MATERIALS CHEMISTRY







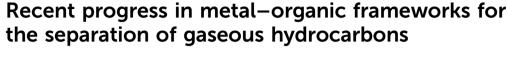
FRONTIERS

REVIEW

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The separation of gaseous hydrocarbons is involved in many important industrial processes for manufacturing chemicals, polymers, plastics, and fuels, and is performed through cryogenic distillation, which is heavily energy-intensive. Adsorption-based gas separation technology by using adsorbent materials can potentially fulfill a much energy-efficient gas separation. As a new generation of adsorbent materials, metal-organic frameworks (MOFs) have been demonstrated to have great potential in addressing important gas separations of hydrocarbons. In this review, we outline the uniqueness of MOF adsorbents for their separation application for gaseous hydrocarbons. A variety of microporous MOFs have been developed for separating gaseous hydrocarbons, which have been achieved by fine-tuning their pore sizes for high molecular sieving effects and/or immobilizing binding sites on their pore surfaces for their specific recognition of small molecules. Herein, we highlight recent important progress in this very important topic, focusing on the purification of ethylene, propylene, and butadiene.

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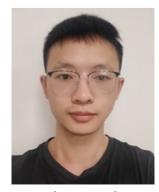
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1. Introduction

Gaseous hydrocarbons involve not only essential fuels for modern society but also are applied as important feedstocks in the chemical industry. Hydrocarbons usually are volatile, invisible, and flammable, and tend to be highly dispersed, easily contain mixtures of low concentration, and thus are difficult to handle. The separation and purification of hydrocarbons are critical industrial chemical processes to produce bulk commodities for fuels, polymers, and plastics. Some of these separation processes are carried out on a very large

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industrial scale. For example, olefin/paraffin separation produces light olefins of over 200 million tonnes. The huge markets of hydrocarbon products make a large contribution (thousands of billions of US dollars) to the annual revenues of the oil and gas industry. Most of the industrial separations of hydrocarbons traditionally rely on thermal-driven technologies, mainly fractional distillation involving numerous evaporation-condensation cycles, which are a high energy-intensity process. In particular, to separate mixed hydrocarbons of similar volatilities for high purity, relevant industrial processes are operated in complicated facilities and under harsh conditions. For the separation and purification of industrial commodities, it is believed that energyintensive processes, such as distillation consume 10-15% of the world's energy production. Adsorptive separation based on porous adsorbents is a promising technology to lower relevant separation



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energy use. For example, alternative technologies, such as adsorptive separation and/or membrane-based technologies, can be up to 10 times more energy-efficient than the traditional distillation methods, which have not been fully realized. These nonthermal technologies can separate hydrocarbon molecules according to their chemical affinities or sizes rather than differences in boiling points, and thus can be carried out under mild conditions, hence greatly reducing the energy inputs.² The core of these candidate technologies is the separation performance of solid porous media or permeable membranes, which are often made of porous materials with nanosized voids and desired internal pore features.

Metal-organic frameworks (MOFs, also known as porous coordination polymers) are an emerging type of crystalline porous solids, which are assembled by metal-containing nodes and organic linkers or struts through coordination bonds to have pore space. MOFs are unique owing to their exceptional porosity, diverse structures, tunable pore size, and ease of functionality.³⁻⁶ After two decades of intensive practices, MOF materials are well demonstrated for their exceptional capability for pore adjustment and interior modification. Today, about 100 000 of MOFs have been synthesized. MOFs can show ultrahigh porosity with the largest pore surface area of over 7000 m² g⁻¹, or with pore sizes ranging from 3 to 100 Å, the highest thermal stability of over 600 °C, or exceptional chemical stability in concentrated acidic/ basic solutions.^{3,7,8} The high modularity of MOFs enables us to construct their isostructural analogues of different pore sizes/ shapes and surfaces (such as functional organic groups, metal open sites, etc.) with the same coordination networks. The key design element for MOFs is thus to functionalize their pore surface with binding sites and/or adjust their pore size/shape for molecular separation. In this context, MOFs have shown great promise that is superior to conventional porous materials (activated carbon and zeolites) in addressing important separations of gaseous hydrocarbons. 9-19

For separation processes in physical adsorbents, their separation mechanism can be roughly categorized into either equilibrium or non-equilibrium adsorption. Equilibrium adsorption processes are thermodynamic and are mainly driven by binding affinity differences dominated by those functional sites (i.e., binding sites) through supramolecular interactions. Pore functionalization with strong binding sites can significantly boost such type of separation performance. For non-equilibrium adsorption processes, 20 including kinetic separation and molecular sieving, the separation is achieved by differing the diffusivity, which is highly affected by the pore sizes and flexibility of adsorbents. The kinetic separation can be amplified after narrowing the pores of adsorbents. There are also cases that the separation is achieved by a combination of both thermodynamic and kinetic processes. In addition, there are gas separation processes that are usually performed with the collaboration of framework flexibility and structural transformation, namely, gate-opening or pore opening. Considering all aspects, it is very important to systematically control the pore size, pore surface and even the flexibility of adsorbents.

On the other hand, hydrocarbons are composed of the same elements with different carbon bonds and carbon/hydrogen ratios. Their physical properties and even chemical properties can be very similar (Table 1). The adsorptive separation by differing their molecular shapes or adsorption affinities in physical adsorbents is thus required to perform with high accuracy, which can be achieved by MOFs. 13 For example, compared with the mixture counterpart propane, propylene, as one major petrochemical product, differs by just two hydrogen atoms, and there is around a 5 K difference in their boiling points. It has been demonstrated that MOFs with embedded binding sites (ranging from open metal sites to polar functional groups, such as anionic fluoride, hydroxyl and amino) can effectively separate olefins/ paraffins owing to the difference in thermodynamic affinity. Another applicable approach is to adjust the pore sizes of MOFs



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Rui-Biao Lin obtained his BSc in Chemistry from Sun Yat-Sen University (SYSU) in 2009. He obtained his PhD in 2014 (SYSU). During 2016-2020, he worked at the University of Texas at San Antonio as a postdoctoral fellow. Since 2021, he has been working as a full professor in SYSU, where he is working on multifunctional porous materials, including metal-organic frameworks and hydrogen-bonded organic frameworks.



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Xiao-Ming Chen received his BS (1983) and MS (1986) degrees from Sun Yat-Sen University and PhD from the Chinese University of Hong Kong in 1992. He is an Academician of the Chinese Academy of Sciences, and Academician of The World Academy of Sciences for the advancement of science in developing countries (TWAS). He is a professor in the School of Chemistry at Sun Yat-Sen University and director of the Institute of Green Chemistry and

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Table 1 Physical parameters of selected gas and vapor hydrocarbons¹²

Adsorbate	Normal boiling point/K	Density/g L ⁻¹ (101.325 kPa, 273.15 K)	Kinetic diameter/Å	Polarizability \times 10^{25} /cm ³	Dipole moment × 10 ¹⁸ /esu cm	Quadruple moment × 10 ²⁶ /esu cm ²
$\overline{\text{CH}_4}$	111.66	0.717	3.758	25.93	0	0
C_2H_4	169.42	1.261	4.163	42.52	0	1.50
C_2H_6	184.55	1.355	4.443	44.3-44.7	0	0.65
C_2H_2	188.40	_	3.3	33.3-39.3	0	_
C_3H_6	225.46	1.914	4.678	62.6	0.366	_
C_3H_8	231.02	2.011	4.3 - 5.118	62.9-63.7	0.084	_
c-C ₃ H ₆	240.34	1.920	4.23-4.807	56.6	0	_
$i-C_4H_{10}$	261.34	2.689	5.278	81.4-82.9	0.132	_
i-Butene	266.25	_	4.84	8.14-8.29	_	_
1-Butene	266.92	_	4.5	79.7-85.2	0.359-0.438	_
1,3-Butadiene	268.62	_	5.2	86.4	0	_
$n-C_4H_{10}$	272.66	2.704	4.687	82.0	0.05	_
trans-2-Butene	274.03	_	_	84.9	0	_
cis-2-Butene	276.87	_	4.23	_	0.253	_
neo-C ₅ H ₁₂ (2,2-dimethylpropane)	282.65	2.334 (70.922 kPa)	6.2-6.464	102.0	0	_
i-C ₅ H ₁₂	300.99	1.120 (34.543 kPa)	5.0	_	0.13	_
$n-C_5H_{12}$	309.22	0.789 (24.455 kPa)	4.5	99.9	0	_
neo-C ₆ H ₁₄ (2,2-dimethylbutane)	322.87	_ ` ´	6.2	_	_	_
i-C ₆ H ₁₄ (2-methylpentane)	333.40	0.343 (8.960 kPa)	5.5	_	0.1	_
3-Methylpentane	336.40	_	5.5	_	_	_
n-C ₆ H ₁₄	341.88	0.231 (6.041 kPa)	4.3	119	0	_
C_6H_6	353.24	0.403 ^a (12.695 kPa)	5.349-5.85	100-107.4	0	_
c-C ₆ H ₁₂ (cyclohexane)	353.93	0.446 ^a (13.019 kPa)	6.0-6.182	108.7-110	0	_
n-C ₇ H ₁₆	371.57	0.067 (15.250 kPa)	4.3	136.1	0	_
$i-C_8H_{18}$ (2,2,4-trimethylpentane)	372.39	_ ` ´	6.2	154.4	0	_
Toluene	383.79	0.037 (0.906 kPa)	5.25	118-123	0.375	_
Ethylbenzene	409.36	_ ` ` `	5.8	142	0.59	_
<i>p</i> -Xylene	411.53	_	5.8	137-149	0.1	_
<i>m</i> -Xylene	412.34	_	6.8	142	0.37	_
o-Xylene	417.59	_	6.8	141-149	0.640	_
^a Density at 298.15 K.						

for size-matching of gas molecules, which is expected to enhance kinetic separation or sieving effect and finally achieve high selectivity. If the pore aperture size of adsorbents is right between the molecular sizes of different gas components, an adsorption cut-off happens along with the inaccessibility of internal pore space to certain gas components, thus leading to molecular sieving. For some MOFs, the adjustment of pore size in MOFs can be done up to a precision level of 0.1 Å. 13 Given that most hydrocarbon gases have their molecular sizes or kinetic diameters between 3 and 5 Å, microporous MOFs with comparable pore sizes have been intensively investigated for separating hydrocarbon mixtures. Usually, MOFs with large pores can show high sorption capacity but low separation selectivity for gas, whereas the ultramicroporous ones can exhibit high selectivity but low sorption capacity (termed sorption capacity versus selectivity trade off). By simultaneously tuning the pore size and incorporating binding sites, the internal pore space of MOFs can integrate molecular shape matching and preferential binding toward the targeted gas molecules, which is expected to address the trade-off for exceptional separation performance. The complicated effects of MOF flexibility for separation of hydrocarbons have also been noted.²¹

By virtue of pore structural and chemical control of MOF materials, namely, tuning pore size, incorporating functional sites, or their combination, significant progress has been made for gaseous hydrocarbon separation. This review focuses on the research progress of MOF materials for separation of gaseous hydrocarbons in about recent five years. In particular, we summarize representative MOF materials with unique pores and functional sites for C₂H₂ and CO₂ separation, C₂H₂/C₂H₄ separation, C2H4 and C2H6 separation, C3H4/C3H6 separation, C₃H₆/C₃H₈ separation, and purification of butadiene, xylenes and other volatile gaseous hydrocarbons.

2. Pore structure control of MOFs for separating gaseous hydrocarbons

The separation performance of adsorbents towards target molecules can be affected by various factors, mainly dominated by the adsorbent-adsorbate and adsorbate-adsorbate interactions in the pore space. The adsorbent-adsorbate interactions for specific gases can be adjusted by controlling the pore chemistry and pore size of porous materials for optimal binding affinity, whereas adsorbate-adsorbate interactions are dependent on the physical properties of gas molecules including molecular polarity or polarizability, sizes and shapes. Therefore, rationally tuning the pore sizes of MOFs and/or functionalizing their pore surface have been demonstrated as efficient approaches to boost the separation performance for gases. Both adsorbent-adsorbate and

adsorbate-adsorbate intermolecular interactions for larger or heavier molecules with high polarizability are usually superior to those for small, light and non-polar ones, due to more supramolecular interactions (ranging from hydrogen bonding to electrostatic interactions and van der Waals forces). In this section, representative examples of MOFs for hydrocarbon separation were presented according to the sequence of the polarizability and boiling points of various gases (Table 2).

2.1. Methane purification

Natural gas is a cleanest fossil fuel and has been widely used due to its natural abundance and high energy intensity, and is usually contaminated with gas impurities such carbon dioxide (CO₂) and nitrogen (N₂). The upgrading of natural gas involves the purification of methane (CH₄). Coal-bed methane (CBM) is an excellent complement to conventional natural gas; the recovery of CH4 from it can also reduce the emission of the greenhouse gas CH4 from CBM as well as enhance the safety of coal mineral.22

Ma et al. used an alkyl MOF, $Cu_2(ATC)$ (ATC-Cu, $H_2ATC =$ 1,3,5,7-adamantane tetracarboxylic acid), as a methane nanotrap that features oppositely adjacent open metal sites (OMSs) and dense alkyl groups for capturing methane molecules.²³ At 1 bar and 298 K, this MOF exhibits the highest methane uptake capacity (2.90 mmol g⁻¹) among reported MOFs, showing a high CH₄/N₂ selectivity of 9.7 for an equimolar mixture under ambient conditions. ATC-Cu thus shows promising potential for capturing methane from CBM with low content of methane (<30%). Structural and computational modelling indicated that pairs of open Cu sites with a Cu···Cu distance of 4.43 Å between two neighboring Cu paddlewheels afford considerable dual Coulombic interactions and act as strong binding sites for methane molecules. Also, there are cavities with an aliphatic surface that can serve as the second binding sites for CH₄, with an average interaction distance of ca. 3.5 Å.

Yang et al. studied four nickel-based coordination networks with functional sites (-NH2) or varied pore sizes for the separation of CH₄/N₂, which supports that the pore size and chemical environment of adsorbents play an important role during methane purification.²⁴ Among those four MOFs, Ni(ina)₂ showed the highest CH₄/N₂ selectivity (15.8) with an adsorption capacity of 1.82 mmol g⁻¹ under ambient conditions. Ni(ina)₂ shows good thermal and moisture stability as well, which can be easily scaled up at a low cost.

The influence of humidity on the separation performances of MOFs for CH₄ separation has been noticed. Li et al. investigated a series of isostructural MOFs, [Zn₂(1,4-NDC)₂(DABCO)], $[Zn_2(ADC)_2(DABCO)]$, $[Ni_2(ADC)_2(DABCO)]$, and $[Cu_2(ADC)_2(-$ DABCO)] (namely, DMOF-N, DMOF-A₁, DMOF-A₂, DMOF-A₃, respectively, H₂1,4-NDC = 1,4-naphthalenedicarboxylic acid, H₂ADC = 9,10-anthracene dicarboxylic acid, and DABCO = 1,4diazabicyclo[2.2.2]octane), for CH₄ purification.²⁵ Altering their aromatic moieties and/or metal centers results in varied pore sizes, hydrophobicity and stability. The hydrophobic pore space suppressed the water sorption and enhanced the moisture resistance of those MOFs, which show high CH4 uptakes and CH4/N2

selectivity. Breakthrough experiments for the CH₄/N₂ mixture under humid conditions indicated that their CH₄/N₂ separation performance can be retained even under high humidity (40% RH).26

Zhang et al. reported two isostructural flexible metal-azolate frameworks (abbreviated as MAFs, a subclass of MOFs with azolate ligands¹⁹) [Zn₃(OH)₂(pzdc)(tz)]·DMA and [Zn₃(OH)₂-(pzdc)(atz)]·DMA (MAF-91·DMA and MAF-92·DMA, respectively, H_3 pzdc = 3,5-pyrazoledicarboxylic acid, Htz = 1,2,4-triazole, and Hatz = 3-amino-1,2,4-triazole), which possess quasi-discrete pores with analogous sizes (MAF-91·DMA: 3.6 \times 2.4 and 4.0 \times 2.1 Å², and MAF-92·DMA: 3.7 \times 1.3 and 4.0 \times 2.1 Å²). ²⁷ Due to the stronger intra-framework hydrogen-bonding interaction in MAF-92, there is a higher gating energy than MAF-91. Thus, MAF-92 showed tremendous shrinkage of apertures (1.0 \times 0.8 and 2.5 \times 1.0 Å²) after guest removal, while those in MAF-91 $(3.5 \times 2.2 \text{ and } 4.4 \times 2.0 \text{ Å}^2)$ showed negligible changes (Fig. 1). Single-component gas adsorption revealed that MAF-92 can adsorb a large amount of CO_2 (2.1 mmol g^{-1} at 273 K and 1 bar), but completely excludes N2 and CH4. The molecular sieving performance was further confirmed by breakthrough experiments for CO₂/N₂ and CO₂/CH₄, giving selectivities of >1500. This work revealed that the controlled gated barrier can be expected to achieve definite and ideal molecular sieve effect. In contrast, the very commonly encountered framework flexibility of MOFs could be an important drawback to size-dependent molecular sieving for separation of similar molecules.

2.2. C₂H₄ and C₂H₆ separation

Ethylene (C₂H₄) is one of the most important chemical raw materials, which is widely used in the production of plastics, rubber, coatings, and other chemical products. It is mainly produced by cracking ethane (C_2H_6) or naphtha; thus, C_2H_6 is a major impurity in the raw mixture. However, the separation of C_2H_4 from the C_2H_4/C_2H_6 mixture is highly challenging due to their small molecular size difference (<0.5 Å) and boiling point difference (ca. 15 K). MOFs have been reported to exhibit significant progress in the separation of C₂H₄/C₂H₆.²⁸⁻⁴¹

Usually, the introduction of OMSs on the pore surface of MOFs enables preferential adsorption of C2H4 over C_2H_6 . ^{28-33,38,41-44} For example, HKUST-1²⁸ and $M_2(dobdc)^{29-31}$ (M-MOF-74; M = Mg, Mn, Fe, Co, Ni, and Zn) exhibit stronger binding enthalpies for olefins than alkanes due to the metal- π interactions. Altering the charge density of the metal centers can improve the olefin adsorption and selectivity as revealed by M₂(dobdc) isomers.³³ The appropriate aperture combined with OMSs of high density can also significantly improve the bonding affinity for olefins. In 2020, Qian et al. reported two microporous MOFs functionalized with different amounts of carboxylate groups, in which the carboxylate groups not only can adjust the aperture size, but also chelate with copper(1) ions via post-synthetic modification. 41 Therefore, Cu^I@UiO-66-(COOH)₂ exhibits optimal apertures and exposed Cu(1) centers to form a strong binding affinity for C2H4, while suppressing the adsorption of C2H6. Compared with other UiO-66 materials, Cu^I@UiO-66-(COOH)₂ showed the highest ideal adsorbed solution

Review

 Table 2
 Summary of representative MOFs for adsorptive separation of important gases

