioactive waste, and, at the same time, produce precious $^3$He and tritium fusion reactor fuel.

3. Liquid Phase Separation

While the majority of essential industrial separation processes are in the gas phase, there are significant demands on liquid phase separations, especially in pollutant removal, petrochemical and pharmaceutical manufacturing. Industrial waste water purification is crucial for environment and public health. Waste water usually contains various organic and inorganic pollutants such as antibiotics from pharmaceutical uses, organic dyes from plastic factories, various inorganic anions and toxic cations from industrial and domestic sources. These species are usually dilute and have to be directly extracted from the liquid mixture. Ionic compounds usually exhibit high boiling point but high solubility in polar solvents, which are suitable for liquid phase separation. In pharmaceutical industry, some organic compound that cannot withstand high temperature (typically required in gas chromatography) have to be separated in the liquid phase under mild conditions. Some compounds (for example, xylene isomers) can be separated in either gas phase above their boiling point, or in a solution at lower temperature. On occasions when these compounds are not in high concentration, separation in the liquid phase can be a good choice due to the lower energy cost.

To date, extensive studies have been carried out by using MOFs for various liquid phase separations. For a comprehensive summary on this topic, De Vos and co-workers reviewed MOFs as liquid phase adsorbents for fuel upgrading, isomer separation, and water purification. Yan and co-workers summarized the use of MOFs in analytical chemistry, which includes a number of studies employing MOFs as the stationary phase in solid phase extraction (SPE) and HPLC for separation of various analytes. Here, we mainly focus on some recent studies on separation of aromatic compounds, dyes, and pharmaceutical compounds.

3.1. Capture of Organic Molecules and Ions from Solutions

Water pollution has attracted increasing attention lately. A large amount of organic species such as phenol, aniline, explosives, and pharmaceuticals have been discharged into various water
products or intermediates for the polymer, agrochemical, pharmaceutical, and flavor industries. The recovery of these phenolics from aqueous environments is challenging. De Vos and co-workers reported the isolation of phenolics from aqueous mixture by liquid phase adsorption with the help of a series of hydrophobic isostructured zirconium MOFs named MIL-140(C/D)\[182\]. All three MOFs showed preferential adsorption of hydroquinone over catechol but with distinct kinetics. Breakthrough experiment in aqueous solution confirmed that the separation can be achieved for capture of pure hydroquinone. Other phenolic combinations such as guaiacol/catechol, guaiacol/\(\alpha\)-creosol, and \(\alpha\)-creosol/catechol were also studied and separations were observed in all cases. Noteworthy is that zirconium MOFs are stable under water, which makes them particularly suitable for this task since the phenolic derivatives are typically associated with aqueous solutions.

In 2016, Li and co-workers reported two highly stable zirconium MOFs (coded as BUT-12 and BUT-13) for detection and adsorption of antibiotics and organic explosives in water.\[183\] The as-synthesized MOFs are constructed by \([\text{Zr}_6\text{O}_4\text{L}_3]_{1.5}\) (H\(_4\)L\(_3\))\(_{10}\) SBU and H\(_2\)CTTA \((5′,7′\text{-carboxyphenyl})\)-\(2′,4′,6′\text{-trimethyl}-\(1′,3′,5′\text{-terphenyl})\)-4,4′-dicarboxylic acid) or H\(_2\)TTNA \((6′,6′\text{-dihydroxy-2,4,6-}\text{trimethylbenzene-1,3,5-triy})\text{tris}(2-naphthoic acid)), respectively, to form the \(\alpha\) topology. There are two types of polyhedral cages. An octahedral cage constructed from six SBU and eight 3-connected ligand, and a cuboctahedral cage constructed from twelve SBU and eight ligands. Pore diameters of two polyhedral cages are \(\approx 17.5 = 24.7\) Å in BUT-12 and \(\approx 21.3 = 30.2\) Å in BUT-13, respectively. The as-prepared MOFs show excellent adsorption ability for antibiotics such as nitrofurazone (NFE) and nitrofurantoin (NFT), and for nitroaromatics such as 2,4,6-trinitrophenol (TNP) and 4-nitrophenol (4-NP). Suitable pore sizes, free hydroxyl groups, and large surface areas lead to the maximum adsorption capacity of TNP at 708 and 865 mg g\(^{-1}\), 4-NP at 414 and 560 mg g\(^{-1}\) in BUT-12 and BUT-13, respectively. Besides, the detection limits of TNP are 23 ppb and 10 ppb in BUT-12 and BUT-13, respectively. Recently, the same group reported selective adsorption and detection of aniline in water by a copper paddle-wheel based MOF \([\text{Cu}_4\text{tdbb}] \ (\text{H}_4\text{tdbb} = 3,3′,5,5′\text{-tetrakis}(3,5\text{-dicarboxyphenyl})-2,2′,4′,6,6′\text{-hexamethylenebiphenyl}))\) (also known as BUT-155).\[184\] This compound exhibits exceptionally hydrolytic stability, and can survive in water for 10 d or boiling water for 24 h without obvious loss of pore properties. This compound can selectively extract aniline and phenol from aqueous solution. Especially, the aniline uptake capacity is high compared to other porous materials. Furthermore, BUT-155 will experience a color change from blue to green upon aniline adsorption, likely due to the change of coordination environment around copper. This phenomenon can be used as a convenient method for detection of aniline in aqueous solution.

