

Review

CO₂-Selective Capture from Light Hydrocarbon Mixtures by Metal-Organic Frameworks: A Review

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Abstract: CO₂ represents a typical impurity in light hydrocarbon feedstocks, which affects the quality of subsequent chemical products. Owing to their highly similar nature, industrial separation requires large amounts of energy. Adsorptive gas separation based on porous materials is considered an efficient alternative, as it can offer faster kinetics, higher selectivity, long-term stability and more energy-efficient regeneration. For the adsorption separation method, preferential CO₂ capture from gas mixtures in one step is more energy-efficient for direct purification than light hydrocarbons, saving about 40% energy by eliminating energy-intensive post-regeneration processes such as countercurrent vacuum blowdown. Therefore, CO₂-selective adsorbents are more sought-after than light hydrocarbon-selective adsorbents. Metal-organic frameworks (MOFs) have been demonstrated as outstanding physisorbents for CO₂ capture due to their configurable channels for CO₂ recognition, structural flexibility and large specific surface area. Many highly selective CO₂ adsorption behaviors of MOFs have been reportedly achieved by precise modulation of pore size, pore chemistry or structural flexibility. In this review, we discuss the emerging development of MOFs for CO₂-selective capture from different light hydrocarbon mixtures. The challenges of CO₂ recognition and the strategies employed to achieve CO₂ selectivity over light hydrocarbon mixtures by MOFs are summarized. In addition, the current challenges and prospects in the field of MOFs for CO₂ capture are discussed and elaborated.

Citation: Huang, H.; Wang, L.; Zhang, X.; Zhao, H.; Gu, Y. CO₂-Selective Capture from Light Hydrocarbon Mixtures by Metal-Organic Frameworks: A Review. *Clean Technol.* **2023**, *5*, 1–24. <https://doi.org/10.3390/cleantechnol5010001>

Academic Editor: Patricia Luis

Received: 18 October 2022

Revised: 12 December 2022

Accepted: 19 December 2022

Published: 20 December 2022



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Keywords: CO₂ capture; metal-organic frameworks; light hydrocarbons; adsorption; separation

1. Introduction

Carbon dioxide (CO₂) is a critical cause of global warming, which is a widespread public concern [1,2]. Global annual CO₂ emissions increased by approximately 130% between 1970 and 2020 and are expected to increase to 48–55 Gt/year by 2050 without intervention [3,4]. Therefore, carbon capture, utilization and storage have been considered key strategies by policymakers and oil companies, of which CO₂ capture is the core issue [5–7]. In the chemical industry, CO₂ is often formed as an impurity during the production of light hydrocarbons. For instance, natural gas or biogas (CH₄) usually contains 5–70% carbon dioxide, which needs to be reduced to less than 2% for pipeline transportation and 50 ppm for liquefied natural gas [8,9]. Acetylene (C₂H₂) is typically produced by partial combustion of CH₄ or hydrocarbon cracking, which generally results in several gaseous impurities such as CH₄ and CO₂ [10]. The presence of CO₂ in light hydrocarbons affects the quality of subsequent chemical products, and it is challenging to trap CO₂ from their mixture due to their highly similar physical properties (Table 1) [11]. Absorption with aqueous amine and cryogenic distillation are traditionally used for CO₂ capture and light hydrocarbon purification, but these methods suffer from large amounts of waste streams and high regeneration energy consumption [12–14]. Comparatively, adsorptive gas separation based on porous adsorbents in hydrocarbon purification is considered more

energy-efficient, as it can offer faster kinetics, higher selectivity and more energy-efficient regeneration [5,15–18]. The adsorption separation process is performed by introducing a gas mixture into a column filled with porous materials, adsorbing the strongly adsorbed components and obtaining the outlet weakly adsorbed components; the strongly adsorbed components are subsequently recovered in the desorption process. However, the desorption process involves energy-intensive steps such as countercurrent evacuation [19–21]. It is estimated to cost approximately 40% more energy to harvest high-purity products through the desorption process than to collect the weakly adsorbed gas product directly at the outlet [22,23]. Therefore, porous materials for CO₂-selective adsorption are more sought-after than hydrocarbon-selective materials, as hydrocarbons are the target products in practical applications. Direct CO₂ capture from light hydrocarbon mixtures is more energy-efficient and effective.