MITCO,	Materials	Gas separation	Strategies	$\begin{array}{c} \text{Uptake}^a \\ (\text{mmol g}^{-1}) \end{array}$	$\mathrm{Selectivity}^b$	Ref.
co_CO_CO_H, CO_LO_H, Optimizing pero sizes (1.0 × 1.8 × 1.8 × 1.2	ATC-Cu	$\mathrm{CH_4/N_2}$	Incorporating adjacent open copper sites	2.9/0.75	9.7	23
COJCH, Optimizing prec sizes (5.3.3) and incorporating parallel aromatic rings 14560.39 77.3 74.6 (2004), Cyll, Cy	$Ni(ina)_2$		Optimizing pore sizes $(5.0 \times 4.8 \text{ Å}^2)$	1.82/0.53	15.8	24
Co.	$DMOF-A_2$		Optimizing pore sizes (5.3 Å) and incorporating parallel aromatic rings	1.65/0.39	7.2	25
Poet-(COOH), C-J.H.CJ.H., Optimizing preve states (1.4. M) and incorporating expert() is not one the pore surfaces C-J.H.CJ.H., Definiting preve state (1.4. M) and incorporating electronegative functional groups C-J.H.CJ.H., Incorporating preve state (1.4. M, 8. M) and incorporating electronegative functional groups C-J.H.CJ.H., Incorporating preve state (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—states C-J.H.CJ.H., Incorporating prevents (1.4. M, 8. M) and incorporating state—state	MAF-92	$\mathrm{CO}_2/\mathrm{CH}_4$	Optimizing pore sizes $(5.0 \times 4.8 \text{ Å}^2)$	2.06/0.06	1.3×10^{7}	27
Child	Cu'@UiO-66-(COOH)2	$\mathrm{C_2H_4/C_2H_6}$	Optimizing pore sizes (4.1 A) and incorporating copper(1) ions onto the pore surfaces	1.9/0.9	80.8	41
CHACH, Encopouning press (CAA, SA, A) and incorporating electronogative functional groups (2.9.1). A comparing press (CAA, SA, A) and incorporating electronogative functional groups (2.9.1). A comparing press (CAA, SA, A) and incorporating genes (CAA, SA, A) and incorporating SIR, sites and dipole repulsion groups (CAA, CAA, CAA, CAA, CAA, CAA, CAA, CAA	UTSA-280		Optimizing pore rigidity and pore size (3.8 A)	2.5/0.098	>10000	35
Cyl.,C.,H., Organizing pore stick (1.4.5.4.4) and incorporating selectoring and of pole repulsion groups (1.20.1.). Cyl.,C.,H., Organizing gove stick (1.4.4.5.4.4) and incorporating Sig.,2 sites (1.2.2.5.4.4.2.4.2.3.2.4.0.4.4.3.4.2.2.0.4.4.4.3.4.2.2.0.4.4.4.4.4.2.2.2.0.4.4.4.4.4.2.2.2.0.4.4.4.4	Co-gallate		Optimizing pore size (5.2 A)	3.37/0.31	52 50 50 40	36
C,JH,C,JH, Properting	m ZII~901		Optimizing pore structure (3.8 A) and incorporating electronegative functional groups	1.92/1.04	36.6 / 12.4	35
Co.H.,C.H., Optimizing pore size (3.3, Å). Co.H.,C.D., C.H.,C.H., Optimizing press size (4.3, Å) and incorporating Sig.* sites (2.4, G.H.,C.D.) C.H.,C.D., Incorporating press size (4.4, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) C.H.,C.D., Incorporating open size (4.4, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) C.H.,C.D., Incorporating open size (4.4, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.3, Å) and incorporating Sig.* sites (2.2, G.H.,C.D.) Suitable pore sizes (4.2, A.A., Å) and incorporating Sig.* sites (2.2, G.H.,C.D.,D.) Suitable pore sizes (4.2, A.A., A., A., A., A., A., A., A., A.,	ZO-901 MAF-49	C.Hc/C.H.	Optimizing port size (3:4 × 4:2 A) Incorporating multiple hydrogen-bonding acceptors and dinole repulsion grouns	1.7/1.69	2.7	65
dobde) Cohi, Chi, Chi, Directpointing pore size (14 4Å) and incorporating Sire ² —sites Cohi, Chi, Chi, Optimizing pore size (14 4Å) and incorporating Sire ² —sites Cohi, Chi, Chi, Optimizing pore size (14 4Å) and incorporating Sire ² —sites Optimizing pore size (14 4Å) and incorporating Sire ² —sites Solution of the cohimacy of the cohimac	Cu(Oc),	Z6, Z4	Optimizing pore size (3.3 Å)	1.85/0.78	3.4	09
2.Chi J. Optimizing prove size (1.4. λ. λ. λ. and morponeting SIR½*- sites 3.650.65 6.20.00 0.0a Optimizing prove size (1.4. λ. λ. λ. λ. and incorponeting SIR½*- sites 3.650.65 6.20.00 0.0a Optimizing prove size (1.4. λ. 2. λ. λ.) and incorporating SIR½*- sites 3.650.63 7.29.1 1.066-(COOH)2 C.5H.5CO2 Incorporating copie Cit. siz. s. λ. λ.) and incorporating SIR½*- sites 4.450.23 7.29.1 1.066-(COOH)2 C.5H.5CO3 Incorporating copie Cit. siz. s. λ. λ.) and incorporating SIR½*- sites 4.450.23 1.81.02.1 1.066-(COOH)2 Suitable pore sizes (1.3. x. 2. λ. λ.) and incorporating SIR½*- sites 4.01.268 4.13 1.066-(COOH)2 Suitable pore sizes (1.3. x. 2. λ. λ.) and incorporating SIR½*- sites 3.680.13 1.19 1.066-(COOH)2 Suitable pore sizes (1.3. x. 2. λ. λ.) and incorporating SIR½*- sites 3.680.13 1.19 1.066-(COOH)2 Suitable pore sizes (1.3. x. 2. x. λ.) and incorporating SIR½*- sites 3.680.13 1.19 1.00 Suitable pore sizes (1.2. x. 2. x. λ. λ.) and incorporating SIR½*- sites 3.680.13 3.580.63 3.580.63 1.00 Suitable pore sizes (1.2. y. 2. x. λ. λ.) and incorporating SIR½*- sites	[Fe,(O,)[dobdc)]		Inconociating Re-peroxo sites	3.29/2.6	4.4	61
000a Ophimizing processing (1.4 × 2.0 Å) and incorporating SiR ₂ *- sites 3.650.653 0.060.04 2 4.670.22 Ophimizing processing (1.4 × 2.0 Å) and incorporating SiR ₂ *- sites 3.650.653 0.060.04 2 4.670.22 Incorporating copped/) ions onto the pore surfaces 1.670.22 0.060.04 4.670.23 1.060.04 1.060.00 1.060.0	SIFSIX-2-Cu-i	C,H,/C,H,	Optimizing pore size (4.4 Å) and incorporating SiF _e ²⁻ sites	4.02/2.19	44.8	70
0040 0040 0040 0040 0040 0040 0040 004	UTSA-200a	*7-7-7-7	Optimizing pore size (3.4 Å) and incorporating SiF ₆ ² sites	3.65/0.63	6320	71
10 dimining open zin ties and ties since and zies and incorporating site, zies and zies zies zies zies zies zies zies zies	UTSA-300a		Optimizing pore size $(1.3 \times 2.8 \text{ Å}^2)$ and incorporating SiF ₆ ²⁻ sites	3.08/0.04	27	72
4. (COOPH), C.J.H., CO., Intropporting opper IX is its so incorporating opper IX is its so incorporating opper IX is its so increporating opper IX is its so incorporating SIF ₂ ²⁻² sites a confine incorporating opper IX is its so incorporating SIF ₂ ²⁻² sites a confine incorporating opper IX is its so incorporating SIF ₂ ²⁻² sites a confine incorporating opper IX is so incorporating SIF ₂ ²⁻² sites a confine incorporating opper ix is so incorporating iX is incorporating iX is so incorporating iX is so incorporating iX is so incor	NCU-100a			4.57/0.32	7291	9/
Figure Cooker C	UTSA-74	$\mathrm{C_2H_2/CO_2}$	Incorporating open Zn sites	4.82/3.03	6	101
Here the componenting amine sites Horoporating size (1.3 × 2.8 Å) and incorporating size, sites Horoporating size size (1.3 × 2.8 Å) and incorporating size, sites Definitioning pore size (1.3 × 2.8 Å) and incorporating size, sites Horoporating size size (1.3 × 2.8 Å) and incorporating size, sites Definitioning pore size (1.3 × 2.8 Å) and incorporating size, sites Definitioning pore size (1.3 × 2.8 Å) and incorporating size, sites Definitioning pore size (1.3 × 2.8 Å) and incorporating size, sites Definitioning pore size (1.3 × 2.8 Å) and incorporating size, sizes Definitioning pore size (1.3 × 2.8 Å) and incorporating size size (1.3 × 3.8 Å) and incorporating size (1.3 × 2.8 Å) and incorporating size (1.3 × 3.8 Å) and incorporating size (1.3 Å) and incorporating size size ($Cu'@UiO-66-(COOH)_2$		Incorporating copper(1) ions onto the pore surfaces	2.44/0.85	185	107
Here, the potenting amine sites and the potential states between sizes (4.7 Å) and incorporating amine sites and proper sizes (4.7 Å) and incorporating sizes (4.7 Å) and incorporating sizes (4.7 Å) and incorporating sizes and proper sizes (4.7 Å) and incorporating sizes and $\mu_{\rm c}$ obtained by the size of the size of the size of the sizes of the size	JNU-4		Incorporating open Cu sites	9.82/7.1	8.2	108
Suitable pore sizes (1.3 k) and incorporating amine sites Poer spee partition Ordinary pore size (1.4 × 2.8 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.4 × 2.8 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.4 × 2.8 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.4 × 2.9 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.4 × 2.9 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.4 × 2.9 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.3 × 2.1 × 1.2 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.3 × 2.1 × 1.2 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.3 × 2.1 × 3.4 k²) and incorporating Sir, $^{-}$ sites Optimizing pore size (1.3 × 2.1 × 3.4 k²) and incorporating Sir, $^{-}$ sites Incorporating electropating electropating sore inclease blocking the priority site for C, $^{+}$ Suitable pore space (6.1 × 4.2 × 4.5 x²), without size (2.900.1 Suitable pore window (4.2 x²) and incorporating sore incorporating size (1.4 × 3.4 x²), without size (2.900.1 Suitable pore window size (2.2 x²) and incorporating sore incorporating size (1.4 × 3.4 x²) and incorporating sore incorporating size (1.4 x²). All and incorporating pore sizes (1.4 x²) and incorporating pore sizes (1.5 x²) and incorporating sizes (1.5 x²) and incorporating Null sizes C, H ₀	$\mathrm{CPL} ext{-}1 ext{-}\mathrm{NH}_2$		Incorporating amine sites	1.84/0.21	119	114
Suitable pore sizes (1.3 × 2.8 Å) and incorporating amine sites Optimizing pore size (1.4 × 2.8 Å) and incorporating Sir ₂ ² sites Optimizing pore size (1.4 × 2.8 Å) and incorporating Sir ₂ ² sites Suitable pore sizes (1.4 × 2.8 Å) and incorporating Sir ₂ ² sites Optimizing pore size (1.4 × 2.8 Å) and incorporating Sir ₂ ² sites Suitable pore sizes (1.4 × 2.8 Å) and incorporating Sir ₂ ² sites Optimizing pore size (1.4 × 2.8 Å) and incorporating Sir ₂ ² sites Optimizing pore size (1.4 × 2.8 Å) and incorporating Sir ₂ ² sites Optimizing pore size (1.4 × 3.8 Å) and incorporating Sir ₂ ² sites Optimizing pore size (1.4 × 3.8 Å) and incorporating sir ₂ site incorporating size incorporating size incorporating size incorporating size incorporating size incorporating electronsities incorporating size	CAU-10-H		Suitable pore sizes (4.7 Å)	4.01/2.68	4	115
Poter space optimizing pore size (1.3 × 2.8 Å) and incorporating Sir $_{a}^{b}$ - sites Optimizing pore size (1.3 × 2.8 Å) and incorporating Sir $_{a}^{b}$ - sites Optimizing pore size (1.3 × 2.8 Å) and incorporating Sir $_{a}^{b}$ - sites NETEPEZ RYTEPEZ RYTEPEZ Optimizing pore size (1.2 × 1.2 Å) and incorporating Sir $_{a}^{b}$ - sites Nether S suitable pore size (1.2 × 1.2 Å) and incorporating Sir $_{a}^{b}$ - sites Nether S suitable pore size (1.2 × 3.4 Å) and incorporating Sir $_{a}^{b}$ - sites Optimizing pore size (1.2 × 3.4 Å) and incorporating con- Size (1.2 × 3.4 Å) and incorporating size (1.2 Å) and incorporating con- Size (1.2 × 3.4 Å) and incorporating size (1.2 Å) and incorporating con- Size (1.2 × 3.4 Å) and incorporating size (1.2 × 3.4 Å) and inc	$CAU-10-NH_2$		Suitable pore sizes (3.8 A) and incorporating amine sites	3.57/2.08	10.8	116
ReTEPE-Zn Suitable pore size $(1.4 \times 3.0 \text{ Å})$ and neorporating SiFe, sites 3.08(0.18 860 and polimizing pore size $(1.4 \times 3.0 \text{ Å})$ and neorporating SiFe, sites 3.08(0.18 860 and polimizing pore size $(1.4 \times 3.0 \text{ Å})$ and neorporating SiFe, sites 3.08(0.18 860 and polimizing pore size $(1.4 \times 3.0 \text{ Å})$ and $8.4 \times 10.2 \text{ Å}^2$, flexible pore structure, incorporating sizes $(1.9 \times 3.0 \text{ Å})$ and $0.00 \times 3.00 $	FJU-90		Pore space partition	8.04/4.6	4.3	122
Suitable pore sizes (12.9 × 12.9 \mathring{A} and incorporating SiFe ² sites Suitable pore sizes (12.9 × 12.9 \mathring{A} and incorporating SiFe ² sites FRTEPEZ Suitable pore size (33. × 3.7 \mathring{A}) and incorporating SiFe ² sites Tochororating electronegative pore surface inclease belocking the priority site for $C_{2}H_{3}$ Tochororating electronegative pore surface inclease belocking the priority site for $C_{2}H_{3}$ Suitable pore space (6.1 × 4.5 × 4.5 \mathring{A}^{3}) window size (3.2 \mathring{A}) and incorporating comporating large pore cage space (pore diameter: 9.46 \mathring{A}_{3}), suitable pore window (4.2 \mathring{A}_{3}) window size (3.4 \mathring{A}_{3}) incorporating gletcropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size (4.1 × 5.3 \mathring{A}_{3}) incorporating gletcropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size (4.1 × 5.3 \mathring{A}_{3}) incorporating gletcropositive sizes (3.0 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.1 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.1 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.1 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.1 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating pore sizes (4.2 × 5.4 \mathring{A}_{3}) and incorporating SiFe ² stopes Chalck, Cha	UTSA-300a		Optimizing pore size $(1.3 \times 2.8 \text{ A}^2)$ and incorporating SiFe.	3.08/0.18	860	72
auting Ni and free N atoms sites RTEPEZ RODO/C2H2 RODOPATING petchorogating petchorogating pore size(1.24 × 10.2 A h), incurbor pore structure, incorpor RODOPATING pore size(1.23 × 2.3 Å) and incorporating SiR ₂ ² sites RODOPATING petchorogating petchorogating pore size(1.2 Å) and incorporating com- Suitable pore space (b. 1.4 Å, 2.4 Å), window size (2.2 Å) and incorporating com- Suitable pore space (b. 1.4 Å, 2.4 Å), window size (2.2 Å) RODOPATING size space (b. 1.4 Å, 2.4 Å), suitable pore window (4.2 Å) RODOPATING size space (b. 1.4 Å, 2.4 Å), suitable pore window size (2.2 Å) RODOPATING size surface and the hydrogen-confined pore cavities with Suitable pore sizes (4.1 Å) RODOPATING size sizes (4.2 Å), and incorporating percurbony open sizes (4.1 Å) RODOPATING sizes sizes (4.2 Å), and incorporating partners Cylug'c3H6/C3H6 RODOPATING sizes sizes (4.2 Å), and incorporating partners Cylug'c3H6/C3H6 RODOPATING sizes sizes (4.2 Å), and incorporating parallelalgined aromatic-based units Cylug'c3H6/C3H6 RODOPATING sizes sizes (4.1 Å) and incorporating parallelalgined aromatic-based units Cylug'c3H6/C3H6 RODOPATING sizes (4.1 Å) and incorporating parallelalgined aromatic-based units Cylug'c3H6/C3H6 RODOPATING sizes (4.1 Å) and incorporating parallelalgined aromatic-based units Cylug'c3H6/C3H6 RODOPATING sizes (4.1 Å) and incorporating RodoParallelalgined aromatic-based units Cylug'c3H6/C3H6 Cylug'c3H6/C3H6 RODOPATING sizes (4.1 Å) and incorporating RodoParallelalgined aromatic-based units Cylug'c3H6/C3H6 RODOPATING sizes (4.1 Å) and incorporating RodoParallelalgined aromatic-based units Cylug'c3H6/C3H6 RODOPATING sizes (4.1 Å) and incorporating NiOrg*- sizes Cylug'c3H6/C3H6 RODOPATING sizes (4.1 Å) and incorporating NiOrg*- sizes Cylug'c3H6/C3H6 RODOPATING sizes (4.2 Å) and incorporating NiOrg*- sizes Cylug'c3H6/C3H6 RODOPATING sizes (4.3 Å) and incorporating sizes Cylug'c3H6/C3H6 R	NCU-100a		Optimizing pore size (1.4 \times 3.0 Å) and incorporating sires	4.57/0.49	1/8/	125
ReTEPE-Zn Incorporating electronegative pore surfaces obtaining prote size (3.3.4.7.4) and incorporating SiPe 2 - sites and popularizing pore size (3.3.4.7.4) and incorporating sice (6.1.8.4.5.4.5.4.9.4), window size (3.2.4.3.4.4) and incorporating complementary electronegative potentials on the pore surface incorporating large pore cage space (6.1.8.4.5.4.5.4.9.4), window size (3.2.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.4.	FJI-H36		Suitable pore sizes (12.9 \times 12.9 A and 8.4 \times 10.2 A), flexible pore structure, incorporation Ni and free N atoms sites	6.46/4.20	3.5	17/
Optimizing pore size $(3.3 \times 3.7 \text{ Å}^2)$ and incorporating Sig. 2 - sites CO ₂ /C ₂ H ₂ Nucoporating residual guest molecules blocking the priority site for C ₂ H ₂ Suitable pore space $(6.1 \times 4.5 \times 4.5 \times 4)$, window size (3.2 Å) and incorporating complexity guest pore cage space (pore diameter 9.46 Å), suitable pore window (4.2 Å) Plementary electrostatic potentials on the pore surface (3.2 Å) and incorporating carporating guest pore cage space (pore diameter 9.46 Å), suitable pore window (4.2 Å) Plementary electrostatic potentials on the pore surface (3.2 Å) and incorporating electrostatic generopositive surface and the hydrogen-confined pore cavities with a paper size (3.2 Å) incorporating electrostatic generopositive surface and the hydrogen-confined pore cavities with a paper size $(4.1 \times 5.3 \text{ Å}^2)$ Proprincing pore sizes (4.5 Å) and incorporating with a size (3.0 Å) and incorporating pore sizes (4.5 Å) and incorporating pore sizes (4.5 Å) and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating pore sizes $(4.5 \times 5.1 \text{ Å}^2)$ and incorporating $(3.5 \times 5.5 \text{ Å}^2)$ an	SOFOUR-TEPE-Zn		Incorporating electronegative pore surfaces	3.98/0.63	16833	97
mo CO ₂ (2,H ₂ higher proporating residual guest molecules blocking the priority site for C ₂ H ₃ 2.09(0.1 > 10 ⁵ sultable pore espace (f.2.4.4.5.4.5.4.5) windows size (3.2.4) and incorporating contraints peletrostatic potentials on the pore surface provided with the pore surface incorporating large pore cage space (fore diameter: 9.46 Å), suitable pore window (4.2.Å) 3.43717	ZUL-330		Optimizing pore size $(3.3 \times 3.7 \text{ Å}^2)$ and incorporating SiFe ²⁻ sites	7.33/1.1	10 086	86
Suitable pore space $(5.1 \times 4.5 \times 4.5 \text{ Å}^2)$, window size $(3.2.\text{ Å}^2)$ and incorporating combinating to precipate the pote surface incorporating large pore cage space (pore diameter: 9.46 Å), suitable pore window size $(3.2.\text{ Å}^2)$ incorporating large pore cage space (pore diameter: 9.46 Å), suitable pore window size $(3.2.\text{ Å}^2)$ incorporating electropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size $(4.1 \times 5.3 \text{ Å}^2)$ incorporating electropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size $(4.1 \times 5.3 \text{ Å}^2)$ incorporating pore sizes $(4.1 \times 5.3 \text{ Å}^2)$ incorporating pore sizes $(4.1 \times 5.3 \text{ Å}^2)$ incorporating pore sizes $(4.1 \times 5.3 \text{ Å}^2)$ and incorporating $(4.1 \times 5.3 \text{ Å}^2)$ incorporating pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating high-density open Ni sites optimizing pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore size $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating No. $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore size $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating pore size $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating No. $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating $(4.1 \times$	Cu-F-pymo	CO ₂ /C ₂ H ₂	Incorporating residual guest molecules blocking the priority site for C, H,	2.09/0.1	$>10^{5}$	143
plementary electrostatic potentials on the pore surface Incorporating large pore eage space (pore diameter: 9.46 Å), suitable pore window (4.2 Å) 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 3363° 3.17/- 337/- 337/- 337/- 337/- 3385/0.15 4.1/114° 3.16/0.27 3.16/0.23 3.17/- 3.15/0.27 3.16/0.27 3.16/0.27 3.16/0.27 3.16/0.23 3.17/- 3.15/0.23 3.11/2.33	Cd-NP	1	Suitable pore space $(6.1 \times 4.5 \times 4.5 \text{ Å}^3)$, window size (3.2 Å) and incorporating com-	2.59/0.43	85	144
Incorporating large pore cage space (pore diameter: 9.46 Å), suitable pore window (4.2 Å) Suitable pore window size (2.2 Å) Suitable pore window size (2.2 Å) Incorporating electropositive surface and the hydrogen-confined pore cavities with a 3.45/15 and proporating electropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size $4.1 \times 5.1 \text{Å}$ incorporating pore sizes (3.0 Å) and incorporating WO ₂ F ₄ ²⁻² sites Optimizing pore sizes (4.7 Å) Optimizing pore sizes (4.5 Å) Optimizing pore sizes (4.1 × 4.4 Å ²) and incorporating high-density open Ni sites Nitiable pore sizes (4.1 × 4.4 Å ²) and incorporating proporating pore sizes (4.1 × 4.4 Å ²) and incorporating pore sizes (3.0 Å) and incorporating pore sizes (4.2 × 5.4 Å ²) and incorporating pore sizes (3.0 Å) and incorporating NbOrs (3.0 Å) and incorporating NbOrs (3.0 Å) and incorporating Sizes (3.0 Å) and incorporating NbOrs (3.0 Å) and incorporating Sizes (3.0 Å) and incorporating NbOrs (3.0 Å) and incorporating NbO			plementary electrostatic potentials on the pore surface			
and μ_{2} -OH amons size 2.2 Å) incorporating betropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size $(4.1 \times 5.3 \text{ Å}^{2})$ incorporating electropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size $(4.1 \times 5.3 \text{ Å}^{2})$ incorporating electropositive surface and the hydrogen-confined pore cavities with appropriate dimensional size $(4.1 \times 5.3 \text{ Å}^{2})$ incorporating pore sizes (3.0 Å) and incorporating WO ₂ F ₄ ² sites optimizing pore sizes (4.7 Å) optimizing pore sizes (4.7 Å) optimizing pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ optimizing pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ incorporating pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ optimizing pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ and incorporating praffille-ligned aromatic-based units solution incorporating pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ and incorporating pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ and incorporating pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ and incorporating pore sizes $(4.2 \times 5.1 \text{ Å}^{2})$ and incorporating pore sizes $(4.3 \times 4.2 \times 5.1 \text{ Å}^{2})$ and incorporating $(4.3 \times 4.2 \times 5.1 \text{ Å}^{2})$ and incorporating $(4.3 \times 4.2 \times 5.1 \text{ Å}^{2})$ and incorporating $(4.3 \times 4.2 \times 5.1 \text{ Å}^{2})$ and incorporating $(4.3 \times 4.2 \times 4$	Y-bptc		Incorporating large pore cage space (pore diameter: 9.46 Å), suitable pore window (4.2 Å)	2.48/1.17	$4.1/114^c$	136
Suntable pore without Size (1.2.4) Suppropriate dimensional size (4.1 × 5.3 Ų) By propriate dimensional size (4.1 × 5.3 Ų) By propriating carbonyl oxygen atoms sites Optimizing pore sizes (4.7 Å) Optimizing pore sizes (4.5 Å) Optimizing pore sizes (4.5 Å) Suitable pore sizes (4.5 Å) Suitable pore sizes (4.1 × 4.4 Ų) and incorporating parallel-aligned atomatic-based units Chal-Chal-Chal-Chal-Chal-Chal-Chal-Chal-	, 11119		and μ_3 -OH anions sites	1	30000	,
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301 Optimizing pore sizes (4.6 Å) late Application of the properties of th	Y-abtc		Optimizing pore sizes (4.7 Å)	2/0.07	.	152
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Suitable pore sizes $(4.7 \times 5.6 \text{ Å}^2)$ and incorporating parallel-aligned aromatic-based units 2.23/2.25 2.48 Fr.2 Optimizing pore sizes (3.0 Å) and incorporating $-CF_3$ groups Suitable pore cavities $(6.1 \times 4.3 \times 4.3 \text{ Å} 3 \text{ and } 6.8 \times 4.0 \times 4.2 \text{ Å}^3)$ and incorporating 2.79/1.45 83 200 Optimizing pore size (3.4 Å) and incorporating SiF_0^{2-} sites Optimizing pore size $(3.96 \times 5.56 \text{ Å}^2)$ and incorporating SiF_0^{2-} sites $(3.46/n-C_4H_8/i-C_4H_8)$ Optimizing pore size (4.31 Å) and incorporating fluoroniobate sites $(4.31.26/n-4.8)$	ZIU-75a		Suitable pore sizes $(4.1 \times 4.4 \text{ Å}^2)$ and incorporating high-density open Ni sites	3.31/2.33	54.2	157
Optimizing pore sizes (3.0 Å) and incorporating $-\text{CF}_3$ groups 2 C ₃ H ₄ /C ₃ H ₆ Suitable pore cavities $(6.1 \times 4.3 \times 4.3 \text{ Å} 3 \text{ and } 6.8 \times 4.0 \times 4.2 \text{ Å}^3)$ and incorporating 20 dynamic dangling OTF groups 200 Optimizing pore size (3.4 Å) and incorporating SiF _c ²⁻ sites Optimizing pore size $(3.96 \times 5.56 \text{ Å}^2)$ and incorporating fluoroniobate sites 2.79/1.45 83 2.6000 3.58/1.20 2.0000 3.04/2.10 2.0000 2.0000 Optimizing pore size $(3.96 \times 5.56 \text{ Å}^2)$ and incorporating fluoroniobate sites 2.64/2.26/0.48	PCP-IPA	$\mathrm{C_3H_8/C_3H_6}$	Suitable pore sizes $(4.7 \times 5.6 \text{Å}^2)$ and incorporating parallel-aligned aromatic-based units	2.23/2.25	2.48	169
2 C ₃ H ₄ /C ₃ H ₆ Suitable pore cavities $(6.1 \times 4.3 \times 4.3 \text{ Å} 3 \text{ and } 6.8 \times 4.0 \times 4.2 \text{ Å}^3)$ and incorporating 2.79/1.45 83 dynamic dangling OTf groups 200 Optimizing pore size (3.4 Å) and incorporating SiF ₆ ²⁻ sites 3.58/1.20 > 20 00 Optimizing pore size $(3.96 \times 5.56 \text{ Å}^2)$ and incorporating NbOF ₅ ²⁻ sites 3.04/2.10 220 C ₄ H ₆ /n-C ₄ H ₈ /i-C ₄ H ₈ Optimizing pore size (4.31 Å) and incorporating fluoroniobate sites 2.64/2.26/0.48 —	FDMOF-2		Optimizing pore sizes (3.0 Å) and incorporating –CF ₃ groups	5.04/4.15	2.18	170
OFFIVE-bpe-Cu-AB C4Hs/h-C4Hs Optimizing pore size (4.31 Å) and incorporating SiF $_6$ ²⁻ sites 3.58/1.20 > 20 000 Optimizing pore size (3.96 × 5.56 Å ²) and incorporating NbOF $_5$ ²⁻ sites 3.04/2.10 220 C4Hs/h-C4Hs Optimizing pore size (4.31 Å) and incorporating fluoroniobate sites 2.64/2.26/0.48 —	ELM-12	$\mathrm{C_3H_4/C_3H_6}$	Suitable pore cavities $(6.1 \times 4.3 \times 4.3 \text{ Å} 3 \text{ and } 6.8 \times 4.0 \times 4.2 \text{ Å}^3)$ and incorporating	2.79/1.45	83	181
OFFIVE-bpe-Cu-AB Optimizing pore size $(3.96 \times 5.56 \text{ Å}^2)$ and incorporating NbOF ₅ $^{2-}$ sites $(4.24/6.76 + 1.06)$ Optimizing pore size (4.31 Å) and incorporating fluoroniobate sites $(4.31.46)$ Optimizing pore size $(4.31.4)$ and incorporating fluoroniobate sites $(4.31.40)$ $($	UTSA-200		Optimizing pore size (3.4 Å) and incorporating SiF ₆ ²⁻ sites	3.58/1.20	>20000	182
C_4H_6/n - C_4H_8/i	sql-NbOFFIVE-bpe-Cu-AB		Optimizing pore size $(3.96 \times 5.56 \text{ Å}^2)$ and incorporating NbOF ₅ ²⁻ sites	3.04/2.10	220	189
	ZU-52	$\mathrm{C_4H_6}/n\text{-}\mathrm{C_4H_8}/\mathrm{i}\text{-}\mathrm{C_4H_8}$	Optimizing pore size (4.31 Å) and incorporating fluoroniobate sites	2.64/2.26/0.48		192