Xu and co-workers reported a mesoporous zinc MOF for column-chromatographic dye separation by size-exclusion effect.\[185\] The as-synthesized MOFs are constructed by \((4,6)\)-connected \(\text{Zn}_4\text{O}(\text{CO}_3)_6\) SBU and tetra-carboxylate ligands. Each ligand connects four \(\text{Zn}_4\text{O}\) clusters, forming a 3D corundum-type structure with the free pore space up to 84.6% (compound 3) (Figure 10a). Compound \(\text{Zn}_4\text{O}(\text{L}^1)_{1.5}\) \((\text{H}_4\text{L}^1 = 6,6′\text{-bis}(6\text{-carboxynaphthalen-2-yl)oxy)methyl}\text{propane-1,3-diyl}[(\text{oxy})(\text{di-2-naphthoic acid)})\) was utilized as adsorbent in basic red 1 (BR1) and food green 3 (FG3) mixture solution. After adsorption for 36 h, concentration of BR1 decreased dramatically and concentration of FG3 changed little (Figure 10b). Then a chromatographic column prepared with compound \(\text{Zn}_4\text{O}(\text{L}^1)_{1.5}\) was used for BR1/FG3 separation and FG3 was completely separated from BR1 (Figure 10c).

Interestingly, chromatography can be done even on a single crystal based on the difference in diffusion rate. Grzybowski et al. utilized a millimeter-sized single MOF-5 crystal as chromatography column to separate organic dyes in 2010.\[186\] MOF-5 is constructed by terephthalate and \(\text{Zn}_4\text{O}(\text{CO}_3)_6\) SBU and the dimension of the channel is \(\approx 8 × 8\) Å. Organic dyes of sizes smaller than 0.8 nm such as Pyronin Y (PY), Pyronin B (PB), Thionin (TH), Toluidine Blue O (TBO), Azure A (AA), Brilliant Green (BG), and Methyl Yellow (MY) could be separated through MOF-5. MOF-5 single crystal was placed on organogel presoaked in mixed dye solutions during separation. For separation of PB/TH mixture, distance between two peaks of dyes increased from \(\sim 50\) to \(\sim 260\) µm at 30 and 180 min, respectively, detected by fluorescence confocal microscopy. Different mixtures of dyes including BG/PB, PY/MY, TBO/MY, and BG/ PB/MY are also separated by MOF-5. Neutral adsorbate MY moves faster in column separation and dyes with primary amino group like AA and TH move slower than other dyes due to hydrogen bond interaction. Besides, MOF-5 is also used as absorbent in PY/AA solution indicating different diffusible rate of dyes inside MOF-5.

In the above cases, the inclusion of guest molecules is more likely to be an adsorption process due to the neutral nature of the frameworks. In practice, many inorganic and organic pollutants are charged species. Bu and co-workers proposed an ion-exchange approach by employing charged frameworks.\[187\] The strong electrostatic interaction between the charged host and charged guest makes it very sensitive to the charge as well as the size of the guests and thus enhances the selectivity. Specifically, the positively charged indium trimer was introduced into the unidual 9-connected \(\text{nbc}\) net, leading to a series of cationic frameworks (Figure 11b). These MOFs exhibit nanometer-sized windows, which allow the ion-exchange of anionic dyes. Interestingly, in a systematic study on the ion-exchange processes with a number of dyes, it was found that the ion-exchange kinetics is very selective to the charge type of the guest due to strong electrostatic interaction. Also, the ion-exchange kinetic is dependent on the specific charge value and the molecule size/molecular weight (Figure 11d). This observation sets up the basis for an ion-exchange-based chromatography process. In certain cases, large sized dye molecules will be completely excluded from the pores due to size exclusion (Figure 11c). The appropriate use of this gating effect can lead to simple one-step separations, which cannot be offered by conventional ion-exchange resins (Figure 11a). This ion-exchange approach is general.
and can be used for separation of any ionic species. It is especially meaningful for separating ionic pharmaceutical species, whose molecular weight is comparable to the dye molecules in this study.

Besides organic ions, many inorganic anions and cations are responsible for water pollution too. Among many types of ionic contaminants, a particular class is inorganic ions with radioactive component such as UO$_2$$^{2+}$, TcO$_4^-$, which have attracted much attention lately.[188,189] For example, $^{99}$Tc comes from the production of weapon grade plutonium ($^{239}$Pu) during irradiated uranium fuel cell reprocessing, and primarily exists in the form of TcO$_4^-$ in nuclear waste.[190] The presence of large amounts of $^{99}$TcO$_4^-$ in stored nuclear waste is an environmental and public health concern mainly due to the long half-life ($t_{1/2} = 2.13 \times 10^5$ year) and environmental mobility of $^{99}$TcO$_4^-$ due to its high water solubility. According to the ionic and water-soluble nature of $^{99}$TcO$_4^-$, ion-exchange can be an efficient method to extract the contaminant from solution. Thallapally and co-workers used the postsynthetic functionalization strategy to introduce the ammonium

Figure 10. a) The crystal structure of compound Zn$_4$O(L$^3$)$_{1.5}$. b) (top) UV–vis spectra of the DMF solution containing BR1 and FG3 dyes, in which crystals of 3 were soaked. (bottom) UV–vis spectra of the effluent during BR1/FG3 mixture passing through the MOF chromatographic column. c) Photograph records for 3-filled column-chromatographic separation process for BR1 and FG3 dyes. Reproduced with permission.[185] Copyright 2013, Wiley-VCH.
terminating group $\text{–CH}_2\text{N}^+\text{(CH}_3\text{)}_3\text{X}$ ($\text{X} = \text{OH}^-$ for PAF-1, $\text{Cl}^-$ for MIL-101(Cr) and PAF-1, respectively) onto MIL-101(Cr) and PAF-1, respectively, to turn the originally neutral framework into charged framework, namely MIL-101-F and PAF-1-F. The resulting charged framework can efficiently remove $\text{ReO}_4^-$ (to simulate radioactive $^{99}\text{TcO}_4^-$) from aqueous solution through anion exchange. A related work reported by the same group used a similar strategy to create cationic framework on a UiO-66 platform.\[191]\] Different from the above work, this time the amino group originally attached to the terephthalic acid was turned into ammonium by acidification.

Recently, Wang and co-workers discovered that a cationic coordination polymer $[\text{Ag(bipy)}]\text{NO}_3$ (denoted as SBN, bipy = 4,4$'$-bipyridine), originally reported by Oliver et al.,\[192]\] can efficiently immobilize $\text{ReO}_4^-$ into the cavity upon ion-exchange.\[193]\] Noteworthy, this ion-exchange process is irreversible. Once captured, almost no $\text{ReO}_4^-$ can be eluted using large excess of nitrate, carbonate, and phosphate anions. An irreversible single-crystal to single-crystal transformation from SBN to SBR (the $\text{ReO}_4^-$-incorporated form) was observed. This extraordinary selectivity for $\text{ReO}_4^-$ is due to the formation of strong $\text{Ag}^+$–$\text{O}$–$\text{Re}$ bond, revealed by the single crystal structure. In addition, the uptake capacity for $\text{ReO}_4^-$ reaches 786 mg g$^{-1}$, a value noticeably higher than state-of-the-art anion-exchange resins and other inorganic or hybrid anion sorbents.

### 3.2. Separation of Aromatic Compounds

Aromatic hydrocarbons including ethylbenzene and xylene are important raw materials for PET (polyethylene terephthalate) or polystyrene production. Together with benzene and toluene, they are known as BTEX. The separation of $\text{C}_8$ aliphatic compounds is quite challenging owing to their similarity in chemophysical properties. Especially, the boiling point for $\text{m}$-xylene, $\text{p}$-xylene, and ethylbenzene is 138–139, 138, and 136 °C, respectively, making it impossible to achieve efficient separation by conventional distillation method. The industrial separation of the xylene isomers is conducted either by a crystallization process or by adsorption on zeolites. In this regard, separation in the presence of MOF adsorbents can be a promising method.\[194]\] Some research efforts have been made using MOFs as the stationary phase in gas chromatography to separate BTEX compounds at temperatures above their boiling point. Alternatively, MOFs can be also used as a stationary phase in HPLC with these compounds dissolved in an organic solvent such as hexane or heptane.\[195–197]\]

In 2007, De Vos and co-workers reported the first systematic study on separation of xylene isomers and ethylbenzene.\[198]\] In this study, three MOF compounds (MIL-47, MIL-53(Al), and HKUST-1) were studied in parallel. It was found that HKUST-1 can only separate $\text{m}$-xylene and $\text{o}$-xylene with a separation factor of 2.4. Both MIL-53 and MIL-47 showed preference for $\text{p}$-xylene
over ethylbenzene with a separation factor of 10.9. However, for the most challenging separation of \( m \)-xylene and \( p \)-xylene, only MIL-47 successfully distinguished them with a separation factor of 2.9. Both breakthrough and chromatography experiments with MIL-47 showed good separation performance for \( m \)-xylene and \( p \)-xylene. In 2012, Millange and co-workers used MIL-53(Fe) as the porous medium to separate BTEX mixture. \(^{[197]}\) They revealed a variety of host–guest and guest-guest interactions for the first time from crystal structure obtained by X-ray diffraction. While the \( \text{ortho} \) - and \( \text{meta} \)-isomers present a similar arrangement when occluded in the MIL-53 host, \( \text{para} \)-xylene shows a distinctly different set of interactions with the host. Baseline separation can be almost reached by pulse chromatogram of BTEX on an MIL-53(Fe) packed column at 323 K, with the elution sequence as: ethylbenzene < benzene < \( p \)-xylene < toluene, \( m \)-xylene < \( o \)-xylene.

In 2015, Stoddard and co-workers reported the use of CD-MOFs to separate BTEX mixtures. \(^{[198]}\) CD-MOF is constructed from alkali metal cations and \( \gamma \)-CD (\( \gamma \)-cyclodextrin) with a large amount of free hydroxyl groups on frameworks (Figure 12a,b). The aperture window is \( \approx 5.1 \) Å. A top-down approach was utilized to prepare CD-MOF-2 HPLC column for benzene, toluene and xylene isomers separation (Figure 12c). The separation factors \( \alpha_{o \text{px}} = 16.4 \) and \( \alpha_{m \text{px}} = 3.44 \) indicate the selectivity of \( o \)- over \( p \) xylene and \( m \)- over \( p \)-xylene respectively. Interestingly, a bottom-up protocol was also used to prepare CD-MOF-1 HPLC column (Figure 12d). CD-MOF-1 column exhibited better resolution (\( R_{m \text{px}} = 2.17, R_{o \text{px}} = 6.43 \)) and separation factors (\( \alpha_{o \text{mx}} = 2.67, \alpha_{o \text{px}} = 17.9, \alpha_{m \text{mx}} = 6.73 \)) in xylene separation. The separation of ethyltoluene and cymene also indicate the same retention order of \( \text{ortho} \)- > \( \text{meta} \>- \text{para} \)-isomers (Figure 12e,f).

In 2012, Zhang and co-workers fabricated a newly synthesized MOF MAF-X8 on stainless fibers through hydrothermal method to separate BTEX (benzene, toluene, ethylbenzene and \( o \)-xylene). \(^{[199]}\) MAF-X8 is constructed by 4-(3,5-dimethylpyrazol-4-yl)benzoic acid and Zn ion and has a twisted-tetragonal, pillared-column 3D structure. Two aperture windows in the

![Figure 12.](image-url)
4.1. Chiral MOFs as Stationary Phase in HPLC

In 2016, Stoddard used CD-MOFs as stationary-phase materials for various organic compound separation by HPLC. The selective factors are 1.72 and 2.26 respectively for \((R)\) and \((S)\)-phenylethanol over their enantiomers. Separation of \(\alpha\), \(\beta\)-pinene and their racemic counterparts also performs well owing to strong interaction between exocyclic double bond and CD-MOF-1. Besides, separations of alkyl-, vinyl-benzenes and haloaromatics are also reported in this work due to geometry orientation of substrates in apertures and hydrogen bonding interaction between analytes and frameworks respectively.