Table 2 (continued)

Motoriole	no jamonoo oo j	Chroteories	Uptake^a	Solootinitab Dof	Dof
Materials	Gas separation	Strategies	(g minin)	Sciectivity	NCI.
ZU-33		Optimizing pore size (4.20 Å) and incorporating GeF_6^{2-} sites	2.67/0.57/0.42	I	
MAF-23	$\mathrm{i\text{-}C_4H_8/}n\text{-}\mathrm{C_4H_8/}\mathrm{C_4H_10/}\mathrm{C_4H_6}$	Incorporating flexible quasi-discrete pores	2/2/2/2	I	193
Zn-bzc-2CH_3	$n ext{-}\mathrm{C}_4\mathrm{H}_{10}/\mathrm{i ext{-}}\mathrm{C}_4\mathrm{H}_{10}$	Optimizing pore size (4.13 Å)	2.42/0.03	1	195
Zr-abtc	nHEX/3MP/23DMB	Suitable pore window size (4.5 Å)	1.28/1.02/0.58	1	197
HIAM-203	nHEX/3MP/22DMB	Suitable pore window size (4.8 Å)	1.7/1.43/0.07		198
CopzNi	$n{ m HEX/2MP/22DMB}$	Incorporating open Ni sites	2.17/1.46/0.08	1	199
Mn-dhbq	pX/mX/oX	Incorporating multiple open Mn sites, rich π -electrons, and structural flexibility	$1.74/1.48/0.22^e$	1	206
ı			$1.33/0.16/0.21^f$		
ZU-61		Incorporating adaptable pore structure and $NbOF_5^{2-}$ sites	$3.44/3.37/3.2^g$	1	207
ZUL-C3	$p_{ m X}/m_{ m X}/o_{ m X}/{ m EB}$	Incorporating nonaromatic low-polar pore environment	3.25/3.35/3.41/3.27	1	208
MAF-41	EB/ST/Tol/Bz	Incorporating structural flexibility	2.31/0.3		500

^a Uptake amount at 1 bar and room temperature. ^b Calculated by IAST at ambient temperature and 1 bar. ^c Kinetic selectivity at ambient temperature. ^d Equilibrium-kinetic combined selectivity at ambient temperature. E Uptake amount at 1.05 bar and 333 K. Uptake amount at 1.05 bar and 393 K. Uptake amount at 7.1 mbar and 333 K.

theory (IAST) selectivity of 80.8 for an equimolar C₂H₄/C₂H₆ mixture at 298 K and 1 bar.

Molecular sieves can show the maximum C₂H₄/C₂H₆ selectivity via molecular size exclusion, though it is quite challenging due to their similar molecular sizes. In 2018, Chen et al. reported a rigid ultramicroporous MOF [Ca(C₄O₄)(H₂O)] (UTSA-280, $H_2C_4O_4$ = squaric acid) with one-dimensional (1D) pore channels for molecular sieving separation of C₂H₄/C₂H₆. UTSA-280, being assembled by calcium oxide chains and squarate linkers, shows 1D pores with the minimum cross-sectional area of 14.4 Å², which falls precisely between the sizes of C₂H₄ and C_2H_6 (13.7 Å² and 15.5 Å², respectively). Therefore, UTSA-280 can adsorb C₂H₄ with an adsorption capacity of 2.5 mmol g⁻¹ at 298 K and 1 bar while blocking the diffusion of the relatively large C₂H₆ molecules (Fig. 2).³⁵ The C₂H₄/C₂H₆ selectivity of UTSA-280 was estimated to be over 10000. The adsorption heat (Q_{st}) of UTSA-280 for C₂H₄ ranges from 20.5 to 35.0 kJ mol⁻¹, which is lower than those of MOFs with OMSs (40-85 kJ mol⁻¹). 30,45 Breakthrough experiments confirmed that high purity (>99.2%) of C₂H₄ can be obtained from an equimolar C₂H₄/C₂H₆ mixture with a productivity of 1.86 mmol g^{-1} . It is worth noting that UTSA-280 is capable of efficiently capturing C2H4 from a quaternary CH4/ C₂H₄/C₂H₆/C₃H₈ mixture (45/25/25/5). Dispersion-corrected density functional theory (DFT-D) calculations and single-crystal X-ray diffraction experiments revealed that C2H4 molecules are adsorbed by UTSA-280 in a linear array with weak C-H···O hydrogen bonding, $\pi \cdot \cdot \cdot \pi$ stacking and van der Waals (vdW) interactions.

In 2018, Ren et al. reported a series of gallate-based MOFs, $[M(C_7O_5H_4)\cdot 2H_2O]$ (termed M-gallates, M = Mg, Ni, and Co), for C₂H₄/C₂H₆ separation with high sieving effect.³⁶ These MOFs contain 3D interconnected zigzag channels and have Brunauer-Emmett-Teller (BET) surfaces of ca. 424 (Ni), 559 (Mg), and 475 (Co) m² g⁻¹. The pore sizes (3.47–3.69 Å) of these MOFs are close to the molecular sizes of C_2H_4 (3.28 × 4.18 × 4.84 Å³) and C_2H_6 (3.28 × 4.18 × 4.84 Å³). Therefore, M-gallates could highly selectively adsorb C₂H₄ over C₂H₆. Among them, Co-gallate displays the highest performance for separation of C₂H₄/C₂H₆. The C₂H₄ uptake capacity of Co-gallate is much higher than that for C_2H_6 (3.37 mmol g^{-1} vs. 0.31 mmol g^{-1}), resulting in a high IAST selectivity of 52 at 298 K and 1 bar for an equimolar C₂H₄/ C₂H₆ mixture. The IAST selectivity of Mg-gallate is about 37.3 for an equimolar C₂H₄/C₂H₆ mixture at 298 K and 1 bar. Breakthrough experiments for a 50/50 C₂H₄/C₂H₆ mixture further demonstrated the excellent C2H4/C2H6 separation performances of these low-cost M-gallates.

In 2020, Xing et al. reported a phosphate-pillared MOF, $[Zn_3(atz)_3(PO_4)]_n$ (ZnAtzPO₄, Hatz = 3-amino-1,2,4-triazole), for C₂H₄/C₂H₆ separation with high selectivity (12.4 at 298 K and 32.4 at 273 K).³⁹ Single-component gas adsorption and kinetic studies revealed that ZnAtzPO₄ has a higher C₂H₄ adsorption capacity (1.92 mmol g^{-1}) than for C_2H_6 (1.04 mmol g^{-1}) at 298 K and 1 bar, as well as a faster adsorption rate for C₂H₄ compared with C₂H₆, giving a kinetic selectivity of 36.6. DFT calculations demonstrated that electronegative groups decorated on the narrow pore apertures of ZnAtzPO4 can effectively capture C₂H₄ and inhibit the diffusion of C₂H₆, resulting in an

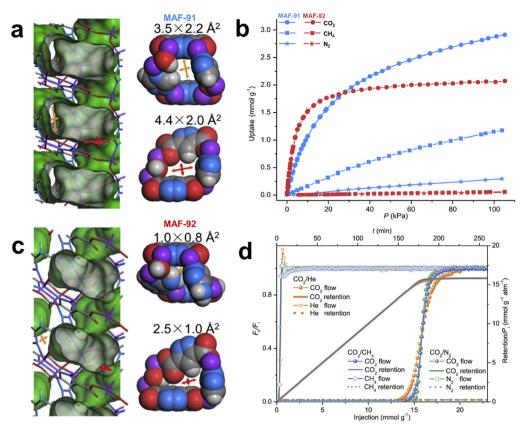


Fig. 1 (a) and (c) Crystal structures of MAF-91 and MAF-92. (b) CO₂, CH₄, and N₂ adsorption isotherms of MAF-91 and MAF-92 at 298 K. (d) Column breakthrough behaviors of MAF-92 for 10:90 CO₂/N₂, 10:90 CO₂/CH₄ and 10:90 CO₂/He mixtures. Reprinted with permission from ref. 27. Copyright 2021 Cell Press.

efficient equilibrium-kinetic C₂H₄/C₂H₆ separation. A flexible ultramicroporous MOF, [Cu₂(pyz-CH₃)(pzdc)₂] (ZU-901, pyz-CH₃ = 2-methylpyrazine, and H₂pzdc = 2,3-pyrazinedicarboxylic acid), with a pore size of 3.4 \times 4.2 Å² was recently reported to show a C₂H₄ adsorption-desorption curve in an S shape with high C2H4 working capacity and facile regeneration. 40 Single-component sorption experiments showed that ZU-901 can adsorb 1.55 mmol g^{-1} C_2H_4 and much less C_2H_6 (0.26 mmol g^{-1}) at 298 K and 1 bar. The adsorption selectivity of ZU-901 calculated for the pressure swing adsorption (PSA) process is 65. The $Q_{\rm st}$ of ZU-901 for C_2H_4 was calculated to be ~ 25 kJ mol⁻¹, which indicates that ZU-901 can be mildly regenerated. The simulated two-bed PSA process revealed that polymer-grade ethylene (ca. 99.5%) can be obtained by ZU-901 with only 1/10 of the energy consumption compared to simulating cryogenic distillation $(2.03 \text{ kJ mol}^{-1} \text{ vs. } 21.84 \text{ kJ mol}^{-1}).$

For C₂H₄-selective MOF materials, multiple adsorption and desorption cycles are typically required to achieve high-purity ethylene. In contrast, C2H6-selective adsorbents can directly give pure ethylene by one single separation operation, making it simple to operate and more energy efficient. Compared to the C₂H₄ molecule, the C₂H₆ molecule has a slightly larger polarizability and two additional hydrogen atoms. MOFs with OMSs usually interact strongly with C_2H_4 molecules via π complexation, whereas MOFs with relatively less polar sites, usually, can preferentially adsorb C₂H₆ over C₂H₄. 46-66

In an earlier study, Gascon et al. firstly reported preferential capture of C₂H₆ over C₂H₄ by utilizing the gate-opening effect of ZIF-7 (also known as MAF-3).58 However, the separation efficiency was low due to the lack of active binding sites. In 2015, Zhang et al. reported a porous MAF [Zn(batz)] (MAF-49, H_2 batz = bis(5-amino-1*H*-1,2,4-triazol-3-yl)methane), which shows a high C₂H₆/C₂H₄ selectivity of 9 at 316 K.⁵⁹ In MAF-49, there are quasi-discrete cages functionalized with a high density of electronegative nitrogen atoms on the surface, which are further interconnected by smaller paths into 1D channels (Fig. 3). DFT calculations and crystallographic study indicated that a C₂H₆ molecule confined in the cage can form stronger and more non-classical C-H···N hydrogen bonds or electrostatic interactions through better structural matching with the cage surface of MAF-49 as compared to the C2H4 molecule, which is beneficial for capture, or stronger binding of C₂H₆ compared with C₂H₄. MAF-49 showed, for the first time, an exceptional reversed selectivity compared with porous materials including MOFs, which conventionally bind more strongly with C₂H₄ vs. C₂H₆. Breakthrough experiments for the C_2H_4/C_2H_6 (15:1) mixture showed that MAF-49 can give highly pure C₂H₄ (99.95%+) within a single breakthrough operation under ambient conditions.

An appropriate combination of pore sites and pore surface can maximize the weak host-guest interactions, thus highly enhancing the performance of MOFs for C₂H₆/C₂H₄ separation.

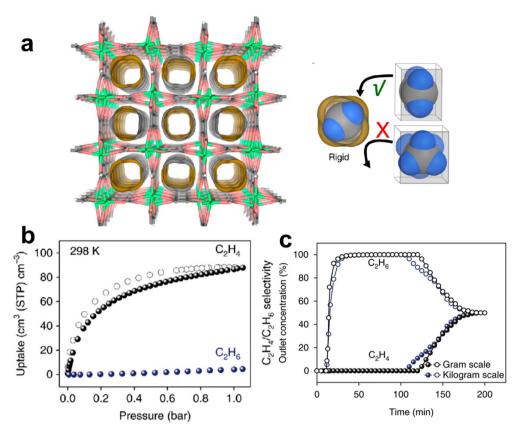


Fig. 2 (a) Structure of UTSA-280. (b) Sorption isotherms of UTSA-280 for C_2H_4 and C_2H_6 at 298 K. (c) Breakthrough curves for UTSA-280 from different scales for an equimolar mixture of C_2H_4/C_2H_6 at 298 K and 1 bar. Reprinted with permission from ref. 35. Copyright 2018 Nature Publishing Group.

In 2018, Chen et al. reported two isoreticular MOFs, [Cu(Qc)₂] (HQc = quinoline-5-carboxylic acid) and [Cu(ina)₂] (Hina = isonicotinic acid), featuring 1D channels with pore sizes of ~ 4.1 and ~ 3.3 Å, respectively, and an array of low-polarity aromatic surfaces with different contact areas on the channels (Fig. 4).⁶⁰ Single-component sorption results demonstrated that [Cu(Qc)₂] shows a higher C₂H₆ uptake than C₂H₄ (60.0 cm³ $cm^{-3} \nu s. 25.3 cm^{3} cm^{-3}$, i.e., 1.85 mmol $g^{-1} \nu s. 0.78 mmol <math>g^{-1}$) at 298 K and 1 bar, thus giving a high C₂H₆/C₂H₄ selectivity of 3.4 for an equimolar C₂H₆/C₂H₄ mixture at 298 K and 1 bar. In contrast, [Cu(ina)₂] shows comparable adsorption capacity for both gases (C_2H_4 : 67.4 cm³ cm⁻³, and C_2H_6 : 64.3 cm³ cm⁻³, *i.e.*, 1.99 mmol g^{-1} vs. 1.90 mmol g^{-1}) due to the smaller polar surface. Neutron powder diffraction and DFT-D calculations showed that the high C₂H₆ selectivity in [Cu(Qc)₂] can be attributed to the more $C-H\cdots\pi$ interactions formed between C₂H₆ and [Cu(Qc)₂]. Breakthrough experiments demonstrated that high purity of C₂H₄ (> 99.9%) can be directly collected from a 50/50 C₂H₆/C₂H₄ mixture by a packed column bed of $[Cu(Qc)_2]$, with a separation productivity of 587 mmol L⁻¹.

The incorporation of the peroxo sites into MOFs can improve the affinity for C₂H₆. In 2018, Chen et al. reported a microporous MOF $[Fe_2(O_2)(dobdc)]$ $(dobdc^{4-} = 2,5-dioxido-1,4$ benzenedicarboxylate) decorated with Fe-peroxo sites that exhibits a high C₂H₆ affinity with a large Q_{st} of 66.8 kJ mol⁻¹ (Fig. 5).⁶¹ Single-component sorption isotherms showed that $[Fe_2(O_2)(dobdc)]$ can adsorb a large amount of C_2H_6 (74.3 cm³ g⁻¹, 3.32 mmol g⁻¹) at 1 bar and 298 K and the IAST selectivity for 50/50 C₂H₆/C₂H₄ was calculated to be 4.4 under the same conditions. High-resolution neutron powder diffraction showed that C₂D₆ molecules can form strong non-classical C-D···O hydrogen bonds with very short D···O distances (~2.17 to 2.22 Å). Therefore, [Fe₂(O₂)(dobdc)] exhibits excellent separation performance, yielding polymer-grade C₂H₄ (≥99.99%) from 50/50 C₂H₄/C₂H₆ mixtures in a single breakthrough operation and a productivity of 0.79 mmol g^{-1} . This result further confirms the unique and important role of non-classical C-H···O hydrogen bonds in the molecular recognition and selective adsorption of ethane by MOFs.

2.3. C₂H₂/C₂H₄ separation

In the petrochemical industry, the production of C₂H₄ involves trace amounts of acetylene (C_2H_2) impurities ($\sim 1\%$). The removal of these impurities is crucial as even small amounts of acetylene during ethylene polymerization can cause catalyst poisoning and highly affect the production of polyethylene. Extensive research has been conducted on the adsorptive separation of MOFs for C₂H₂/C₂H₄ mixtures. 67-78 Chen et al. first reported a series of M'MOFs for separation of C2H4 from C2H2/C2H4.67 However, these M'MOFs show modest selectivity for C₂H₂ over C₂H₄. In 2015, they further reported an amino-functionalized microporous MOF (UTSA-100) with 1D channels (4.3 Å) and small cages (4.0 Å), showing a moderately high C₂H₂ uptake of

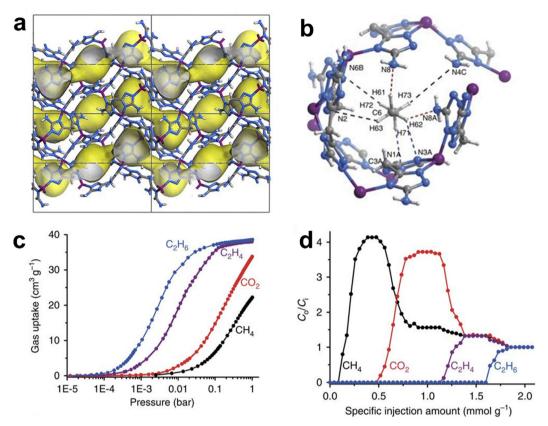


Fig. 3 (a) Crystal structure of MAF-49. (b) Preferential adsorption sites for C_2H_6 in MAF-49 revealed by DFT calculations. (c) Gas adsorption isotherms for and 1 bar. Reprinted with permission from ref. 59. Copyright 2018 Nature Publishing Group.

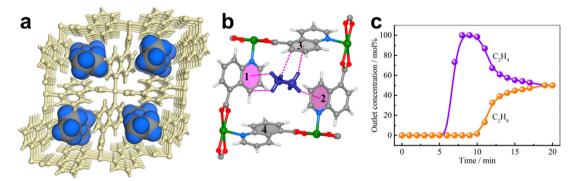


Fig. 4 (a) Neutron diffraction crystal structure of $[Cu(Qc)_2] \cdot 0.41C_2D_6$. (b) Preferential binding sites for the C_2D_6 molecule and the close vdW contacts within the rhombic cavity of aromatic rings, highlighting $C-H\cdots\pi$ interactions in pink dashed bonds. (c) Experimental column breakthrough curves for an equimolar C₂H₆/C₂H₄ mixture (298 K, 1 bar) in an adsorber bed packed with Cu(Qc)₂. Reprinted with permission from ref. 60. Copyright 2018 American Chemical Society.

95.6 cm 3 g $^{-1}$ (4.27 mmol g $^{-1}$) at 296 K but with a much lower $\mathrm{C_2H_4}$ uptake (37.2 cm 3 g $^{-1}$, 1.66 mmol g $^{-1}$). The calculated IAST selectivity of UTSA-100 for a 1/99 C₂H₂/C₂H₄ mixture is 10.7. This work well demonstrates that suitable pore sizes and binding sites can highly improve the separation performance of MOFs for removing trace C₂H₂ from C₂H₄.⁶⁸

To obtain materials with high C2H2 adsorption capacity and high selectivity, in 2016, Chen et al. reported a series of SIFSIX

MOFs, namely, SIFSIX-1-Cu, SIFSIX-2-Cu, SIFSIX-2-Cu-i, SIFSIX-3-Ni, and SIFSIX-3-Zn, which allow preferential capture of C₂H₂ from the C₂H₂/C₂H₄ mixture with high selectivity and adsorption capacity. 70 These materials possess different pore sizes, which can be systematically fine-tuned by replacing ligands, metal nodes, inorganic anions or framework interpenetration. Among them, SIFSIX-2-Cu-i with a two-fold interpenetrated framework and pore size of 5.2 imes 5.2 $imes^2$ (BET surface area

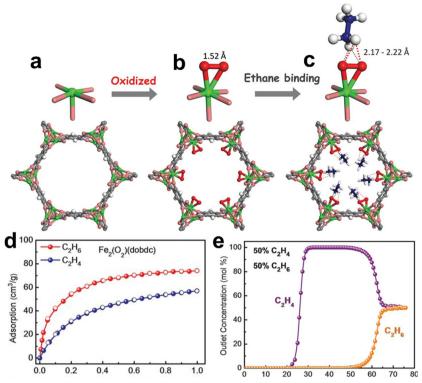


Fig. 5 Crystal structures of (a) pristine $[Fe_2(dobdc)]$ and $[Fe_2(O_2)(dobdc)]$ (b) after oxidization and (c) after final C_2D_6 -loading. (d) Sorption isotherms of $[Fe_2(O_2)(dobdc)]$ for C_2H_6 and C_2H_4 under ambient conditions. (e) Breakthrough curves of $[Fe_2(O_2)(dobdc)]$ for an equimolar C_2H_6/C_2H_4 mixture under ambient conditions. Reprinted with permission from ref. 61. Copyright 2018 the American Association for the Advancement of Science.

503 m² g⁻¹) exhibits a high uptake for C_2H_2 (2.1 mmol g⁻¹, *i.e.*, 47 cm³ g⁻¹) at a low pressure of 0.025 bar, indicating its strong binding affinity for C₂H₂ (Fig. 6). The IAST selectivity of SIFSIX-2-Cu-i for C₂H₂/C₂H₄ (1/99) is up to 44.54. SIFIX-2-Cu with a pore size of 8.0 \times 8.0 Å² (BET surface area: 1178 m² g⁻¹) shows the highest C₂H₂ uptake of 8.5 mmol g⁻¹ and a moderate IAST selectivity for C₂H₂/C₂H₄ (1/99) of 10.6. Breakthrough experiments demonstrated that all these SIFSIX MOFs can produce polymer-grade C₂H₄ from C₂H₂/C₂H₄ (1/99 or 50/50 mixtures). DFT-D calculations and high-resolution neutron powder diffraction studies reveled that SiF₆²⁻ pillars in the framework can form strong hydrogen-bonding interactions with C2H2, resulting in the high selectivity and adsorption capacity for C₂H₂. This work revealed that the combination of optimal pore size and multiple active sites can greatly improve the selectivity and adsorption capacity of the MOFs.

In 2017, Chen et al. reported a 2-fold interpenetrated MOF SIFSIX-14-Cu-i (UTSA-200) with a smaller pore size (3.4 Å) than SIFSIX-2-Cu-i (4.4 Å) and also functional as SiF₆²⁻ sites that can enhance the binding affinity for C₂H₂ (Fig. 7).⁷¹ The pore size of the activated structure (UTSA-200a) ideally falls between the kinetic diameter of C₂H₄ (4.2 Å) and C₂H₂ (3.3 Å), endowing UTSA-200a with a high performance of molecular sieving separation of C₂H₂/C₂H₄. Single component equilibrium adsorption isotherms showed that UTSA-200a exhibits a high low-pressure uptake (58 cm³ cm⁻³) for C₂H₂ at 0.01 bar but a negligible uptake (~ 0.25 mmol g⁻¹) for C₂H₄ below 0.2 bar, which is significantly lower than the absorption of SIFSIX-2-Cu-i (2.28 mmol g^{-1}). The IAST selectivity for a 1/99 C_2H_2/C_2H_4 mixture of UTSA-200a was calculated to be 6000 at 298 K and 1 bar. High-resolution neutron powder diffraction further revealed that the strong binding affinity of UTSA-200a for the C2D2 molecule was achieved by short C-D···F hydrogenbonding interactions (1.921 Å). Breakthrough experiments revealed that UTSA-200a can efficiently separate C2H2 from a 1/99 C₂H₂/C₂H₄ mixture to give an extremely high purity C₂H₄ (99.9999%) with a productivity of 87.5 mmol g^{-1} .

In 2017, Chen et al. reported an ultramicroporous SIFSIX- $MOF [Zn(dps)_2(SiF_6)] (UTSA-300, dps = 4,4'-dipyridylsulfide)$ with small apertures $(2.4 \times 3.3 \text{ Å}^2)$ for specific recognition of C₂H₂ from C₂H₄.⁷² The desolvated structure UTSA-300a (aperture size: 3.3 Å) exhibits large affinity toward C_2H_2 with a $Q_{\rm st}$ of up to 57.6 kJ mol⁻¹ and thus can be selectively gate opened by C_2H_2 . It should be noted that UTSA-300 shows complete size exclusion of C₂H₄, giving IAST selectivity for the equimolar C₂H₂/C₂H₄ mixture up to $>10^4$ at 298 K. Breakthrough experiments confirmed its good separation performance for an equimolar C2H2/C2H4 mixture. Subsequently, an isostructural framework of UTSA-300 [Cu(dps)₂(SiF₆)] (NCU-100 or UTSA-300-Cu) was reported.⁷⁶ In contrast to UTSA-300, NCU-100 possesses elongated Cu(II)-F bonds, showing a larger cavity size $(3.6 \times 4.3 \times 4.2 \text{ Å}^3 \text{ vs. } 3.5 \times 4.2 \text{ Å}^3 \text{ vs. } 3.2 \times 4.2 \times 4.2 \text{ Å}^3 \text{ vs. } 3.2 \times 4.2 \times 4.2 \text{ Å}^3 \text{ vs. } 3.2 \times 4.2 \times$ $3.9 \times 4.1 \,\text{Å}^3$) in the closed-pore phase. Single-component sorption experiments revealed that NCU-100a shows not only higher lowpressure uptake (0.73 mmol g^{-1} vs. 0.04 mmol g^{-1}) for C_2H_2 at 0.01 bar and 298 K but also a higher total uptake capacity $(4.57 \text{ mmol g}^{-1} \text{ vs. } 3.08 \text{ mmol g}^{-1})$ at 298 K and 1 bar, resulting

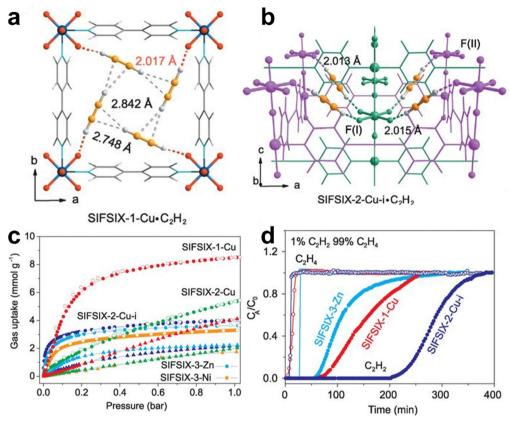


Fig. 6 (a) Crystal structure of SIFSIX-1-Cu·C₂H₂. (b) DFT-D simulated structure of C₂H₂-loaded SIFSIX-2-Cu-i. (c) Single-component sorption isotherms of SIFSIX-1-Cu, SIFSIX-2-Cu, SIFSIX-2-Cu-i, SIFSIX-3-Zn, and SIFSIX-3-Ni for C₂H₂ and C₂H₄ under ambient conditions. (d) Breakthrough curves of SIFSIX-1-Cu, SIFSIX-2-Cu, and SIFSIX-3-Zn for a 1/99 C₂H₂/C₂H₄ mixture. Reprinted with permission from ref. 70. Copyright 2016 the American Association for the Advancement of Science.

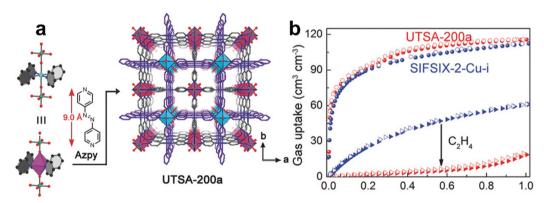


Fig. 7 (a) Crystal structure of UTSA-200. (b) C_2H_2 and C_2H_4 adsorption isotherms of UTSA-200a at 298 K. Adapted from ref. 71 with permission from Wiley-VCH, Copyright 2018

in an IAST selectivity for 1/99 C₂H₂/C₂H₄ up to 7291 (298 K and 1 bar). This excellent performance for C₂H₂/C₂H₄ separation can also be attributed to the combination of optimal pore size and strong binding sites, as confirmed by DFT calculations and crystallographic studies. Breakthrough experiments confirmed that high purity C₂H₄ (>99.99%) can be obtained from a 1/99 C_2H_2/C_2H_4 mixture with a productivity of 14.9 mmol g⁻¹.

Recently, Zhai et al. synthesized a series of cluster-based MOFs, $[M_9(\mu_4\text{-TAZ})_6(\mu_3\text{-HTAZ})_x(\mu_3\text{-TAZ})_{12-x}(A)_v]$ solvent (SNNU-98-M, M = Mn, Co, Ni, and Zn), for the purification of C_2H_2 , in which the tetrazolate (TAZ) ligands coordinate with metal centers in tridentate (µ3-TAZ) and tetradentate (µ4-TAZ) bridging modes.⁷⁸ These MOFs of acs topology show high framework densities and high stabilities, as well as small pore sizes of

5.2 Å (Mn), 4.8 Å (Co), 4.8 Å (Ni), and 4.2 Å (Zn), respectively, which are expected to increase the separation selectivity and volumetric storage capacity. Single-component gas adsorption revealed that SNNU-98-Mn exhibits the highest volumetric C₂H₂ uptake (222.9 cm³ cm⁻³) at 298 K and 1 bar, and a high uptake for C₂H₂ (175.3 cm³ cm⁻³) at 298 K and 0.1 bar, whereas SNNU-98-Co shows the highest C₂H₂/C₂H₄ IAST selectivity (2405.7) under room temperature and 1 bar. Column breakthrough experiments revealed that all these materials show good C₂H₂/ C₂H₄ separation performance, with SNNU-98-Mn displaying a higher C₂H₄ productivity of 64.6 mmol g⁻¹ from a 1/99 C₂H₂/ C₂H₄ mixture and a longer breakthrough retention time (1362 min g^{-1} and 701 min g^{-1} at 273 K and 298 K, respectively, with a gas flow rate of 2 mL min⁻¹).

The separation of C₂H₄ from multicomponent mixtures in one step is significant for obtaining polymer-grade C2H4 due to the presence of multiple impurities in the cracking gas. Recently, more MOFs have been revealed to be capable of such multicomponent separation.⁷⁹⁻⁹⁴ In 2018, Lu et al. reported the highly selective adsorption of C₂H₄ from a C₂H₂/C₂H₄/C₂H₆ mixture by a stable MOF, $(Me_2NH_2)[Co_3(DCPN)_2(\mu_3-OH)(H_2O)]\cdot 11H_2O$ (T]T-100, DCPN = 5-(3',5'-dicarboxylphenyl)nicotinate). ⁷⁹ TJT-100 exhibits a 1D channel (pore size: ~8.0 Å) decorated with a high density of carboxylate oxygen atoms. Single-component adsorption showed that the adsorption capacities of TJT-100 for C2H2, C2H4, and C_2H_6 were 127.7 cm³ g⁻¹, 98.1 cm³ g⁻¹, and 105.4 cm³ g⁻¹, respectively. The breakthrough experimental results of TJT-100 for the C₂H₂/C₂H₄/C₂H₆ mixture (0.5:99:0.5) confirmed the preferential capture of C₂H₂ and C₂H₆, giving C₂H₄ with an excellent purity of 99.997%. DFT calculations revealed that C2H2 and C2H6 have multiple electrostatic interactions with the framework, which facilitates preferential adsorption of C₂H₂ and C₂H₆ by TJT-100.

In 2019, Zaworotko et al. reported a synergistic sorbent separation technique (SSST), which enables the one-step production of polymer-grade C₂H₄ from a ternary (C₂H₂/C₂H₆/C₂H₄) gas mixture, and even a quaternary (CO₂/C₂H₂/C₂H₆/C₂H₄) gas mixture (Fig. 8).80 Three microporous MOFs, TIFSIX-2-Cu-I, SIFSIX-3-Ni, and Zn-atz-ipa, were placed in tandem on the sorbent bed, offering selective adsorption of C₂H₂, CO₂, and C₂H₆, respectively. Notably, Zn-atz-ipa shows a rare, higher uptake of C₂H₆ than CO₂, C₂H₂ and C₂H₄ at 0 to 0.4 bar. Breakthrough experiments showed that the packing order of the three MOFs in the sorbent bed has a significant impact on the separation performance, whereas the particle size and amount of the adsorbent have a minor effect. When the packing order is SIFSIX-3-Ni@Znatz-ipa@TIFSIX-2-Cu-i, high purity C_2H_4 can be gained from a 1/49.5/49.5 $C_2H_2/C_2H_4/C_2H_6$ or 1/33/33/33 C₂H₂/C₂H₄/C₂H₆/CO₂ mixture and the working capacities are 0.32 and 0.10 mmol g⁻¹, respectively. This work provides a new path for selective separation of a specific component molecule from a multicomponent gas mixture.

2.4. C₂H₂ and CO₂ separation

Acetylene (C₂H₂) is an important chemical raw material that is mainly produced by thermal cracking of hydrocarbons or the

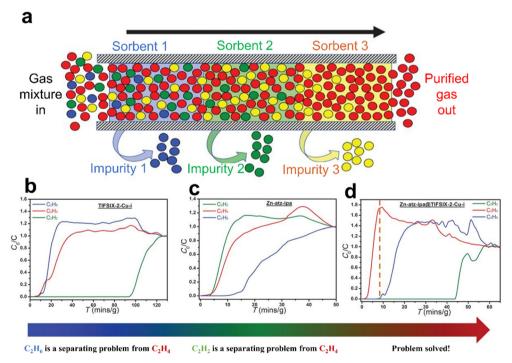


Fig. 8 (a) SSST involves an adsorption bed with three task-specific physisorbents to purify the commodity (red) with specific binding sites for each trace impurity (blue, green, and yellow). (b) and (c) Experimental column breakthrough curves for $C_2H_2/C_2H_4/C_2H_6$ separation (1:1:1 mixture) on TIFSIX-2-Cu-i and Zn-atz-ipa at 298 K and 1 bar. Breakthrough experiments were conducted in a column (inner diameter, 8 mm) at a flow rate of 2.1 ml min^{-1} . (d) Experimental column breakthrough curves for $C_2H_2/C_2H_4/C_2H_6$ separation (1:1:1 mixture) on a tandem-packed column of TIFSIX-2-Cu-i (~250 mg) and Zn-atz-ipa (~600 mg) at 298 K and 1 bar. Reprinted with permission from ref. 80. Copyright 2019 the American Association for the Advancement of Science.

partial combustion of methane. The resulting gas stream contains various impurities, with carbon dioxide (CO2) being the major one. Thus, the separation of C₂H₂ from CO₂/C₂H₂ mixtures is important in industry. Although CO2 and C2H2 have similar sizes (CO₂: $3.18 \times 3.33 \times 5.36 \text{ Å}^3$, and C₂H₂: $3.32 \times 3.34 \times 5.7 \text{ Å}^3$) and physical properties (boiling point of CO₂ = 194.7 K and of $C_2H_2 = 189.3$ K), the opposite quadrupole moments and slightly discrepant polarizabilities between C₂H₂ and CO₂, as well as the stronger π -bonding ability with metal sites and hydrogenbonding donor ability of C₂H₂, allow the realization of their separation by means of rational design of pore surfaces and flexible framework amplification. 72,95-98

In the early studies, Kitagawa et al. reported that a microporous MOF material, Cu₂(pzdc)₂(pyz), with non-coordinated oxygen atoms on the pore surface forms strong hydrogen-bonding interactions with C₂H₂, showing high C₂H₂/CO₂ separation potential.⁹⁹ This study firstly demonstrates the effective role of Lewis base sites in enhancing the affinity of a MOF for C₂H₂. In addition, MOFs with high density of OMSs can facilitate the recognition of acetylene. 100-108 In 2016, Chen et al. reported a MOF-74 isomer, namely, UTSA-74, which has two different (octahedral and tetrahedral) metal coordination geometries along the 1D channel.¹⁰¹ Each octahedrally coordinated metal ion provides two OMSs upon removal of the coordinated water molecules, leading to enhanced C₂H₂/CO₂ separation. The single-component adsorption isotherms showed that UTSA-74 has a comparable C₂H₂ uptake capacity (145 cm³ cm⁻³) to Zn-MOF-74 but a smaller CO₂ uptake capacity (90 cm³ cm⁻³ vs. 146 cm³ cm⁻³), resulting in UTSA-74 with a good C₂H₂/CO₂ separation performance. This result can be attributed to that each open Zn site can bind with two C2H2 molecules, whereas two oxygen atoms of a CO₂ molecule occupy two adjacent OMSs, as demonstrated by the single-crystal X-ray structures and molecular modeling studies. Breakthrough experiments for a 50/50 C₂H₂/CO₂ mixture further demonstrate its good practical separation performance. This is also the first example of using breakthrough experiments to demonstrate the separation performance of MOFs for the C₂H₂/CO₂ mixture.