In 2015, Liu and co-workers utilized a newly synthesized chiral MOF as CSP for racemic ibuprofen separation by HPLC. The enantiopure ligand D-camphorate (D-cam) and planar Mn\(_6\)O cluster lead to a homochiral structure, \((\text{Me}_2\text{NH})_2\text{Mn}_4\text{O(D-cam)}_4\cdot(\text{H}_2\text{O})_5\), in which 1D channel with \(\approx4.8\) Å square aperture size is constructed by \([\text{Mn}_6\text{O(D-cam)}]^{12+}\). Selectivity factor and resolution are 6.48 and 2.02 respectively for separation of racemic ibuprofen by HPLC.

In 2014, Cui and co-workers synthesized and structurally characterized two chiral MOFs constructed by enantiopure frameworks are of sizes \(8.8 \times 8.8\) Å\(^2\) and \(6.7 \times 6.7\) Å\(^2\). The highly oriented and crystalline MAF-X8 fibers were eluted by NaCl saturated water solution. The extraction time for 200 ng mL\(^{-1}\) BTEX is \(\approx7\) min and the detection limit is as low as 0.006-0.06 μg L\(^{-1}\). The RSD of run-to-run (\(n = 6\)) and column-to-column (\(n = 3\)) is 4.1% and 8.0%, respectively. It is worth noting that compared to commercial PDMS/DVB (65 μm) and PDMS (100 μm), the relative extraction efficiency of MAF-X8 is 18–157 times and 2–8 times higher, respectively. Besides, MAF-X8 fibers exhibit much higher absorbent selectivity of BTEX than the other two fibers. There is no obvious decrease of BTEX or increase of phenols extraction even in 1:5 (concentration) BTEX/Phenols solution compared to PDMS/DVB and PDMS fibers.

In 2016, Stoddard and co-workers further reported the use of CD-MOFs for separation of alkylaromatic and haloaromatic compounds. The \(\gamma\)-CD torus and 40 stereogenic centers lead to separation of versatile reagents. The triangular pores with \(\approx5.1\) Å size between \(\gamma\)-CD, cubes are ideal sites for benzene/toluene retention in CD-MOF-2; however, xylenes are not possible to pass through these pores due to kinetic diameter limitation. Utilization of CD-MOF-1 column for saturated and unsaturated aromatic and alicyclic compounds separation is also achieved. Interaction between copper sites and exocyclic double bonds enables longer retention time of \(\delta\)-terpinene and \(\beta\)-pinene than other terpenines and \(\alpha\)-pinene respectively. Eluting ethylbenzene from styrene with a separation factor \(\alpha = 1.75\) is due to \(\pi\)-complexation of styrene with metal sites. Besides, CD-MOF-1 column could also be used to separate haloaromatic compounds. Different strengths of C-H···X and C-OH···X noncovalent bonding interactions and shape/size of extended framework give a retention order of haloaromatic rings: fluorobenzene > chlorobenzene > bromobenzene > benzene > toluene > iodobenzene and the elution times in range of \(\approx50\) to 140 min; 1,2-dibromobenzene > 1-bromo-2-iodobenzene > 1,2-dichlorobenzene > 1,2-diiodobenzene and elution time in range of \(\approx92\) to 253 min. The retention orders of dibromo- and bromiodobenzene are as follows: 1,2-isomers > 1,4-isomers > 1,3-isomers. CD-MOF-1 column possesses a commercial potential for separation of isomers and enantiomers owing to its versatile separation abilities.

4. Enantioselective Separation

Isolation of racemic mixtures to afford enantiopure compounds has great significance in medicine and fine chemical production. However, due to almost identical chemical and physical properties of the racemates, enantioselective separation is an extremely challenging task. Chiral chromatography using chiral stationary phase is a commonly used method for chiral separations. Many common chiral stationary phases (CSP) are based on oligosaccharides such as cellulose or cyclodextrin. However, none of the currently used CSP materials can address a variety of chiral separation needs and low separation efficiency issues are still frequently encountered. Thus, the development of new CSP materials is in demand. Chiral porous solids can be good candidates for CSP materials since they combine both chirality and sieving effect. Chiral zeolite materials were studied for enantioselective separation. However, these are several limitations for chiral zeolite materials. For example, there are limited chiral topology types for zeolites and it is not easy to produce homochiral zeolite materials. In addition, the pore size of zeolites is usually limited and thus not feasible for large organic molecules, which are typical for pharmaceutical molecules. MOFs represent a more diverse class of porous materials that can be more easily made homochiral with the pore size tailored for separation purpose. For example, a homochiral MOF compound can be simply obtained by inclusion of an enantiopure ligand. Recently, some reports have revealed that in the presence of appropriate chiral induction agent, homochiral MOFs can be even obtained with achiral components only. The great success in the synthesis of homochiral MOFs has inspired many studies on their use for applications for enantioselective separations. Aoyama and co-workers reported the first homochiral MOF in 1999, and numerous chiral MOFs have been reported since then. MOFs are competitive materials for enantioselective separation due to the adjustable homochiral frameworks and structural diversities. Although a number of chiral separation methods have been exploited, MOFs are mostly utilized as chiral stationary phase for HPLC and GC or as absorbents in solutions and solid-phase extractions (SPE). Many chiral MOFs have been studied as absorbents for enantioseparation. Analytes include amino acids, sulfoxides, amines, alcohols and pharmaceutical molecules such as naproxen. Even though various works have been reported in MOF-based enantioseparation, the categories of analytes are still limited and most reported analytes are small molecules with kinetic diameters less than 10 Å. Further studies would also need to focus on large enantiomer separations and analyte varieties.