Based on copper(1)-alkynyl chemistry, anchoring Cu(1) on the surface of a MOF can significantly improve its specific recognition for C₂H₂. Qian et al. reported a Cu(1)-modified porous MOF, Cu(1)@UiO-66-(COOH)2, which exhibits significantly enhanced C₂H₂/CO₂ separation performance with a high C₂H₂/CO₂ IAST selectivity of 185, compared to the prototype UiO-66-(COOH)₂. ¹⁰⁷ The strong π -complexation between the π electrons on C_2H_2 and Cu ions enables Cu(1)@UiO-66-(COOH)2 to adsorb a large amount of C₂H₂ (0.9 mmol g⁻¹) at low pressure (0.01 bar) and exhibit a high $Q_{\rm st}$ of 74.5 kJ mol⁻¹. Breakthrough experiments demonstrated its highly efficient separation performance for C₂H₂/CO₂. In addition, optimal distribution of OMSs on the pore surface of MOFs can achieve the maximum utilization of these sites. Recently, Li et al. reported a microporous MOF (JNU-4) with high-density OMSs. 108 These sites consist of square-planar copper centers separated by organic ligands, allowing each metal center to effectively bind with C2H2; thus, JNU-4 achieves a high C₂H₂ adsorption capacity (222 cm³ g⁻¹, 9.91 mmol g⁻¹) and a moderate IAST selectivity of 8.2 for an equimolar C2H2/CO2

mixture. Notably, this material absorbs C₂H₂ up to 200 cm³ g⁻¹ (8.93 mmol g⁻¹) at 298 K and 0.5 bar, but demonstrates a low $Q_{\rm st}$ of 26.8 kJ mol⁻¹. Grand Canonical Monte Carlo (GCMC) simulations demonstrated that C2H2 molecules can bind on both sides of OMSs, while CO2 molecules can only bind on one side. Breakthrough experiments revealed that it has a high C₂H₂ absorption capacity (160 cm³ g⁻¹, 7.14 mmol g⁻¹) from an equimolar C₂H₂/CO₂ mixture and can provide fuel-grade C2H2 gas.

Although a high density of OMSs can improve the selectivity for C₂H₂, electrostatic interactions between CO₂ and metal also exist simultaneously. 109-111 This requires a rational distribution of metal sites or the combination of multiple functions such as the pore size and shape to achieve a better C2H2 selectivity. 100,105,112 However, OMSs of high density may result in a high Q_{st} , thus leading to an increase of the energy consumption for adsorbent regeneration. In addition to OMSs, the introduction of functional groups (-NH₂, -F, -Cl, -Br, -CF₃, etc.) on organic ligands is also an effective strategy to promote selective adsorption of C₂H₂. ¹¹³⁻¹¹⁶ In 2021, Zhao et al. reported that an amine-functionalized flexible MOF (CPL-1-NH₂) with a 1D channel (3.8 \times 4.4 Å²) exhibits a high IAST selectivity of 119 for a 50/50 C₂H₂/CO₂ mixture at 298 K and 1 bar. 114 Theoretical calculations showed that the high selectivity of CPL-1-NH2 for C2H2 can be attributed to the NH2 functionalization that enhances C₂H₂ interaction with the framework, but blocks the stronger interaction between the noncoordinated oxygen atoms and CO2 molecules by occupying the adsorption site of CO₂. In the same year, Qian et al. reported an Al-MOF (CAU-10-H) with a pore size of 4.7 Å, exhibiting a high C₂H₂ storage density (392 g L⁻¹) and a separation factor (3.4). 115 GCMC simulations showed that the suitable pore size not only enhances the interaction of C2H2 with high density oxygen atoms and aromatic rings on the pore surface, but also enables synergistic interaction between adjacent C2H2 molecules. Subsequently, CAU-10-H was functionalized with amine to furnish a new MOF (CAU-10-NH₂). 116 The later study showed that the amine groups can improve the uptake capacity of C2H2 at low pressure, and significantly enhance the stacking density (0.46 cm³ g⁻¹) and C₂H₂/CO₂ selectivity (10.8) compared with the prototype MOF. In addition, these materials have the advantages of high stability, low Q_{st} , easy scale-up, and low cost.

It is well known that pore size and shape play an important role in the separation process, as an appropriate pore size can enhance the strength of interactions between the pore surface and adsorbate, as well as among adsorbates themselves. 97,100,112,117-123 MOFs can be designed and modified to alter the pore sizes, even at the sub-nanometer scale, through substitutions of metal ions, organic ligands, or inorganic anions. Strategies such as building self-interpenetrated networks and pore space partition (PSP) can also be used for the pore size or space modulation. 13,124 In 2019, Chen et al. reported a PSP approach for highly efficient C₂H₂/CO₂ separation. The new porous MOF (FJU-90) was synthesized by inserting a triangular ligand (2,4,6-tris(4-pyridyl)pyridine) into the cylindrical channel of prototype FJU-88.122 The 1D channel of FJU-88 was separated into a number of aperture cavities with the aperture size decreasing from 12.0 \times 9.4 to 5.4 \times 5.1 \mathring{A}^2 .

Thus, the combination of optimized pore space and oxygen atom sites endows FJU-90a with a high C₂H₂ adsorption capacity (180 cm³ g⁻¹, 8.04 mmol g⁻¹). The separation performance of the activated MOF (FJU-90a) for a 50/50 C₂H₂/CO₂ mixture was further confirmed by breakthrough experiments with a productivity of 1.87 mol kg^{-1} .

In 2017, Chen et al. reported a SIFSIX-MOF UTSA-300 that exhibits not only efficient separation of C₂H₂/C₂H₄ but also a high selective uptake for C₂H₂ from the C₂H₂/CO₂ mixture.⁷² Single-component adsorption isotherms revealed that the activated MOF (UTSA-300a) shows a high capacity for C2H2 adsorption (68.9 cm³ g⁻¹, 3.08 mmol g⁻¹) but adsorbs negligible CO_2 (3.25 cm³ g⁻¹, 0.14 mmol g⁻¹) at 298 K and 1 bar, resulting in a high IAST C₂H₂/CO₂ selectivity of 743 (298 K and 1 bar) (Fig. 9). Due to the strong C-H···F interactions formed between C₂H₂ molecules and SIF₆²⁻, C₂H₂ can easily diffuse into UTSA-300a, while CO₂ is restricted because of electrostatic repulsion, as confirmed by DFT calculations and neutron powder diffraction studies. The separation performance of UTSA-300a for a 50/50 C₂H₂/CO₂ mixture was further demonstrated by breakthrough experiment in a packed column bed of UTSA-300a. Subsequently, systematic fine-tuning of the pore size of UTSA-300 was performed by replacing the fluoride anionic linkers and metal ions. 125 Three new SIFSIX-type MOFs, namely SIFSIX-dps-Cu (NCU-100), GeFSIX-dps-Cu, and NbOFFIVE-dps-Cu, were reported to exhibit different pore sizes (1.4 \times 3.0 Å^2 , 1.5 \times 3.0 Å^2 , and 2.2 × 2.7 Å^2 , respectively) and interlayer distances (4.10 Å, 4.06 Å, and 3.69 Å, respectively). Single-component adsorption isotherms indicated that SIFSIX-dps-Cu shows the highest C₂H₂ uptake (4.57 mmol g⁻¹) with a high IAST C₂H₂/CO₂ selectivity up to 1787 at 298 K and 1 bar. In addition, the gate-opening pressure of SIFSIX-dps-Cu for C2H2 is 0.035 bar, which is lower than those of GeFSIX-dps-Cu (0.05 bar), NbOFFIVE-dps-Cu (0.3 bar), and UTSA-300 (0.06 bar), probably because of its larger interlayer distance. DFT and grand canonical Monte Carlo simulations further revealed that C2H2 molecules have multiple host-guest interactions (H...F hydrogenbonding interactions) in both inter- and intra-layer cavities. Breakthrough experiments confirmed that high purity C2H2 (\geq 99.9%) can be obtained from C₂H₂/CO₂ (50/50) with a high productivity of 2.48 mmol g⁻¹.

A suitable pore size combined with active sites and a flexible structure can greatly improve the adsorption capacity of a material for C₂H₂. ^{95,106,114,125–127} Recently, Hong et al. reported that a flexible MOF, namely, [Ni(DTBDA)(MeOH)₂(DMA)(H₂O)₂] (FJI-H36, DTBDA = 3',5'-di(1*H*-1,2,4-triazol-1-yl)-[1,1'-biphenyl]-3,5-dicarboxylic acid), with adaptive channels shows efficient adsorption of C₂H₂. ¹²⁷ FJI-H36 contains two types of cavities with the size of 12.9 \times 12.9 Å² and 8.4 \times 10.2 Å², respectively, as well as high-density active sites of open Ni^{II} (4.52 mol L⁻¹) and

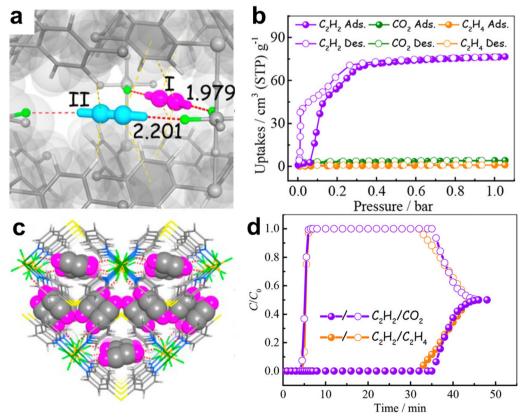


Fig. 9 (a) and (c) Neutron diffraction crystal structure of UTSA-300 \supset C_2D_2 and (b) C_2H_2 , CO_2 , and C_2H_4 sorption isotherms for UTSA-300a at 273 K. (d) Experimental column breakthrough curves for equimolar C_2H_2/CO_2 (purple) and C_2H_2/C_2H_4 (orange) mixtures (298 K, 1 bar) in a fixed-bed packed with UTSA-300a. Reprinted with permission from ref. 72. Copyright 2017 American Chemical Society.

free N atoms (9.04 mol L^{-1}). Single-component sorption experiments confirmed that FJI-H36 shows a high C2H2 uptake of 159.9 cm³ cm⁻³ at 298 K and 1 bar, and an ultra-high C₂H₂ storage density of 561 g L⁻¹. Breakthrough experiments for a 50/50 C₂H₂/CO₂ mixture further demonstrated its high adsorption capacity for C_2H_2 (3.82 mmol g^{-1}). The structure of FJI-H36 adaptively changes with the adsorption of C2H2, leading to a dense packing of C₂H₂ in it, as demonstrated by the X-ray crystal structure of C₂H₂@FJI-H36.

Recently, Wang et al. reported a sulfate-pillared MOF $[Zn(tepb)(SO_4)]$ (SOFOUR-TEPE-Zn, TEPB = tetra(4-pyridyl)benzene), which possesses dense electronegative pore surfaces to highly promote the separation of C₂H₂/CO₂ (Fig. 10). 97 SOFOUR-TEPE-Zn is an isostructural framework with SOFOUR-1-Zn, ¹²⁸ but with more electron-rich pore surfaces due to the higher electronegative ethylene groups in the TEPE ligand in contrast to the phenyl ring in the TEPB ligand. Single-component sorption results of SOFOUR-TEPE-Zn reveled a higher C₂H₂ uptake (89.1 cm³ g⁻¹, 3.98 mmol g^{-1}) than SOFOUR-1-Zn (69.4 cm³ g⁻¹, 3.10 mmol g⁻¹) at 1 bar and 298 K, but a much lower CO₂ uptake (14.1 cm³ g⁻¹, 0.63 mmol g⁻¹), resulting in a very high IAST selectivity of 16833 for 50/50 C₂H₂/CO₂. Breakthrough experiments for 50/50 C₂H₂/CO₂ of SOFOUR-TEPE-Zn give a productivity of 60.1 cm³ g⁻¹ $(2.68 \text{ mmol g}^{-1}) \text{ of } 99.5\% \text{ purity or } 33.2 \text{ cm}^3 \text{ g}^{-1} (1.48 \text{ mmol g}^{-1}) \text{ of }$ 99.99% purity in its desorption process by stepped helium purging and mild heating. Moreover, SOFOUR-TEPE-Zn also maintains a high C₂H₂ productivity of 75.5 cm³ g⁻¹ (3.37 mmol g⁻¹) of 99.5% purity with 99.82% C₂H₂ recovery in the simulated pressure swing adsorption processes. DFT-D and GCMC simulation studies revealed that the preferential binding of C2H2 in SOFOUR-TEPE-Zn can be mainly attributed to electron-rich pore surfaces, providing multiple optimal adsorption sites for C₂H₂.

CO2-selective adsorbents can yield high purity C2H2 in one step rather than multiple adsorption-desorption steps, making the operation simple and more energy efficient. Currently, only a limited number of CO2-selective MOF materials have been reported, manifesting the challenge in the design of CO2selective materials. 129-148 Fortunately, several strategies have been reported to promote the selective adsorption of CO2 in MOFs. For example, Chen et al. introduced hydroxyl functional groups into MOF frameworks, enabling selective capture of CO₂ from C₂H₂, with a high IAST selectivity of 118.7 for CO₂/C₂H₂ (1:2, v:v) at 0.1 bar and ambient temperature. 137 In 2021, Chen et al. reported an ultramicroporous MOF [Cu(F-pymo)₂]·1.25H₂O (Cu-F-pymo, F-pymo = 5-fluoropyrimidin-2-olate) with zeolitic gismondine (GIS) topology exhibiting a high selective adsorption of CO2 over C2H2, which depends on activation temperature (Fig. 11). 143 Cu-F-pymo contains two distinct pore environments, namely, spherical cavities and 1D helical channels, both of which are occupied by removable water molecules. Single-component adsorption isotherms revealed that partially dehydrated Cu-F-pymo can adsorb 1.19 mmol g⁻¹ C₃H₆

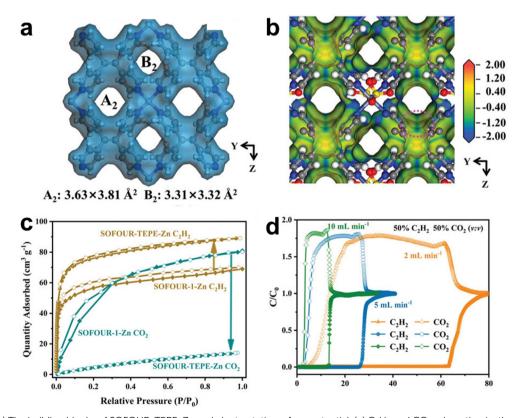


Fig. 10 (a) and (b) The building blocks of SOFOUR-TEPE-Zn and electrostatic surface potential. (c) C₂H₂ and CO₂ adsorption isotherms for SOFOUR-1-Zn and SOFOUR-TEPE-Zn at 298 K. (d) Breakthrough curves of SOFOUR-TEPE-Zn for C₂H₂/CO₂ (50/50, v/v) at different flow rates at 298 K. Reprinted with permission from ref. 97. Copyright 2023 Wiley-VCH.

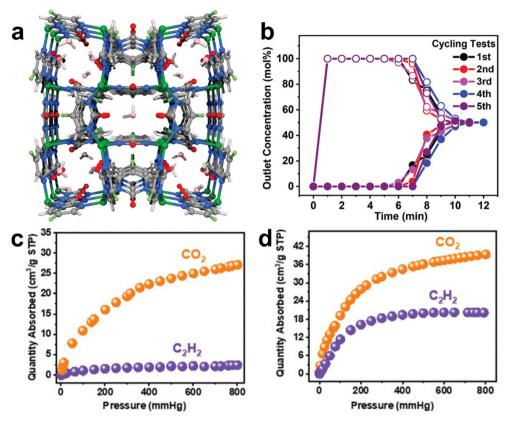


Fig. 11 (a) Schematic structure of Cu-F-pymo MOF with residual water molecules. (b) Breakthrough cycling tests of the equimolar CO₂/C₂H₂ mixture. (c) and (d) Separation performance toward CO₂ and C₂H₂ in Cu-F-pymo under different activation conditions. Reprinted with permission from ref. 143 Copyright 2021 Wiley-VCH.

and show negligible C₂H₂ uptake (0.1 mmol g⁻¹) at 298 K and 1 bar. Breakthrough experiments revealed that highly pure acetylene (>99.9%) can be obtained directly from a 50/50 CO₂/C₂H₂ mixture by a single separation operation. Modeling studies demonstrated that CO2 can be preferentially adsorbed in the 1D channels, while C₂H₂ primarily occupies the spherical cavities. Therefore, the remaining water molecules in the spherical cavities blocked the preferential site, leading to the molecular sieving effect of Cu-F-pymo for CO₂/C₂H₂.

Besides size-matching between gas molecules and the pore structure, reasonable charge distribution would also facilitate the selective recognition of CO₂ over C₂H₂. Chen et al. reported an ultramicroporous porous material Cd[Fe(CN)₅NO] (Cd-NP) that exhibits stronger affinity for CO₂ in contrast to C₂H₂. Cd-NP contains quasi-discrete ellipsoidal cavities (6.1 \times 4.5 \times 4.5 Å^3) connected by small apertures (3.2 Å), and its BET surface area is 305 m² g⁻¹ (Fig. 12). 144 Thanks to suitable pore sizes and electrostatic distribution on pore surfaces, Cd-NP shows a high CO_2 uptake of 58.0 $cm^3\ g^{-1}$ (2.59 $mmol\ g^{-1})$ but a lower C_2H_2 uptake of 9.7 cm 3 g $^{-1}$ (0.43 mmol g $^{-1}$) at 1 bar and 298 K, thus showing a high IAST selectivity (85) for an equimolar CO_2/C_2H_2 mixture. The $Q_{\rm st}$ of ${\rm CO_2}$ was calculated to be 27.7 kJ ${\rm mol}^{-1}$, which would facilitate regeneration of the material under mild conditions. The breakthrough process showed that Cd-NP was capable of producing a high purity C₂H₂ (99.9%) directly from $50/50 \text{ CO}_2/\text{C}_2\text{H}_2$ with a productivity of 2.34 mol L⁻¹. GCMC simulations and neutron powder diffraction experiments showed that the preferential adsorption of CO₂ in Cd-NP can be attributed to the confinement effect of the pore cavity and electrostatically complementary pore surface.

CO₂/C₂H₂ inverse separation can also be achieved using synergistic effects of thermodynamics and kinetics. Li et al. reported an ultramicroporous MOF, Y-bptc, to achieve one-step C₂H₂ purification from a CO₂/C₂H₂ mixture. Y-bptc processes small windows (4.2 Å) interconnected with large cubic cages with ftw topology. Equilibrium and kinetic adsorption studies reveled that Y-bptc absorbs 55 $\text{cm}^3~\text{g}^{-1}$ (2.45 mmol g^{-1}) CO_2 and a lower C₂H₂ uptake at 298 K and 1 bar with an IAST selectivity of 4.1 for 50/50 CO₂/C₂H₂.¹³⁶ Moreover, CO₂ diffuses faster than C₂H₂ in Y-bptc, and the calculated kinetic separation coefficient reaches 114 at 298 K. Breakthrough experiments confirmed that CO₂ in a 1:1 CO₂/C₂H₂ mixture can be readily removed by Y-bptc, giving C_2H_2 with a purity of >99% and productivity of 1.52 mmol g^{-1} in a one-step separation process. GCMC simulations further revealed the high affinity of Y-bptc for CO2 resulting from the formation of hydrogen-bonding interactions between μ_3 -OH⁻ groups of the framework and CO₂ molecules.

In 2023, Wade et al. reported two isostructural MOFs $[Zn_5Cl_4(bbta)_3]$ (MUF-4, bbta²⁻ = benzo-1,2,4,5-bistriazolate) and MUF-4-F, which exhibited completely opposite adsorption

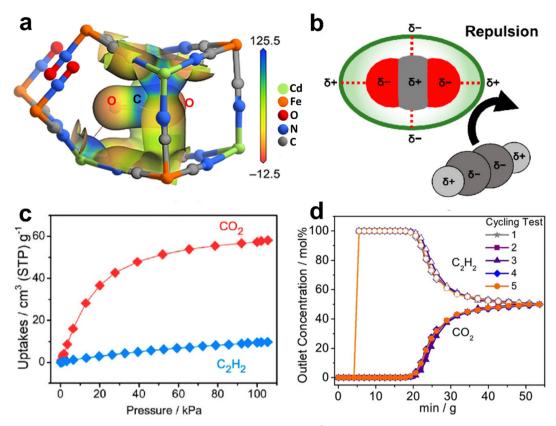


Fig. 12 (a) Electrostatic potential (ESP) of Cd-NP \supset CO₂ mapped onto the 0.15 e⁻Å⁻³ electron density isosurface. (b) Electrostatically driven adsorption mechanism towards CO₂ and C₂H₂ molecules. (c) CO₂ and C₂H₂ sorption isotherms for Cd-NP at 298 K. (d) Cycling tests of the equimolar CO₂/C₂H₂ mixture in a column packed with Cd-NP at 298 K and 1 bar. Reproduced with permission from ref. 144. Copyright 2021 Wiley-VCH.

selectivity for CO₂/C₂H₂. MUF-4-F can be derived by F⁻ to Cl⁻ ligand exchange of MUF-4. 139 Both MUF-4-F and MFU-4 possess alternating large pore and small pore cavities but have different connecting windows (~ 3.7 Å and ~ 2.2 Å, respectively). C_2H_2 molecules can easily enter MFU-4-F. Equilibrium and kinetic adsorption studies revealed that MFU-4-F exhibits a higher C_2H_2 (6.66 mmol g^{-1}) uptake than CO_2 (3.24 mmol g^{-1}) at 300 K and 1 bar and shows a fast adsorption rate for both gases. In contrast, MFU-4 exhibits high kinetic selectivity for uptake of CO₂ over C₂H₂ up to 3360 at 300 K. Computational studies revealed that C2H2 was blocked by the smaller windows created by the Zn-Cl groups in MUF-4. Breakthrough experiments demonstrated that high purity (>98%) C₂H₂ can be obtained directly from a 50/50 CO₂/C₂H₂ mixture in MUF-4.

2.5. C₃H₆ and C₃H₈ separation

Propylene (C₃H₆) is also an essential industrial feedstock with large demand that is only lower than that of ethylene. The industrial production of C₃H₆ inevitably contains a certain amount of propane (C₃H₈) impurity. However, they have very similar molecular sizes (C_3H_6 : 3.8 × 4.0 × 6.5 Å³, and C_3H_8 : $3.8 \times 4.2 \times 6.8 \text{ Å}^3$), kinetic diameters (C₃H₆: 4.0 Å, and C₃H₈: 4.2 Å) and physical properties (boiling points of 189.3 and 194.7 K, respectively). Therefore, it is more challenging to tune the pore size for sieving separation of C₃H₆/C₃H₈, because they

have highly similar molecular sizes and kinetic diameters, whereas possible changes of the size and shapes of MOF apertures may occur in the adsorption process, as many MOFs are actually flexible. Fortunately, significant research progress about highly efficient separation of C3H6/C3H8 has been recently realized by MOFs through rational structural design and modification of the pore size and pore surface. 149-168

The incorporation of active sites in MOFs' pore surface improves not only kinetic selectivity but also thermodynamic selectivity for gas separation. In 2019, Zhang et al. reported a MAF, MAF-23-O, which can be easily synthesized by heating the flexible prototype $[Zn_2(btm)_2]$ (MAF-23, $H_2btm = bis(5-methy-1H-1)$ 1,2,4-triazol-3-yl)methane) under oxygen gas flow (Fig. 13). 149 Single-crystal structure analyses showed that MAF-23-O is isostructural to MAF-23 and contains half the amount of the oxidized btm²⁻ ligands, namely, btk²⁻ (H₂btk = bis(5-methyl-1,2,4-triazol-3yl)methanone). This in situ ligand oxidative modification makes the framework more rigid and more hydrophilic. The IAST selectivity for C₃H₆/C₃H₈ in MAF-23-O was calculated to be 8-9, which was higher than that of MAF-23 (3-4). Moreover, C₃H₆ and C₃H₈ exhibit similar diffusion rates in MAF-23, but show very different diffusion rates in MAF-23-O with a high kinetic selectivity of 71. Theoretical calculations demonstrated that the exposed oxygen atoms in the framework of MAF-23-O can form strong C-H···O/N interaction with C₃H₆, improving the thermodynamic selectivity of

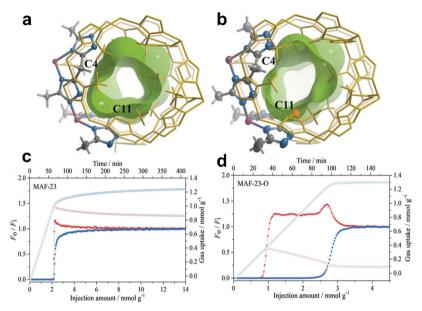


Fig. 13 Crystal and pore structures of (a) MAF-23 and (b) MAF-23-O. Breakthrough curves (filled symbols) and adsorption kinetic curves (open symbols) for (c) MAF-23 and (d) MAF-23-O using an equimolar C_3H_6/C_3H_8 (blue/red) mixture at 298 K and 1 bar. Reprinted with permission from ref. 149. Copyright 2019 Wiley-VCH.

MAF-23-O for C₃H₆. Additionally, the decreased flexibility of the framework slows down the diffusion of C₃H₆, thus improving the kinetic selectivity. Breakthrough experiments revealed that MAF-23-O exhibits efficient separation for an equimolar C₃H₆/ C₃H₈ mixture at 298 K and 1 bar with an adsorption selectivity of 15, which is 10 times that of MAF-23.

In 2016, Eddaoudi et al. reported a oxyfluoride-based MOF $[Ni(pyr)_2(NbOF_5)] \cdot 2H_2O$ (NbOFFIVE-1-Ni, or KAUST-7, pyr = pyrazine) for selective adsorption of C₃H₆ from C₃H₈. ¹⁵⁰ KAUST-7 is isostructural to SIFSIX-3 and composed of Ni(II)pyrazine square-grid layers and (NbOF₅)²⁻ pillars with **pcu** topology, exhibiting 1D channels with an aperture size of 3.0 Å and a periodic array of fluoride anions on the pore surface. Singlecomponent sorption experiments revealed that KAUST-7 can adsorb $\sim 60 \text{ mg g}^{-1} (1.43 \text{ mmol g}^{-1}) \text{ C}_3\text{H}_6 \text{ but negligible C}_3\text{H}_8$ uptake at 298 K and 1 bar. Breakthrough experiments demonstrated that C₃H₈ of 97% purity can be obtained from C₃H₆/C₃H₈ 50/50 mixed-gas by a packed column bed of KAUST-7, with a separation productivity of 0.6 mol g⁻¹. KAUST-7 also can adsorb C₃H₈ by pore-opening sorption behavior at 273 K.

In 2023, Chen et al. reported another SIFSIX MOF [Ni(WO₂F₄)-(pyz)₂] (UTSA-400) featuring 1D channels that can exclude C₃H₈ molecules and adsorb C₃H₆ molecules with a high binding affinity (Fig. 14).151 UTSA-400 shows an isostructural framework with SIFSIX-3 and NbOFFIVE-1-Ni, but with highly tilted pyrazine linkers owing to larger $WO_2F_4^{\ 2-}$ in contrast to $SiF_6^{\ 2-}$ and NbOF₅²⁻. The pore cavities in UTSA-400 are $6.7 \times 5.5 \times 3.7 \text{ Å}^3$ with exposed oxide/fluoride pairs on the pore surface (BET surface area: 226 m² g⁻¹) that can serve as the binding sites for propylene molecules. Single-component sorption results of UTSA-400 indicated a much higher C₃H₆ capacity $(92.1 \text{ cm}^3 \text{ cm}^{-3}, 2.62 \text{ mmol } \text{g}^{-1}) \text{ than NbOFFIVE-1-Ni}$ (54.3 cm³ cm⁻³, 1.34 mmol g⁻¹) by 63%, at 1 bar and 298 K, which is also higher than those of Y-abtc (64.6 cm³ cm⁻³, 1.98 mmol g^{-1}) and Co-gallate (66.6 cm³ cm⁻³, 1.79 mmol g^{-1}). Under the same conditions, UTSA-400 showed negligible C₃H₈ uptake because of inaccessible inward diffusion of propane molecules. The $Q_{\rm st}$ of UTSA-400 for C_3H_6 is 60.5 kJ ${\rm mol}^{-1}$, being comparable to those of MOFs with OMSs (44-57 kJ mol⁻¹). 30,45 Breakthrough separation experiment demonstrated that polymergrade (99.7%) propylene can be obtained from an equimolar C₃H₆/ C_3H_8 mixture with a productivity of 56.7 L L⁻¹. Besides size exclusion, the separation performance of UTSA-400 can also be attributed to strong C-H···O/F interactions, as confirmed by in situ infrared spectroscopy and DFT-D calculations.

In 2018, Li et al. studied four microporous MOFs, namely, Zr-bptc, Zr-abtc, Y-bptc, and Y-abtc, which were obtained by the combination of two analogous metal clusters (Zr₆ and Y₆ clusters) and two different ligands (abtc = 3,3',5,5'-azobenzenetetracarboxylates, and bptc = 3,3',5,5'-biphenyltetracarboxylates). 152 Among these materials, Y-abtc has cage-like pores connected through small windows, exhibiting ftw topology and optimal pore size (4.72 Å) that enables it to adsorb small C₃H₆ molecules (4.48 Å) with fast kinetics but completely exclude larger C3H8 molecules (5.1 Å). Single-component sorption experiments revealed that Zr-bptc exhibits similar adsorption capacities for C₃H₆ and C₃H₈, whereas its isostructural Y-bptc excludes both gases, attributable to the presence of equilibrium cations (dimethylammonium) in the Y-bptc affecting its pore size. In contrast, Y-abtc with the optimal pore size shows a high adsorption capacity for C_3H_6 (~ 2 mmol g^{-1}) and a negligible C_3H_8 uptake at 298 K. Column breakthrough experiments indicated that polymer-grade C₃H₆ (99.5%) can be obtained from 5/95 C₃H₆/C₃H₈ mixtures by Y-abtc. Recently, the same group reported a new Y-based MOF, $Y_6(OH)_8(eddi)_3(DMA)_2$ (HIAM-301, $H_4eddi = 5.5'$ -(ethene-1,2-diyl)diisophthalic acid, and DMA = dimethylammonium), also

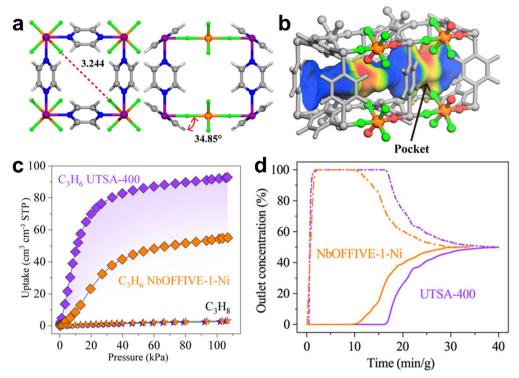


Fig. 14 (a) Crystal structure of UTSA-400. (b) Connolly surface of UTSA-400 mapped with electrostatic potential with a probe of 1.2 Å. (c) Singlecomponent adsorption isotherms of C_3H_6 and C_3H_8 for UTSA-400 and NbOFFIVE-1-Ni at 298 K. (d) Breakthrough curves for NbOFFIVE-1-Ni and UTSA-400 for an equimolar binary mixture of C_3H_6 (solid line)/ C_3H_8 (dashed line) at 298 K and 1 bar. Reprinted with permission from ref. 151. Copyright 2023 American Chemical Society.

exhibiting the molecular sieving separation of C₃H₆/C₃H₈ mixtures. HIAM-301 is composed of 12-connected Y₆(OH)₈(COO)₁₂ clusters bridged by 4-connected eddi4- linkers to form a 3D framework with ftw topology and a pore size of 4.6 Å. 153 It is isostructural to Y-abtc and possesses distorted cubic cages (size: $10\times 10\ \mbox{Å}^2)$, which provides better control over guest accessibility. Single-component adsorption isotherms revealed that HIAM-301 can adsorb 3.16 mmol g⁻¹ C₃H₆ and exhibit minor C₃H₈ adsorption (<0.3 mmol g⁻¹) at 298 K and 1 bar, resulting in a high IAST selectivity (>150) for equimolar C_3H_6/C_3H_8 under the same condition. The practical performance for separation of 5/95 C₃H₆/C₃H₈ was confirmed by dynamic breakthrough experiments with a high productivity of 46.4 cm 3 g $^{-1}$ (>99.5% purity).

In 2020, Chen et al. reported an ultramicroporous Co-gallate MOF [Co(C₇O₅H₄)] (Co-gallate) with 3D channels, which exhibits efficient C₃H₆/C₃H₈ separation by molecular sieving effect. 154 Co-gallate shows elliptical windows (size: 4.2 × 5.1 Å²), which are precisely between the sizes of C₃H₈ and C₃H₆ (Fig. 15). Single-component adsorption isotherms showed that Co-gallate has a high adsorption capacity of C₃H₆ (66.6 cm³ cm⁻³, 1.79 mmol g^{-1}), whereas the adsorption of C_3H_8 (5.2 cm³ cm⁻³, 0.14 mmol g^{-1}) is minor at 298 K. The IAST selectivity of Co-gallate for a 50/50 C₃H₆/C₃H₈ mixture was calculated up to 330 at 1 bar and 298 K. Fixed-bed breakthrough experiments further confirmed its molecular sieving separation performance for 50/50 C₃H₆/C₃H₈, with a C₃H₆ productivity of 36.4 cm³ cm⁻³, 0.98 mmol g⁻¹ (97.7%+ purity).

In 2021, Li et al. reported a MOF (JNU-3a) featuring 1D channels (size $\sim 4.5 \times 5.3 \text{ Å}^2$) attached with small pockets arranged on both sides for C₃H₆/C₃H₈ separation, where 1D channels could facilitate fast adsorption-desorption kinetics (Fig. 16). 155 In addition, the small pockets were connected with the 1D channel through small apertures (~ 3.7 Å) that can undergo gate-opening for C3H6 and C3H8 at different partial pressures. JNU-3a exhibits a stepwise adsorption isotherm and shows temperature-dependent gate-opening for C₃H₆ and C₃H₈, where C₃H₈ exhibits a higher gate-opening pressure than C₃H₆. Therefore, the high selectivity of JNU-3a for C₃H₆/C₃H₈ can be obtained at optimal temperature (303 K). JNU-3a can adsorb 58.6 cm 3 g $^{-1}$ (2.62 mmol g $^{-1}$) $C_{3}H_{6}$ at 303 K, and the $C_{3}H_{6}$ packing density inside JNU-3a was calculated to be 404 g L^{-1} . The dynamic feature of pore aperture was further revealed by singlecrystal X-ray diffraction and theoretical calculation studies. Breakthrough experiment revealed that high-purity C₃H₆ (≥99.5%) can be obtained from a 50/50 C₃H₆/C₃H₈ mixture by JNU-3a. After applying helium purge to those adsorbed gases, C₃H₆ was collected with a maximum productivity of 53.5 L kg⁻¹. The unique pore structure reported in this work would inspire future design of novel MOFs for application in adsorptive separation.

In 2023, Bai et al. reported a supertetrahedral-cluster ($Cu_{10}O_{13}$)based MOF (NTU-85) which possesses square-shaped 1D channels that host lattice water molecules. 156 The partial lattice water molecules can be precisely removed to form a

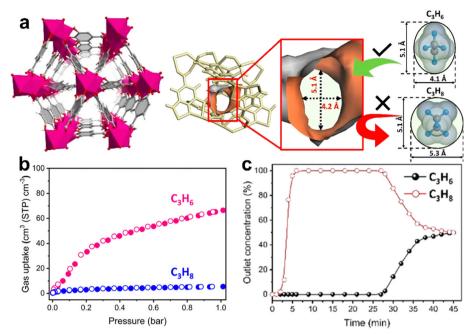


Fig. 15 (a) Structure of the Co-gallate MOF and rationale for C_3H_6/C_3H_8 separation. (b) Gas sorption isotherms of propylene and propane at 298 K for Co-gallate. (c) The breakthrough experiments were carried out in a packed column. Reprinted with permission from ref. 154. Copyright 2020 American Chemical Society

MOF (NTU-85-WNT) of pore surface decorated with water nanotubes (~4.5 Å). Single-component sorption results of NTU-85-WNT indicated a rapid C_3H_6 uptake (20.9 mL mL⁻¹, 0.45 mmol g^{-1}), while the adsorption of C_3H_8 (0.13 mL mL⁻¹, $0.003 \text{ mmol g}^{-1}$) at 298 K can be neglected. The IAST selectivity of NTU-85-WNT for an equimolar C₃H₆/C₃H₈ mixture reaches up to 1570. Fixed-bed breakthrough experiments further confirmed its molecular sieving performance for an equimolar C₃H₆/C₃H₈ mixture, with a C₃H₆ productivity of 1.6 mL mL⁻¹ (98.8%+ purity). It is worth noting that high purity C₃H₈ (>99.5%) can be obtained in one adsorption-desorption cycle due to the efficient sieving performance.

An optimal pore size combined with high-density binding sites can efficiently separate C₃H₆/C₃H₈, allowing for highdensity stacking of C₃H₈ and maximizing its adsorption capacity. Recently, Chen et al. reported a robust Hofmann-type MOF, $[Co(pyz-NH_2)Ni(CN)_4]$ (ZJU-75a, pyz-NH₂ = 2-aminopyrazine), with high-density binding sites, showing excellent separation performance for C₃H₆/C₃H₈. ¹⁵⁷ ZJU-75a exhibits an isostructural framework with [Co(pyz)Ni(CN)₄] (ZJU-74a, pyz = pyrazine), decorated with amino groups. ZJU-75a exhibits an appropriate pore size $(4.1 \times 4.4 \text{ Å}^2)$ and OMSs of high density $(8.89 \text{ mmol cm}^{-3})$. Single-component sorption isotherms showed that ZJU-75a and ZJU-74a exhibit comparable C₃H₆ uptakes of 104.3 cm⁻³ cm³ $(3.31 \text{ mmol g}^{-1})$ and $111.4 \text{ cm}^{-3} \text{ cm}^{3}$ $(3.68 \text{ mmol g}^{-1})$ at 1 bar and 296 K, respectively, whereas the C3H8 adsorption capacity of ZJU-75a (73.5 cm $^{-3}$ cm 3 , 2.33 mmol g $^{-1}$) is obviously smaller than that of ZJU-74a (103.6 cm $^{-3}$ cm 3 , 3.42 mmol g $^{-1}$). Thus, the IAST selectivity of ZJU-75a for C₃H₆/C₃H₈ was calculated to be 54.2 at 296 K and 1 bar, much higher than that of ZJU-74a (4.3). The breakthrough studies indicate that ZJU-75a can yield C₃H₆ of high-purity (99.5%+) with a productivity of 18.7 L kg⁻¹ and separation factor of 14.7. Structural and computational studies indicated that high-density OMSs and nitrogen atoms (from [Ni(CN)₄]₂ units and -NH₂ groups) in ZJU-75a contribute jointly to the strong adsorption of C₃H₆, thus resulting in a high C₃H₆ storage density (0.818 g mL^{-1}).