In 2010, Cui and co-workers published a review about homochiral MOFs catalysis and enantioselective separation. Chen and co-workers also reviewed recent progress in this topic. Here, we summarize some latest advances on this topic.
ligands and Mn\(^{2+}\) (Figure 13a).\(^{[210]}\) The as-prepared MOF contains 1D channels modified by chiral dihydroxyl groups (L\(^1\)) or chiral dimethoxy groups. Nanoscale aperture window size is \(\approx 1.5 \text{ nm} \times 1.0 \text{ nm}\). Utilizing L\(^1\)-MOF as a CSP for HPLC gives selective factor (\(\alpha\)) and chromatographic resolution (Rs) as high as 1.4 and 2.7, respectively, within 0.5 h for separating benzoylated 1-PEA and derivatives. Thermostable and robust frameworks enable recycling and reutilization of the material without obvious decrease in performance.

### 4.2. Chiral MOFs as Absorbents in SPE and solutions

Adsorption was also reported in the same work by Cui and co-workers.\(^{[210]}\) Adsorption preference of (R)-L\(^1\)-MOF for S-enantiomers overcomes racemic counterparts and vice versa. This is because the different orientations and binding strength between racemic components within MOF channels. When (S)-L\(^1\)-MOF and (R)-L\(^1\)-MOF are utilized as adsorbents, ee values of 91% (R) and 88.3% (S) for racemic 1-PEA separation

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Figure 13. a) Structure illustration of the chiral ligand and compound (S)-1a. b) Enantiosorption of (S)-1a toward benzyl amine and its derivatives. Reproduced with permission.\(^{[210]}\) Copyright 2014, Macmillan Publishers Ltd.
are achieved respectively (Figure 13b). Various para position substituted derivatives, aromatic amines, and aliphatic amines also give high ee values through (S)-L-1-MOF adsorption.

Martí-Gastaldo and co-workers utilized a homochiral MOF Cu(GHG) for enantioselective separation of EP and MA by SPE.[211] Cu2+ is tetrahedrally coordinated by amino, methylamino, carboxylate group and imidazole from ligand GHG respectively. Cu-GHG-Cu linked by carboxylic acids forms a fourfold spiral chain. MC simulation indicates that (+)-MA and (-)-EP are more favorable for stereoselective separation from enantiomer mixture owing to H-bonds forming between reagents and ligands on frameworks. Besides, (+)-EP-Cu(GHG) interaction is enhanced by additional H-bond. 54 ± 2% of (+)-EP is separated from 1:1 racemic mixture by a 4 min SPE/MOF separation, and 44% of (+)-EP is extracted by chiral MOF through direct soaking adsorption.

Zhang and co-workers reported an achiral SURMOF-template method to prepare chiral polymer films for enantiomer separation in 2017.[212] Initially, HKUST-1 was grown on QCM substrate and then 1-DOPA was introduced into MOF pores. After self-polymerization of 1-DOPA, MOF template was removed by acid etching. The as-prepared chiral porous polymer film achieves ≈32% (R) for enantioselective separation of naproxen.

In 2015, Wang and co-workers introduced d-histidine into ZIF-8 frameworks through one-pot ligand substitution strategy.[213] The prepared d-his-ZIF-8 achieves enantioseparation with ee values of 78.52% and 79.44% for alanine and glutamic acid respectively. S-alanine and S-glutamic acids are homochiral due to the enantiopure Cu-salen ligand. These compounds were further used to encapsulate the enantiopure Cu-salen ligand. d-his-ZIF-8 is stable after three cycles without obvious decrease in racemic separation.

Chen and co-workers developed a mixed MOF strategy by using a metallo-salen based bipyridine ligand and a dicarboxylate ligand, leading to two MOF compounds M’MOF-2 (with benzenedicarboxylate or BDC) and M’MOF-3 (with cyclohexanedicarboxylate or CDC) (Figure 14a).[114] The two compounds are homochiral due to the enantiopure Cu-salen ligand. These compounds were further used to encapsulate the racemic mixture of (R)- and (S)-1-phenylethanol (PEA) by liquid phase adsorption. It was found that M’MOF-3 exclusively takes up S-PEA to form M’MOF-3S-PEA (Figure 14b). Chiral HPLC analysis of the desorbed PEA from the PEA-adsorbed M’MOF-2 revealed an ee value of 21.1%. The smaller chiral pores within the enantiopure M’MOF-3 have significantly enhanced its enantioselectivity for the separation of R/S-PEA with the much higher ee value of 64%. The same team further expanded the structure series through similar strategy.[115] M’MOF-7 with more bulky substitution group toward the chiral cavity shows even higher ee value of 82.4% for 1-PEA separation owing to the narrower but more selective pore restricted by the tert-butyl groups. The organic struts occupy chiral pore space and decrease nonselective passing through.

In 2016, Cui and co-workers reported an enantioselective adsorption of sulfoxides by a newly synthesized chiral MOF.[214] The as-prepared MOF is constructed by Zn2+, BDC ligand, and DHIP-bases ligand (L). L-Zn-L forms spiral chains along the b axis. The size of 1D channel along the c axis is ≈4.7 Å × 5.4 Å. The best performance achieved is 37.1% (R) ee% for 3-methoxyphenyl methyl sulfoxide. A cadmium chiral MOF was also prepared in this work, but shows no racemic recognition and separation ability.

4.3. Chiral MOFs as Stationary Phase in GC

In 2016, Zhang et al. utilized a LPE layer-by-layer method to grow homochiral SURMOFs on functionalized GC capillary columns for methyl lactate enantioseparation.[215] The chiral MOFs Cu2([cam],P) (P = dabco and bipy) grown on surface of poly(1-DOPA) functionalized column is along the direction. This is because the exposed −COOH groups on column surface replace acetate groups in Cu-paddlewheels. The high orientation and homogeneity of Cu2([cam],dabco)@poly(1-DOPA) decorated columns lead to a remarkable improvement of methyl lactate enantioselective separation compared to Cu2([cam],dabco) poly (1-DOPA) modified columns, and retention times for three columns are 2.63/3.61, 2.91/3.12 and 2.95/2.95 respectively.