C₃H₈-selective adsorptive separation would be a relatively simple and energy-efficient way to get pure propylene. However, the differences of the molecular size ($\sim 0.5 \text{ Å}$) and polarizability $(C_3H_6: 62.6 \times 10^{-25}, and C_3H_8: 62.9-63.7 \times 10^{-25} cm^3)$ between C₃H₆ and C₃H₈ are smaller than those between C₂H₄ and C₂H₆. So far, only a few C₃H₈-selective MOFs have been reported. 169–180

In 2022, Xing et al. reported an ultramicroporous pillared layered MOF $[Co(IPA)(DPG)]_n$ (PCP-IPA, IPA = isophthalic acid, and DPG = $meso-\alpha$, β -di(4-pyridyl)glycol) featuring 1D pores (size $\sim 4.7 \times 5.6 \text{ Å}^2$) and periodic parallel-aligned isophthalic acid units on the pore surface, exhibiting an excellent selectivity for C₂H₆ and C₃H₈. ¹⁶⁹ Although C₂H₆ and C₃H₈ have different molecular sizes, the suitable pore size of PCP-IPA facilitates their directional adsorption and maximizes the interaction between PCP-IPA and C₃H₈/C₂H₆. Therefore, PCP-IPA exhibits not only a C₃H₈/C₃H₆ (50/50) IAST selectivity of 2.48 but also a relatively high adsorption selectivity (2.80) for C_2H_6/C_2H_4 (50/50) at 1.0 bar and 298 K. Both C₃H₈ and C₂H₄ can be directly obtained with high purity (99.99%) through a fixed-bed column from C_3H_8/C_3H_6 (50/50) and C_2H_4/C_2H_6 (50/50) mixtures, respectively, affording a high C₃H₆ productivity (15.23 L kg⁻¹) and excellent C_2H_4 productivity (26.2 L kg⁻¹). Modeling simulation studies revealed that tighter and more multiple vdW interactions (C-H···O/C) can be formed between paraffins and PCP-IPA compared to olefins.

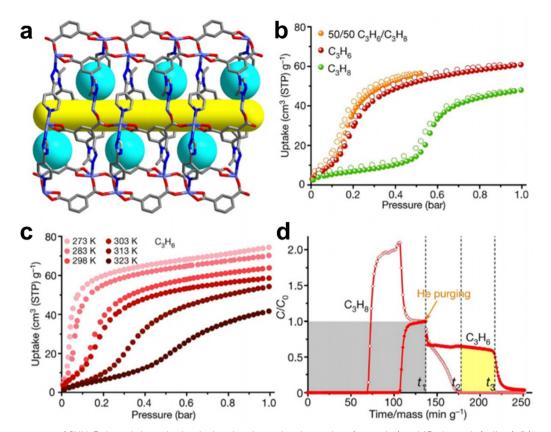


Fig. 16 (a) Pore structure of JNU-3 viewed along the b axis showing the molecular pockets (turquoise) and 1D channels (yellow); (b) pure C₃H₈ (green), JNU-3a at different temperatures; (d) breakthrough curves (starting at t = 0) of an equimolar C_3H_6/C_3H_8 mixture (1.0 mL min⁻¹) on JNU-3a, followed by desorption curves (starting at $t = t_1$) under helium gas (10.0 mL min⁻¹) sweeping at 303 K. C_3H_8 , open diamonds; C_3H_6 , solid diamonds. C and C_0 are the concentrations of each gas at the outlet and inlet, respectively. Grey area, mixed gas input; yellow area, C_3H_6 gas output; t_1 , the beginning of desorption; t_2 , starting point of collecting C_3H_6 ; t_3 , the end point of collecting C_3H_6 . Reprinted with permission from ref. 155. Copyright 2021 Nature Publishing Group

Very recently, Li et al. reported two isostructural MOFs (FDMOF-1 and FDMOF-2) functionalized with different amounts of fluorinated functional groups (-CF₃), showing strong affinity for C₃H₈ over C₃H₆ (Fig. 17). ¹⁷⁰ Compared with the protype MOF $Zn_2(BDC)_2(DABCO)$ (Zn-DMOF, BDC = 1,4-benzenedicarboxylate), the introduction of different amounts of -CF₃ groups into a MOF not only increases its stability but also adjusts the pore size/ shape. Therefore, FDMOF-2 with the maximal amount of -CF₃ groups shows the smallest aperture (5.1 Å) and exhibits the optimal C₃H₈ affinity. Single-component sorption isotherms showed that FDMOF-2 displays a higher C₃H₈ uptake of $140~\mbox{cm}^{3}~\mbox{cm}^{-3}$ (5.04 mmol $\mbox{g}^{-1}\!)$ but a lower $\mbox{C}_{3}\mbox{H}_{6}$ uptake of 115 cm³ cm⁻³ (4.14 mmol g⁻¹), resulting in the IAST selectivity for 50/50 C₃H₈/C₃H₆ up to 2.18 at 298 K and 1 bar. Breakthrough experiments revealed that high purity (>99.99%) C₃H₆ can be directly produced from 50/50 C₃H₈/C₃H₆ mixtures, affording 0.501 mol L^{-1} production of C_3H_6 . It is worth pointing out that the excellent separation performance of FDMOF-2 for C₃H₈/C₃H₆ can be maintained under 70% relative humidity conditions. Single-crystal X-ray diffraction and theoretical calculation studies confirmed that the strong affinity of UTSA-400 for C₃H₈ can be attributed to strong non-classical C-H···π/F hydrogen-bonding

interactions, resulting in a stronger binding affinity for C₃H₈ vs. C_3H_6 with an initial Q_{st} value difference of -3.7 kJ mol⁻¹.

2.6. C_3H_4/C_3H_6 separation

The removal of traces of propyne (C_3H_4 of $\sim 1\%$) from propylene is essential to obtain high purity propylene (C₃H₆). However, it is very difficult to separate trace amounts of C₃H₄ from C₃H₆, because their chemical/physical properties and molecular sizes $(C_3H_4: 6.2 \times 3.8 \times 3.8 \text{ Å}^3; C_3H_6: 6.5 \times 4.0 \times 4.2 \text{ Å}^3)$ are highly similar. Nevertheless, some MOFs have been reported to show great potential for the separation of C_3H_4/C_3H_6 . ^{181–189}

In 2017, Chen et al. reported a flexible-robust MOF [Cu(bpy)₂-(OTf)₂] (ELM-12, bpy = 4,4'-bipyridine, and OTf = trifluoromethanesulfonate) which exhibits excellent performance for removing trace C₃H₄ from a 1/99 C₃H₄/C₃H₆ mixture. ELM-12 composed of 2D square-grid sheets with dynamic dangling OTf groups exhibit two kinds of cavities of different shapes and sizes $(6.1 \times 4.3 \times 4.3 \text{ Å}^3 \text{ and } 6.8 \times 4.0 \times 4.2 \text{ Å}^3)$, which were comparable with the size and shape of C_3H_4 (6.2 × 3.8 × 3.8 Å³) (Fig. 18). 181 Single-component adsorption isotherms revealed that ELM-12 shows a sharp increasing adsorption for C₃H₆ with an uptake of 1.83 mmol g^{-1} at 298 K and 1 bar, as well as a large $Q_{\rm st}$

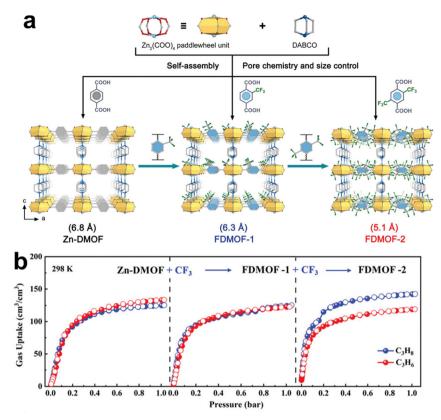


Fig. 17 (a) Crystal structures of Zn-DMOF, FDMOF-1, and FDMOF-2. (b) Single-component gas adsorption isotherms of the samples at 298 K. Reprinted with permission from ref. 170. Copyright 2023 Wiley-VCH.

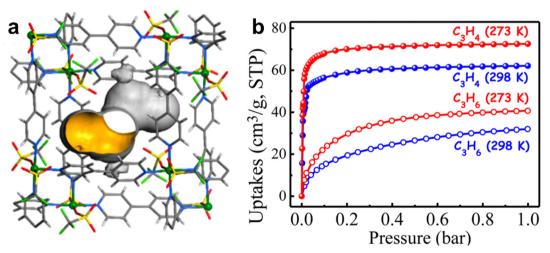


Fig. 18 (a) Crystal structure of ELM-12. (b) C₃H₄ and C₃H₆ adsorption isotherms of ELM-12. Reprinted with permission from ref. 181. Copyright 2017 American Chemical Society.

of 60.6 kJ mol⁻¹ for C₃H₆, indicating its strong interaction with the C₃H₆ molecule. In contrast, both the uptake capacity $(0.67 \text{ mmol g}^{-1} \text{ at } 0.1 \text{ bar and } 298 \text{ K}) \text{ and } Q_{\text{st}} (15.8 \text{ kJ mol}^{-1})$ of ELM-12 for C₃H₈ are significantly lower. The multiple interactions, such as weak or non-classical C-D···O hydrogen bonds, between ELM-12 and C₃D₄ molecules were further confirmed by high-resolution neutron powder diffraction studies. Breakthrough experiments demonstrated that high purity (99.9998%) of C₃H₆ can be obtained from a 1/99 C₃H₄/C₃H₆ mixture.

In 2018, Chen et al. studied a series of MOFs with different types of structures, functionalities, and pore sizes (Fig. 19). 182 Besides for highly selective C₂H₂/C₂H₄ separation, ^{70,71} SIFSIXtype MOFs such as SIFX-1-Cu, SIFSIX-2-Cu-i, SIFSIX-3-Ni, and UTSA-200 also exhibit strong binding affinities for C3H4 compared to C₃H₆ and show high C₃H₄ adsorption capacities at very

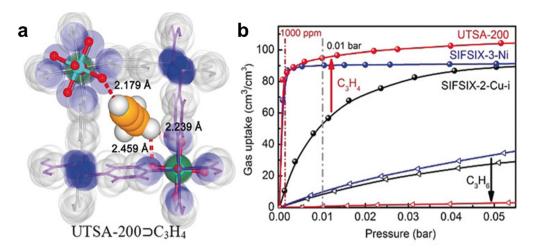


Fig. 19 (a) DFT-D optimized structure and binding sites of UTSA-200 ⊃ C₃H₄. (b) C₃H₄ and C₃H₆ adsorption isotherms of UTSA-200 at 298 K. Reprinted with permission from ref. 182. Copyright 2018 Wiley-VCH.

low pressure. The former three SIFSIX-MOFs show slightly larger pore sizes than both C₃H₄ and C₃H₆, which lead to moderate C₃H₄/C₃H₆ selectivity. The activated UTSA-200 with the optimal pore size (3.4 Å) and strong binding sites has the best separation performance for C₃H₄/C₃H₆. Single-component adsorption isotherms revealed that UTSA-200 exhibits the highest C_3H_4 uptake capacity of 95 cm³ cm⁻³ (2.99 mmol g⁻¹) at 0.01 bar and 298 K, while adsorbs negligible C₃H₆ (0.33 mmol g⁻¹, at 298 K and 0.4 bar), resulting in an extremely high IAST selectivity of 20 000 for $1/99 C_3H_4/C_3H_6$ at 298 K and 1 bar. Breakthrough experiments demonstrated that high purity (99.9999%) C₃H₆ can be yielded from 1:99 and 0.1:99.9 C_3H_4/C_3H_6 mixtures with a productivity of 62.9 mmol g⁻¹ and 143.8 mmol g⁻¹, respectively. Neutron powder diffraction studies and DFT-D calculations revealed that C3H4 molecules can open the pores of UTSA-200 and form strong C-H···F interactions with the framework.

In 2022, Xing et al. reported a flexible MOF GeFSIX-14-Cu-i (ZU-33, GeFSIX = hexafluorogermanate, and 14 = 4,4'- azopyridine), which exhibits guest/temperature-dependent structural dynamics and shows strong binding affinity towards acetylene and propadiene. 188 ZU-33 featuring a 2-fold interpenetrated structure is composed of Cu(II)-4,4'-azobipyridne 2D layers and GeF₆²⁻ pillars, and its pore size (3.08–5.04 Å) was dynamically adjustable by the rotational motion of GeF₆²⁻ pillars and the organic ligands. Single-component gas adsorption experiments revealed that ZU-33 shows a steep uptake for alkynes (acetylene and propyne) and propadiene at low pressure (0.01 bar) and 303 K, while there is a threshold pressure for olefin adsorption and a size exclusion effect for alkanes. In addition, for C2H4 that is smaller than propyne and propadiene regarding the kinetic diameters, ZU-33 nearly inhibits C₂H₄ molecules to diffuse into its pores, suggesting the inverse size sieving below 0.5 bar at 303 K. Molecular simulations and single-crystal X-ray diffraction revealed that the interactions between the alkyne molecules (propyne and propadiene) and ZU-33 are more intense, thus requiring less input energy to overcome the energy barrier for the structural deformation. Breakthrough tests on a ZU-33 packed column verified that acetylene and propadiene can be directly removed from simulated cracking gases.

2.7. C₄ hydrocarbon separation

C₄ olefins including 1,3-butadiene (1,3-C₄H₆), 1-butene (n- C_4H_8) and isobutene (i- C_4H_8) are important raw materials for the production of synthetic rubbers and chemicals. However, C₄ olefin separation represents one of the great challenges in hydrocarbon purification owing to the similar structures and physical properties. 190,191

Xing et al. reported several interpenetrated anion-pillared ultra-microporous MOFs, such as GeFSIX-2-Cu-i (ZU-32), NbFSIX-2-Cu-i (ZU-52) and GeFSIX-14-Cu-i (ZU-33), and realized highly efficient separation of C4 olefins through molecular recognition. 192 This series of materials show ultrafine-tuning of the pore size/shape (4.20-4.83 Å) by replacing pillared inorganic anions with different bulks and different lengths of organic ligands. Among them, NbFSIX-2-Cu-i with a pore aperture size of 4.31 Å (F···F distance) exhibits high C_4H_6 (2.64 mmol g^{-1}) and n- C_4H_8 (2.26 mmol g^{-1}) uptake but negligible i-C₄H₈ uptake (0.48 mmol g⁻¹), showing uptake selectivities of about 5.00 and 5.74 for n-C₄H₈/i-C₄H₈ and C₄H₆/i-C₄H₈, respectively. In contrast, GeFSIX-14-Cu-i shows a smaller pore size of 4.20 Å (F \cdots F distance), resulting in negligible adsorption of n-C₄H₈ (0.57 mmol g⁻¹) and i-C₄H₈ $(0.42 \text{ mmol g}^{-1})$, but still retaining large uptake for C_4H_6 (2.67 mmol g^{-1}), accompanying a gate-opening adsorption behavior for C₄H₆. Breakthrough experiments demonstrated that these materials can efficiently separate C₄H₆ from C₄H₆/ n-C₄H₈/i-C₄H₈/He (50/15/30/5) mixtures, as well as efficiently separate C_4H_6/n - C_4H_8 (50/50) and n- C_4H_8/i - C_4H_8 (50/50) mixtures.

Because of its high degree of unsaturation and strong coordination ability, 1,3-C₄H₆ is commonly adsorbed preferentially over other C₄ hydrocarbons by MOFs with functional sites. It is thus energy-intensive and might induce undesired polymerization as the purification involves capture of 1,3-C₄H₆ and

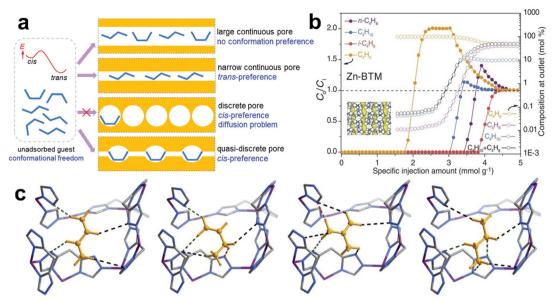


Fig. 20 (a) Schematic diagrams of controlling the guest conformation through the guasi-discrete pore in MAF-23. (b) Breakthrough curves of MAF-23 for a 5:2:2:1 C_4H_6/n - C_4H_8/i - C_4H_8/i - C_4H_8/i mixture. (c) Crystal structures of host—guest complexes of C_4H_6 , n- C_4H_8 , i- C_4H_8 , and C_4H_{10} . Reprinted with permission from ref. 193. Copyright 2017 the American Association for the Advancement of Science.

its subsequent release through heating in general. Zhang et al. noticed that the collaborative interactions between the host framework and guest flexibility can significantly change the conformation of certain C4 hydrocarbons and thus exhibit abnormal adsorption and reversed selectivity (Fig. 20). 193 In particular, a hydrophilic pore of a MAF with free N atoms, namely, [Zn₂(btm)]₂ (MAF-23), with 1D quasi-discrete pores (aperture size 3.6 Å, and cage size ca. 6 Å) was employed for separation of four hydrocarbons, n-C₄H₈, i-C₄H₈, C₄H₁₀ and 1,3-C₄H₆. As revealed by experimental and DFT calculations, n-C₄H₈, the most similar one to 1,3-C₄H₆ among these gas molecules, adopts a metastable cis conformation to form stronger non-classical C-H···N interactions, and hence has a significantly stronger binding affinity, whereas 1,3-C₄H₆ adopts the stable trans conformation and has the weakest binding affinity because of the unfitting configuration for forming stronger non-classical hydrogen-bonding interactions. In other words, MAF-23 with a unique pore structure and surface serves as a guest conformationcontrolling adsorbent to achieve preferential adsorption of n-C₄H₈, i-C₄H₈ and C₄H₁₀ over 1,3-C₄H₆. Therefore, 1,3-C₄H₆ can be first eluted during the breakthrough operation under ambient conditions, and directly purified for the desired purity (\geq 99.5%) to meet the industrial requirement in one single separation operation.

The separation of C₄ geometric isomers is also a challenging separation process, among which the separation of trans/cis-2butene is of prime importance to increase the value of C4 olefins. Ren et al. reported that M-gallate (M = Ni, Mg, and Co), featuring oval-shaped pores, are ideally suitable for shapeselective separation of trans/cis-2-butene through their difference in the minimum molecular cross-section sizes, in addition to a highly efficient separation of 1,3-butadiene, 1-butene, and i-butene. 194 Mg-gallate displays a narrow pore window size of $3.6 \times 4.6 \text{ Å}^2$, capturing the smaller trans-2-butene ($3.5 \times 4.6 \text{ Å}^2$) while excluding the slightly larger cis-2-butene (3.6 \times 4.9 Å²), affording a high trans/cis-2-butene uptake selectivity of 3.19 at 298 K and 1.0 bar in single-component adsorption isotherms. DFT-D study showed that Mg-gallate interacts with trans-2butene and 1,3-butadiene through short distances of intermolecular C···H-O interactions (C···H distances 2.57-2.83 and 2.45-2.79 Å, respectively).

The separation of isomeric C_4 paraffins is also an important task in the petrochemical industry. Zhong et al. regulated the pore aperture of the cage-like Zn-bzc by stepwise installation of methyl groups on its narrow aperture to achieve both molecularsieving separation and a high n-C₄H₁₀ uptake. The resulting Zn-bzc-2CH3 is not only a new benchmark adsorbent featuring molecular sieving for n-C₄H₁₀/iso-C₄H₁₀ separation and a high n-C₄H₁₀ adsorption capacity (2.42 mmol g⁻¹), but also hydrophobic to eliminate the negative effect of water vapor on gas separation under humid conditions. Breakthrough tests proved that high-purity i-C₄H₁₀ (99.99%) can be collected. The minimum energy path of n-C₄H₁₀ and i-C₄H₁₀ from cage to cage passing through the narrow aperture was determined for $Zn-bzc-nCH_3$ (n = 0, 1, 2), and the results suggested easy transports of both n-C₄H₁₀ and i-C₄H₁₀ for the larger apertures of the parent Zn-bzc MOF and Zn-bzc-CH₃ due to the low energy barrier together with a small barrier difference, while kinetic forbiddance with a dramatical increase of the diffusion energy barrier from 23.8 to 131.6 kJ mol⁻¹ for *n*-C₄H₁₀ to migrate through Zn-bzc-2CH₃.

2.8. Linear/branched alkane separation

The branched C₅-C₆ paraffins are major components in highoctane gasoline, which have relatively higher Research Octane Number (RON) values than their normal counterparts. To boost octane ratings in gasoline, the separation of linear alkanes

from their branched isomers is very important in the petroleum industry, which is traditionally done by energy-intensive distillation processes.

Eddaoudi et al. reported two new 12-connected rare-earth metal (Y³⁺ and Tb³⁺) fumarate based fcu-MOFs with both octahedral and tetrahedral cages that were solely interconnected with triangular windows of aperture size ca. 4.7 Å, and discovered that both of them can act as a adsorbate-size cut-off for the total sieving of C₄ and C₅ branched paraffins. 196

In addition, Li et al. prepared two Zr-MOF compounds, Zr-bptc and Zr-abtc, which are highly stable with optimal pore structures for the separation of C₆ alkane isomers (Fig. 21). 197 For instance, Zr-abtc featuring an scu-type structure with 1D channels (d = 7 Å) accommodates all C₆ alkane isomers (n-hexane, 3-methylpentane and 2,3-dimethylbutane), but favors *n*-hexane because of its stronger interactions with the pore surface, resulting in a mono/ dibranched separation factor (\sim 1.3) in the breakthrough test.

In 2020, Li et al. reported a new flexible MOF, calcium chloranilate (HIAM-203), which specially possesses chlorodecorated 1D channels. 198 HIAM-203 exhibits structural flexibility upon adsorption of C₆ alkanes with different branching, as well as similar temperature-dependent adsorption behavior toward alkane isomers. It can take up a plentiful amount of n-hexane and 3-methylpentane at 30 °C, but completely excludes 2,2-dimethylbutane, while at 150 °C 3-methylpentane is also excluded. This phenomenon may be rationalized by the significant difference in

binding affinity near the pore aperture of HIAM-203. As the pore size of HIAM-203 (5.6 Å) is between the kinetic diameters of 3methylpentane (5.5 Å) and 2,2-dimethylbutane (6.2 Å), it thus inhibits the diffusion of 2,2-dimethylbutane.

In 2023, Bao et al. employed the Hofmann-type MOFs, $[M(pz)Ni(CN)_4]$ (M = Co and Ni) to demonstrate similar temperature-swing molecular exclusion for separation of hexane isomers. 199 CopzNi displays excellent separation efficiency for linear/mono-branched and mono-branched/di-branched alkanes with the highest adsorption capacity to date. CopzNi exhibits lower-energy regeneration, scalability, recyclability and high stability, representing a promising candidate for relevant separation processes.

There are also needs for purification of valuable C₅-C₇ olefins. Isoprene, which accounts for 15-25% of C₅ fractions including important olefins like 1-pentene and trans-2-pentene, is widely used in the production of synthetic rubber, pharmaceutical and pesticide intermediates.²⁰⁰ The regeneration and desorption efficiency should also be taken into account for separation.²⁰¹ Cui et al. found that anion-pillared hybrid porous materials, namely, ZU-62 (also termed NbOFFIVE-2-Cu-i) and TIFSIX-2-Cu-i, exhibit a good separation performance for C5 olefin mixtures (trans-2-pentene, 1-pentene and isoprene).202 Owing to a contraction of pore aperture originating from the rotation of 4,4'-dipyridylacetylene ligand, ZU-62 excludes the relatively large molecule of isoprene in the low pressure range (0-6 kPa), while

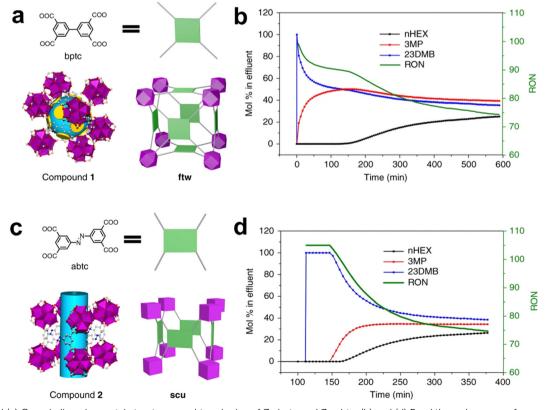


Fig. 21 (a) and (c) Organic ligands, crystal structures, and topologies of Zr-bptc and Zr-abtc. (b) and (d) Breakthrough curves of an equimolar ternary mixture of C₆ alkane isomers at 150 °C for Zr-bptc (top) and Zr-abtc (bottom). The green curve represents the real-time RON of the eluted products. Reprinted with permission from ref. 197. Copyright 2018 Nature Publishing Group.

TIFSIX-2-Cu-i is able to distinguish the three C5 olefins with a high uptake of trans-2-pentene (3.1 mmol·g⁻¹), superior to that of zeolite 5A (2.0 mmol·g⁻¹). DFT-D calculations confirmed that the selective adsorption was achieved by a favorable electrostatic environment as well as suitable pore confinement. Also, the regeneration tests showed that C₅ olefins can be easily desorbed from ZU-62 and TIFSIX-2-Cu-i at 298 K.

2.9. Aromatic isomer separation

The separation of C₈ aromatic compounds (xylene isomers, ethylbenzene and styrene) is also one of the important separations.¹ Tremendous efforts have been devoted to developing MOF adsorbents for relevant separations. Most of these adsorbents contain aromatic organic ligands, in which the phenyl or heterocycle rings allow strong π - π stacking interactions with C_8 aromatic molecules to facilitate the adsorption. 203,204

MOFs featuring structural flexibility like breathing or gate-opening have been applied for separation of aromatic isomers. 18,37,205 Li et al. reported that a stacked 1D manganesebased MOF $[Mn(dhbq)(H_2O)_2]$ $[Mn-dhbq, H_2dhbq = 2,5-dihydroxy-$ 1,4-benzoquinone) exhibits temperature-dependent discriminative adsorption of xylene isomers owing to reversible framework swelling.²⁰⁶ At 363 K, pX can be fully intercepted from the pX/mX/oX ternary mixture by a column of Mn-dhbq, whereas the effluent of the mX/oX mixture can be further separated by another column of Mn-dhbq at a lower temperature (303 K) where mainly oX finally flows out. The purity of pX is over 97% collected during the desorption cycle when using 1,4-diethylbenzene as an eluent at 433 K for 1 hour after liquid-phase adsorption of a quaternary mixture (pX/mX/oX/EB, 22/22/50/6) at 393 K. DFT calculations indicated that the temperature-dependent flexibility between 1D coordination chains (different degrees of swelling at different temperatures) endows such selective adsorption of xylene isomers through π - π stacking interactions with the aromatic ligand.

Xing et al. reported a flexible anion pillared MOF [Ni(bpy)₂(NbOF₅)] (ZU-61) with **pcu** topology and a pore size of 7.8 Å exhibiting efficient separation performance for xylene isomer.²⁰⁷ Single-component adsorption revealed that ZU-61 shows a higher low-pressure uptake for mX and oX than pX at

0.01 bar and 333 K, as well as a high capacity for mX (3.4 mmol g^{-1}) and oX (3.2 mmol g^{-1}). Breakthrough experiments for a 1:1:1 pX/mX/oX mixture confirmed that high purity (>99.9%) pX can elute from the column first, and then followed by mX and oX. The excellent performance for xylene isomer separation can be attributed to the rotational NbOF₅²⁻ anions, which allows adaptive hostguest interaction (C-H···F interactions) depending on the shape of the xylene isomer, as confirmed by DFT calculations and crystallographic studies. These results showed that ZU-61 exhibits great potential for the purification of pX.

Given that all xylene isomers contain phenyl rings for π - π stacking interactions, another approach to enhance the separation selectivity would be utilizing the difference of their alkyl groups while inhibiting the interactions with phenyl rings. Yang et al. constructed a pillar-layered MOF Cu(bpdc)(ted)_{0.5} (ZUL-C3) by using poly-cycloalkane-type ligands to show a nonaromatic pore environment for xylene separation.²⁰⁸ The pore space of the MOF magnifies the difference of host-guest interactions with xylene isomers and ethylbenzene owing to their different distribution of methyl (ethyl) groups. Liquidphase batch experiment indicated that this MOF can separate xylene isomers and ethylbenzene from each other, showing separation potential for oX/pX and oX/mX separation.

A flexible MOF, $[Cu_2(fbdim)] \cdot p$ -xylene (MAF-41·pX), showing a 3D hinged-fence-like framework and 1D channels (4.2 \times 9.8 \times 10.1 Å³ cavities and 3.9 \times 6.7 Å² apertures), was demonstrated by Zhang et al. to exhibit unprecedented inversed molecular sieving (so called intermediate-sized molecular sieving) for the purification of styrene (Fig. 22).²⁰⁹ The framework structure can transform to a nonporous one upon removal of template molecules. The activated MAF-41 can adsorb styrene (ST) to restore the as-synthesized structure while totally excluding ethylbenzene (EB), toluene (Tol), and benzene (Bz). Styrene with a purity of 99.9%+ can be obtained from the multicomponent mixture after one single adsorption-desorption cycle because the pores are individually opened and simultaneously occupied by the target guest. The aperiodic pore opening is believed to avoid co-adsorption of guest molecules smaller than the opened pores. Kinetic sorption studies revealed that the EB/Tol/Bz

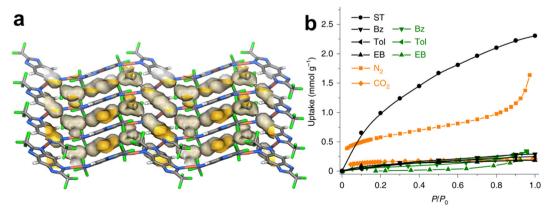


Fig. 22 (a) Crystal structure of guest-free MAF-41. (b) Adsorption isotherms of activated MAF-41 for ST (styrene, 298 K), EB (ethylbenzene, 298 K), Tol (toluene, 298 K), Bz (benzene, 298 K), N2 (77 K), and CO2 (195 K). Reprinted with permission from ref. 209. Copyright 2019 Nature Publishing Group.

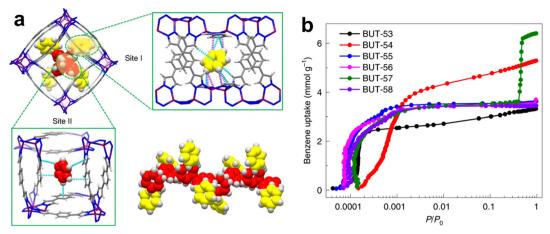


Fig. 23 (a) Structures of C_6H_6 @BUT-55 and benzene-benzene interactions. (b) Logarithmic-scale plots of P/P_0 to view the benzene adsorption of BUT-53 to BUT-58 at low partial pressure. Reprinted with permission from ref. 210. Copyright 2022 Nature Publishing Group.

adsorptions stayed quite low all the time, while the ST uptake of MAF-41 significantly increased for both the single-component and mixtures, which confirms no EB/Tol/Bz co-adsorption or replacement of ST in MAF-41. Although Cu(I) complexes and Cu(1)-based MOFs may have poor stability in air and/or water, guest-free MAF-41 did not collapse not only at temperatures up to 500 °C, but also in boiling water for at least one week, and even remained stable in a solution of pH 3-14 at room temperature for at least 3 days.

In 2022, Li et al. reported a family of double-walled metaldipyrazolate frameworks (BUT-53 to -58) composed of divalent metal ions and dipyrazolate ligands with different symmetries, lengths, and functionalities for trace benzene removal (Fig. 23).²¹⁰ In this study, multiple merits, e.g., high stability, tunable pore, high adsorption capacity and selectivity, were integrated into these hydrophobic MOFs, which all exhibited high benzene uptakes (2.47–3.28 mmol g⁻¹) at room temperature and ultra-low pressures (<10 Pa). BUT-55 is the bestperforming adsorbent for the capture of trace benzene among them. It shows an extremely long breakthrough time of $\sim 8000 \text{ h g}^{-1}$ for a benzene-containing (10 ppm, 10 mL min⁻¹) gas mixture under both dry and humid (relative humidity = 50%) conditions. When the

relative humidity was 80%, the breakthrough time decreased to $\sim 6000 \text{ h g}^{-1}$, which is still much higher than that of other previously reported materials. After adsorption of benzene, BUT-55 can be regenerated under mild heating. As revealed by both the single-crystal structure of benzene-loaded BUT-55 and DFT calculations, multiple non-classical hydrogen-bonding $C-H\cdots X$ (X = N, O, π) interactions are the key to its strong affinity and high sensitivity toward benzene. The high benzene binding energy of BUT-55 contributes to its high adsorption selectivity of benzene over water or other volatile organic compounds (VOCs), such as cyclohexane and ethanol. It should also be pointed out that the BUT-55 sample is able to work continuously around one year under the breakthrough experiment conditions. In other words, a certain amount of BUT-55 can be used to capture trace airborne benzene for a long time due to its high benzene adsorption capacity under ultra-low pressures and high adsorption selectivity. The performance of these MOFs demonstrates high potential in the removal of benzene from ambient air.

Very recently, Mo et al. reported a flexible MOF, [Sr₂(BIN- $DI(H_2O)_2$ (WYU-62, $H_4BINDI = N,N'-bis(5-isophthalic acid)$ naphthalenediimide) with electron-deficient NDI cores, which shows fast adsorption of trace benzene vapor at low pressure,

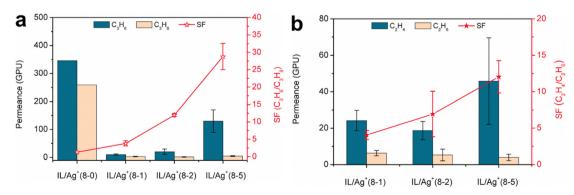


Fig. 24 (a) C_3H_6/C_3H_8 separation performance of $Zn_2(bim)_4$ membranes modified by diversified composites, $IL/Ag^+(8-0)$, $IL/Ag^+(8-2)$ and $IL/Ag^{+}(8-5)$. (b) C_2H_4/C_2H_6 separation performance of Zn_2 (bim)₄ membranes modified by diversified composites, $IL/Ag^{+}(8-1)$, $IL/Ag^{+}(8-2)$ and $IL/Ag^{+}(8-1)$ 5). Reprinted with permission from ref. 217. Copyright 2021 Elsevier.

accompanying a fluorescence-enhanced sensing (limit of detection = $0.133 \text{ mg} \,\mathrm{L}^{-1}$). 211 WYU-62 could be easily obtained by immersing the as-synthesized MOF [Sr₂(BINDI)(DMF)(H₂O)] (MYU-61) in water, during which discrete 0D pores of MYU-61 have transformed to 1D channels (aperture size = $5.1 \times 9.1 \text{ Å}^2$). Aromatic hydrocarbon vapor adsorption isotherms revealed that WYU-62a can show high benzene uptake at very low pressure ($P/P_0 < 0.01$). DFT calculations and crystallographic studies indicated that electron-rich benzene was tightly wrapped between the two electron-deficient NDI moieties with strong π - π and C-H··· π interactions. Therefore, it has excellent benzene adsorption capacity, whereas the accompanying host-guest charge transfer enables visual detection of trace benzene vapor.

3. MOF-based membranes for separating gaseous hydrocarbons

Though a variety of MOFs have been extensively studied for light-hydrocarbon purification in recent two decades, only a few have been fabricated into MOF-based mixed matrix membranes (MMMs), which may integrate the advantages of the separation performance of MOFs and processability of polymers for olefin/ paraffin separation.²¹² For example, MAF-4 (or ZIF-8) and Zr-fum-fcu-MOF (or MOF-801) have been incorporated with membranes for C_3H_6/C_3H_8 separation. ^{213,214}

Modification of MOF membranes with the composite ionic liquid/Ag⁺ (IL/Ag⁺) can efficiently improve their olefin/paraffin separation properties. Yang et al. synthesized layered Zn₂(bim)₄ membranes²¹⁵ using the in situ interfacial assembly (ISIA)²¹⁶ method and further modified them with varied IL/Ag+ composites.²¹⁷ Adsorption isotherms for Zn₂(bim)₄ powder and its IL/Ag+ modified sample showed that the adsorption capacity for olefin can significantly improve after modification with IL/Ag⁺ but the adsorption for paraffin shows negligible changes, which is attributed to the strong π -complexation of olefins with Ag+. Further study revealed that the pristine Zn₂(bim)₄ membrane showed a C₃H₆/C₃H₈ separation factor of 1.14 with a C_3H_6 permeance of 106 GPU ($SF_{C_3H_4}/C_{C_3H_4}$: 1.42, and P_{C,H₄}: 311) (Fig. 24). In contrast, the modified membranes exhibited a significant improvement in olefin/paraffin separation with the optimized C_3H_6/C_3H_8 separation factor of 28.8 \pm 3.8 with the C_3H_6 permeance of 129.8 \pm 40.4 GPU ($SF_{C_2H_4}/C_{2H_6}$: 12.0 \pm 2.2, and P_{C,H_a} : 45.6 \pm 23.7 GPU). The preferential binding affinity of Ag⁺ in IL for olefins facilitates the delivery of olefins in the modified Zn₂(bim)₄ membranes. On the other hand, Ag⁺ filling in the space of laminated modified Zn₂(bim)₄ membranes further blocks paraffin penetration and thus improves the olefin/paraffin selectivity. In addition to the composite modification membrane strategy, intrinsic structural regulation of MOF membranes is also crucial. Recently, a series of Zn₂(bim)₄ membranes functionalized with different amounts of amino groups, namely, $Nx-Zn_2(bim)_4(x represents the molar$ ratio of raw 5-aminobenzimidazole, bim) were also investigated for separation.²¹⁸ Among them, the N10-Zn₂(bim)₄ membrane exhibits the highest H₂/CO₂ separation performance with a

separation factor of 1158 and a H₂ permeance of 1417 GPU. Moreover, its ideal selectivities for H₂/CO₂, H₂/CH₄ and H₂/C₃H₈ were 829, 99, and 33, respectively, showing a distinct size exclusion effect for relatively large molecules.

Long et al. fabricated a series of membranes with M₂(dobdc) (M = Co, Ni, Mg, and Mn) as fillers and 6FDA-DAM as the primary polymer by reducing the filler size to the sub-100 nm level to specially improve the filler-polymer compatibility and dispersion.²¹⁹ Among them, Ni₂(dobdc) showed the best C₂H₄/ C₂H₆ separation performance without reduction in selectivity even under high-pressure owing to the presence of strong and multiple nanocrystal-polymer interactions, which suppresses plasticization by reducing polymer chain mobility.

Polycrystalline MOF membranes are less explored but also important. Liu et al. 220 have recently prepared a polycrystalline Co-gallate membrane with a reported freezing contra-diffusion protocol²²¹ that can enable more accurate control over the reaction kinetics between metal ions and ligands to effectively tune the MOF nucleation and growth in the bulk solution. Maintaining the frozen state of the metal precursor inside the macroporous α-Al₂O₃ substrate resulted in the formation of the preferred c-oriented and well-intergrown Co-gallate membrane with not only abundant open metal sites (at the increased missing-linker defects), but also reduced the thickness of the membrane. The multiscale structure endows the Co-gallate membrane with an outstanding C₂H₄/C₂H₆ separation performance superior to those of state-of-the-art membranes including polycrystalline MOF membranes, MOF-based MMMs, and polymeric membranes. The optimized C₂H₄/C₂H₆ selectivity is 8.3 with a C₂H₆ permeance of 72.6 GPU. The resultant membrane also shows a negative correlation with the operation temperature and high long-term stability.

4. Conclusion and outlook

MOF materials have made significant progress in the separation of gaseous hydrocarbons in the past few years, which was achieved by rational control over their pore chemistry/size, affording an alternative separation technology for relevant applications. The high crystallinity of MOFs facilitates systematic and deep investigation on the exact adsorbent-adsorbate interactions in the type of porous materials for high separation performance, as demonstrated by their crystallographic studies on the host-guest interactions. Controlling of the pore structure of MOF materials at high-accuracy level is applicable due to the high modularity and diverse functionality of MOFs, which facilitates highly efficient separation of methane, olefin/paraffin, alkyne/olefin, alkane isomers and aromatics. As outlined in this review, the collaborative control of the pore size and pore surface has been explored for the potential of MOFs for hydrocarbon separation. MOFs with high separation selectivities and large gas uptakes have been documented. The development of this realm has gradually turned to evaluate the potential of MOFs in practical separation processes, which required continuous research endeavors.

There are many important issues remaining unaddressed before further industrial and commercial usage of MOFs. Shaping/pelleting of MOFs would be the first step in actual processes given engineering considerations, but that would lead to loss of adsorption capacity; thus, further study on mechanical stabilities of MOFs might be necessary. Simultaneously, the diffusion kinetics of MOF pellets should be comprehensively investigated. There are also concerns on current research for evaluations of their separation performances through swing adsorption or membrane separation processes, as these evaluations mainly focus on evaluating candidate materials under simulated conditions rather than the actual applications. In relevant simulated evaluations, the presence of contaminants such as water has gradually got involved. In contrast, the actual gas streams would be more complicated, while the separation condition can be even harsher (under elevated pressures/temperatures), which require the adsorbents to show good stability and durability, including good water resistance and impurity tolerance. The long-term durability and regeneration of MOFs during separation processes have been rarely involved in current research. Moreover, systematic evaluation of materials production, including capital and operating costs, should be performed prior to large-scale deployments of MOF-based adsorptive separation technology. Solvent-free and continuous synthesis methods have been demonstrated to be applicable for MOFs, which show great potential for large-scale production of MOF materials. In addition, new technical issues such as thermal management during the adsorption process would come out when sorption is scaled up. For membranebased separation, there are also several challenges although it is capable of direct production of pure gas and can be simply operated under mild conditions. Several mixed-matrix MOFbased membranes have been developed, which show large permeance differences for hydrocarbon separation. However, the processability, defect, compatibility, and scaling up in membrane fabrication as well as the permeability-selectivity trade-off are still quite challenging. In terms of membrane separation, molecular sieving of hydrocarbons is still highly desirable. As the structure numbers of MOFs keep growing, there are also emerging technologies like machine learning under artificial intelligence for the computational design and discovery of novel MOF materials, while automated chemistry for high-throughput screening is also possible by combination with robotics.

As promising adsorbent materials for hydrocarbon separation, MOFs with high separation performance can be synthesized by combination of rational control of their pore size and pore surface. Continuous collaborative efforts among scientists, engineers and industrial partners will promote the application of MOF adsorbents to scientifically and technologically important industrial hydrocarbon separation, which would reap great benefits for society.

Conflicts of interest

There are no conflicts to declare.

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