In 2016, Yan et al. coated a series of chiral Tp-COFs on capillary columns by in situ synthesis method and the as-prepared columns showed excellent enantioselective separation ability, recyclability and reproducibility in GC.[116] Initially, they utilized a chiral molecule (+)-Ac-i-T to modify ligand Tp in achiral Tp-COFs. After decoration of inner surface of fused silica column with APTES, exposed amino groups were connected by Tp and Pa-RR1 for chiral Tp-COFs construction. The Reynolds constants are in range of 101.9–128.1 for Tp-COF columns, and as-prepared chiral COF columns possess better separation factor and resolution than commercialized β-DEX 225 and Cyclosil B columns. It is worth noting that the repeatability and reproducibility of Tp-COF modified columns are remarkably high, demonstrated by RSD of retention time that varies little after 7 times usage, 5 d utilization and by 3 columns respectively.

5. Separations with MOF Membranes

Membranes for gas separation have attracted broad attention since the first industrialized H2-separating Prism membrane.[217] Currently, polymeric membranes are ahead of other membranes in market due to their low preparation cost, mechanical flexibilities, adjustable thickness, and excellent permeabilities. Numerous polymeric membranes were reported in separation of different gas pairs like N2/O2, N2/H2, H2/CH4, CO2/olefin, CO2/paraffin, and olefin/paraffin.[218] Robeson’s upper bound is an important correlation between gas selectivity and permeability, two criteria for evaluation of gas separation performance by membranes.[219,220] MOF materials are prepared into membranes for gas separation due to their tunable pore aperture sizes and adjustable functionalities. MOF-membranes surpassed Robeson’s upper bounds in most reported works. This is because selectivity and permeability are enhanced in those cases.
Selectivity is dependent on pore size, cavity size and interlayer distances. Apertures are partially occupied by hindering groups on ligands through postsynthetic modification or one-pot in situ synthesis processes.[221] Ionic liquid cavity occupation is a useful strategy to reduce nonselective permeation in MOFs.[222] Interlayer distance decreasement caused by interaction between free rotating groups in a heating process is also an interesting discovery enhancing gas selective passing through.[223]

To obtain high permeabilities, membranes are normally prepared with thickness less than $\approx 0.5 \, \mu m$. [218] Thus, permeability of hybrid membranes is strongly influenced by size and morphology of MOFs. As a result, membranes from 2D MOFs or nano-, sub-microscale MOFs have been more commonly reported. Exfoliation of layered ZIF to prepare molecular sieving membranes is an efficient approach.[224] In situ preparation of 2D MOF is also a novel method.[225] Besides, layer-by-layer method preparing COF-MOF membrane[226] and

Figure 14. a) The building scheme of compounds M'MOF-2 and M'MOF-3. b) (left) The 3D pillared framework with chiral pore cavities for M'MOF-3. Right: The 3D pillared framework exclusively encapsulating S-PEA molecules to afford M'MOF-3S-PEA. Reproduced with permission.[134] Copyright 2011, Macmillan Publishers Ltd.
self-conversion approach growing ZIF between layered double hydroxide (LDH)\[227\] are also novel synthetic strategies for MOF membranes. Yang and co-workers\[228\] and Qiu et al.\[229\] have published reviews on separation by MOF-based membranes. Here we focus on gas separation according to different gas pairs.

5.1. CO$_2$/H$_2$ separation

Yang et al. utilized highly crystalline layered Zn$_2$(bim)$_4$ as components for building molecular sieving membranes (MSMs) (Figure 15).\[224\] The as-prepared MSM shows excellent H$_2$/CO$_2$ separation performance. Instead of using physical exfoliation or soft-chemical exfoliation, they developed a mild physical process combining wet ball-milling and volatile solvent ultrasonication. Zn$_2$(bim)$_4$ is composed of benzimidazole-zinc tetrahedral units and layers are connected by van der Waals interaction. The soft-physical process keeps the 2D structure intact without introducing any other chemical reagents after exfoliation. Due to aperture size and structural flexibility, the prepared MSN excludes the permeation of CO$_2$ and permits the passing through of H$_2$. A hot-drop coating process enables a disordered stacking of exfoliated nanosheets on α-Al$_2$O$_3$ substrate. The MSM shows H$_2$/CO$_2$ selectivity at around 290 and H$_2$ permeation at about 3000 GPU, which surpasses the Robeson’s upper-bound for H$_2$/CO$_2$ gas pair. Besides, the as-prepared hybrid membranes are intact after 400 h utilization.

Zhao et al. utilized freeze–thaw approach to exfoliate a layered MOF (MAMS-1) to prepare molecular sieving membranes.\[223\] They observed an uncommon temperature-dependent behavior for H$_2$/CO$_2$ separation in prepared MSM. MAMS-1 possesses two gas pathways (PW). PW1 is favorable for selective permeation due to aperture size and orientation compared to PW2. Initially, hot water bath is alternated with liquid nitrogen bath for several times to exfoliate layered MAMS-1. Then a hot-drop casting method is utilized to fabricate MSM on porous anodic aluminum oxide. Selectivity is improved and permeance is reduced with the augment of membrane thickness. For 20/80 H$_2$/CO$_2$ mixture, the selectivity of 167 and H$_2$ permeance of 790 GPU surpass other reported membranes. Interestingly, H$_2$ permeation contradicts with classic transport theory for MSM mechanism in range of 40 and 100 °C. The increase in temperature leads to selectivity improvement and vice versa. This unusual thermoswitchable process is due to tert-butyl interaction between layers changing lattice distance of (002) plane. Lattice distance variation was observed by in situ variable temperature PXRD.

Qiu et al. first reported a COF-MOF hybrid membrane and the as-prepared membrane surpassed the 2008 Robeson’s upper bound for H$_2$/CO$_2$ gas pair separation.\[226\] They grew COF-300, [Zn$_2$(bdc)$_2$(dabco)] or ZIF-8 layer by layer on porous

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Figure 15. a) Architecture of Zn$_2$(bim)$_4$. b) TEM image of exfoliated Zn$_2$(bim)$_4$. c) Structural illustration of layered Zn$_2$(bim)$_4$. d) Space-filling illustration of aperture size. Reproduced with permission.\[224\] Copyright 2014, AAAS.
SiO$_2$ plate. The as-prepared membranes perform better selective separation than single-component layered membranes owing to synergistic interaction between interface of COF and MOF.

Caro et al. used a postsynthetic modification method to prepare ZIF-90 molecular sieving membranes through condensation reaction between aldehyde group on ligand and amino group on APTES.[221] The as-prepared MSM exhibits excellent H$_2$/paraffin (CH$_4$, C$_2$H$_6$, C$_3$H$_8$) selectivity with negligible loss in H$_2$ permeability. This is because APTES hinders the pore window, and H$_2$ is unable to permeate into the ZIF-90 cage owing to the length of propyl chain. Thermostability of both ZIF-90 and APTES enable prepared membrane to work under 225 °C over 80 h.

Caro et al. reported a partial self-conversion approach to prepare a ZIF-8-ZnAl(NO$_3$)$_3$ LDH composite membrane resulting in significantly improved H$_2$/CH$_4$ separation performance and H$_2$ permeance.[222] This strategy has the following advantages: (1) Original membrane provides Zn$^{2+}$ source for ZIF-8 growth. (2) The formation of ZIF-8 decreases the thickness of original membrane. (3) ZIF-8 fills in the ≈4.2 Å gallery height reducing nonselective permeance. (4) Partial conversion does not change the compact binding between LDH and γ-Al$_2$O$_3$ substrate. The H$_2$/CH$_4$ separation factor is enhanced by about 5 times and H$_2$ permeance is improved by two times compared to ZnAl(NO$_3$)$_3$ LDH membrane.

Li and co-workers used the oriented Ni$_3$S$_2$ and Co$_3$O$_4$ nanomicrostructure arrays on the Ni foam as substrate to grow continuous membranes for HKUST-1 and M$_6$(HCOO)$_6$.[228] The obtained membranes were firmly anchored on the Ni foam since the nano-microstructure can act as nucleation centers and anchor bars for the MOF growth. Particularly, fabrication of MOF membranes can be achieved in a controllable manner since these oriented nano-microstructure arrays can adjust the growth orientation of the MOF crystals on the substrate. Furthermore, the thickness of the membranes can be controlled by adjusting the reaction time and/or precursor concentration of MOFs. It was also demonstrated that the CO$_2$ permeance through these M$_6$(HCOO)$_6$ MOF membranes is slow compared with CH$_4$, N$_2$, and H$_2$, thereby representing a good separation performance, especially for the H$_2$/CO$_2$ mixture.

### 5.2. CO$_2$/CH$_4$ separation

Gascon and co-workers reported a bottom-up synthesis strategy and prepared 2D Cu(BDC) nanosheets/polyimide (PI) membranes for CO$_2$/CH$_4$ separation.[225] The pore size of Cu(BDC) is ≈5.2 Å. Different with interfacial synthesis strategies, liquid layers in this approach are composed by miscible solvents in mediated ratios. The Cu$^{2+}$ and BDC solutions are separated by an intermediate layer. Due to the diffusion-mediated process, layered MOF grows in interspace and quits growth after precipitation. MOF-polymer membranes are prepared by casting the solution of nanosheets and polyimide on plate. The separation property is improved when cross-section is perpendicular to the gas flow direction. What is more, selectivity of nanosheet-Cu(BDC)@PI membrane is 30%-80% higher than PI membrane and 75%-800% higher than bulk-Cu(BDC)@PI.

Nair and co-workers reported micrometer-sized ZIF-90/polyimide mix matrix membranes for CO$_2$/CH$_4$ separation.[230] The sodalite structure with ≈3.5 Å aperture size permits the permeation of CO$_2$ and prohibits the passing through of CH$_4$. Initially, they introduce H$_2$O and methanol during crystallization process and get micrometer-sized ZIF-90 crystals. The synthesized high crystalline thermostable microcrystals are further incorporated into Ultem, Matrimid and 6FDA-DAM individually. For two commercial membranes loaded with ZIF-90, CO$_2$ permeability is enhanced without any loss in selectivity. For ZIF-90/6FDA-DAM membrane, both permeability and selectivity increase significantly. The ZIF-90/6FDA-DAM MMM surpasses the upper bound 1991 and is near the predicted upper bound 2008.

Yang and co-workers introduced room temperature ionic liquid [bmim][Tf$_2$N] into the cavity of ZIF-8 by a one-pot ionothermal synthesis strategy (Figure 16).[231] As-prepared mixed matrix membranes (MMM) containing IL@ZIF-8 nanocrystals surpass the 2008 Robeson’s upper bound for both CO$_2$/CH$_4$ and CO$_2$/N$_2$ gas pairs. ZIF-8 with 11.2 Å cavity size and 3.4 Å aperture window size is constructed by mim anions and zircon cations. These [bmim][Tf$_2$N] ions not only occupy ZIF-8 cavity to reduce CH$_4$ and N$_2$ gas pathway, but also enhance CO$_2$ capture property. Ideal adsorption selectivity of CO$_2$/N$_2$ increases from 19 to 100 and CO$_2$/CH$_4$ gas pair increases from 7.5 to 40 after cage modification. IL@ZIF-8/PSF MMM performs better gas permeability than PSF membranes without IL@ZIF-8 or ZIF-8 loading. Highly selective separation of CO$_2$ from CH$_4$ at elevated pressure is also observed in as-prepared MMM.

### 5.3. C$_2$H$_4$/C$_2$H$_6$ separation

Long and co-workers developed an MOF-74/6FDA-DAM composite membrane to address C$_2$H$_4$/C$_2$H$_6$ gas separation challenge (Figure 17).[231] The hexagonal channels in MOF-74 contain high density of unsaturated metal sites. Both ethylene permeation and ethylene/ethane selectivity are significantly improved after loading nanocrystals. This is because nanocrystals increase MOF-polymer interface and diminish nonselective gas flow. It is noticeable that four different metal compositions MOF-74/polyimide mix-matrix membranes in this work all surpass upper bound.

### 5.4. Membrane for Liquid Phase Separation

Besides gas separations, MOF-based membranes can be employed for liquid phase separation as well.[232] Li and co-workers reported a UiO-66 membrane with excellent abilities in separating water from certain biofuels and organics.[233] They utilized prestructured yttria-stabilized-zirconia hollow fibers (YSZ HFs) as substrate and zirconium source to grow UiO-66 MOF membranes on the outside surface of hollow fibers by an in situ solvothermal method. The sub-micrometer sized UiO-66 grains fabricate the membrane with a thickness ≈1.0 μm. The as-prepared membrane achieves 99.60 wt% water concentration in the permeate with a total flux ≈1.2 kg m$^{-2}$ h$^{-1}$ for n-butanol aqueous solution purification (5 wt% water). For i-butanol, furfural and THF solution (10 wt% water), the separation...
factors are higher than 45,000 with the best total flux up to ≈6 kg m⁻² h⁻¹. The robustness of prepared membrane enables a continuous pervaporation over 300 h and keeps intact after exposing to boiling water, boiling benzene and ≈pH = 2 sulfuric acid solutions. Besides, the UiO-66 membrane is also able to separate water from other biofuels like ethanol and organics like propanol and acetone.

Cohen and co-workers utilized a drawdown coating method to prepare a series of mechanically stable and flexible free-standing MMMs for dye separation. [234] The reported MOF-PVDF (polyvinylidene fluoride) polymer MMMs contain over seven MOFs including UiO-66, UiO-66-NH₂, MIL-101(Cr), MIL-101(Fe), HKUST-1, MIL-53(Fe), ZIF-8. As a binder, PVDF enables MOF loading to achieve ≈67 wt% in MMMs. The as-synthesized UiO-66 MMM was used as a syringe filter (0.95 cm²) for methyl orange and Coomassie brilliant blue R-250 separation. In a mixed solution containing 10 μM Coomassie dye, over 99% of Coomassie blue was removed and ≈80% of methyl orange went through the MMM, and more than 95% of Coomassie dye was separated from liquid mixture in the second run.

Li and co-workers reported an in situ self-assembly method to prepare ZIF-8/PSS hybrid membranes for removal of methyl blue (MB) from water. [235] Zinc ions were coordinated with carboxylate groups from hydrolyzed polyacrylonitrile (PAN) substrate and then substrate was immersed into a mixed solution.
of 2-methylimidazole (Hmim) and poly(sodium 4-styrene-sulfonate) (PSS) to form ZIP-8 particles and to expose sulfonate groups on PSS for further assembling of Zn\(^{2+}\) and hydrophilicity enhancement. The repeating process enables multilayer growth. The as-prepared two-layered membrane performs a MB retention of 98.6% at a flux of 265 Lm\(^{-2}\)h\(^{-1}\)MPa\(^{-1}\). The retention of MB could be improved to 99.8% by tuning concentration of Zn\(^{2+}\), but flux decreases to 53 Lm\(^{-2}\)h\(^{-1}\)MPa\(^{-1}\) due to smaller particle sizes and increase in membrane thickness.

6. Conclusion

Separation plays essential roles in a broad range of industrial processes and has enormous economic and environmental impact. However, some important separation processes remain a challenge with current technology. Separation with the assist of advanced porous adsorbents has already shown some advantages over conventional methods such as distillation. Especially, the emerging class of MOFs offers new opportunities to address these challenges. Through a selection of recent studies, we have illustrated how MOFs can be used as a solid-state separation medium for various separation applications. Compared to other classes of materials, MOFs are versatile platforms with great tunability and allow precisely controlled crystal engineering and modifications to meet specific separation needs.

During the past decade, research on separation by metal-organic framework materials has undergone rapid development. The IAST calculation and column breakthrough experiments have been more frequently adopted to evaluate the separation performance on MOF materials, which better mimics real applications and provides more relevant results. In a number of separation occasions, MOFs already exhibit superior performance compared to commercially used materials such as zeolites, in terms of some core parameters including selectivity and capacity. Also, consistent improvement of separation performance has been observed from the study of new MOFs materials. For example, the capacity of acetylene captured from ethylene has been improved more than 10 times over the past five years. Given the fact that the majority of existing and hypothetical MOF compounds have not been studied for separation yet, continual discovery of MOF materials with better separation performance can be expected. In practice, it is impossible and unnecessary to test every MOF material experimentally. The computer-assisted screening of MOF candidates can be a useful approach. In this regard, a complete and public accessible database of MOF structures with key parameters of pore features is desired. Meanwhile, a better understanding of specific separation process is equally important, which can provide more accurate guideline for materials screening. In previous studies, various mechanisms for enhanced separation performance were proposed with either experimental or theoretical support, which has improved our understanding on a variety of host–guest interactions. However, further studies are still needed to better reveal the relationship between MOFs structures and the separation performance. Based on thorough understanding of these mechanisms, more effective strategies can be developed toward designing better separation materials.

Finally, for real applications, some important properties other than the separation efficiency need to be taken into account. Thus, more aspects need to be taken into consideration during material design, such as the stability under specific application conditions, separation kinetics, the regeneration cost, and the cost for scaled-up materials synthesis.

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Conflict of Interest

The authors declare no conflict of interest.

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