Table 1. Main physicochemical properties of CO₂ and common light hydrocarbons [24,25].

Property	CO ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
Kinetic diameter (Å)	3.30	3.76	3.30	4.16	4.44
Boiling point (K)	194.7	111.6	189.3	169.4	184.5
Polarizability ($\times 10^{-25}$ cm ³)	29.11	26.0	33.3–39.3	42.52	44.3–44.7
Quadrupole moment ($\times 10^{26}$ esu cm ²)	−4.30	0	7.50	1.5	0.65

The development of porous materials has explosively grown in the last few decades, the most promising of which are metal-organic frameworks (MOFs), also referred to as porous coordination polymers (PCPs). MOFs assembled from organic linkers and metal cluster based secondary building units (SBUs) generally possess high surface areas and easily controlled pore sizes and environments, with infinite possibilities. MOFs have been demonstrated as outstanding physisorbents for CO₂ capture due to their highly configurable channels for CO₂ molecular recognition (Figure 1) [24,26–32]. Therefore, a detailed update on the current status of MOFs with CO₂ selectivity for CO₂/light hydrocarbon separation is urgently needed and would provide insight into their future development. Through this review, we aim to discuss the advancement of MOFs for the selective capture of CO₂ from different light hydrocarbon mixtures (CO₂/CH₄, CO₂/C₂H₂, CO₂/C₂H₄, etc.) in one-step purification of light hydrocarbons. As a departure from other reviews, we focus on evaluating MOFs with CO₂ selectivity. Herein, we describe the challenges of CO₂-selective recognition and summarize the strategies adopted to achieve CO₂ selectivity. Furthermore, we discuss the current challenges and prospects in the field of MOFs for CO₂ capture.

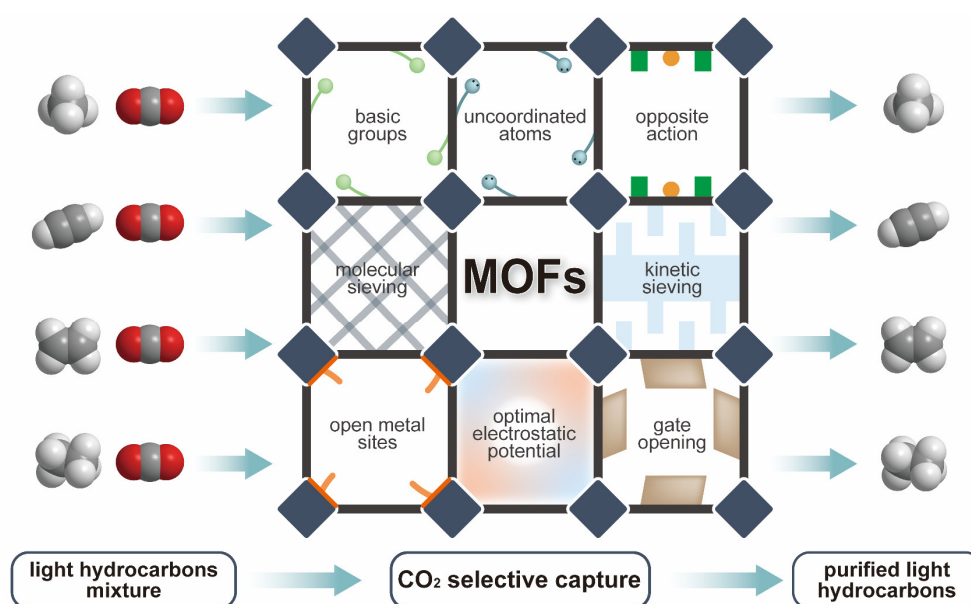


Figure 1. Schematic diagram of the process and typical strategies of CO₂-selective capture from light hydrocarbon mixtures by metal-organic frameworks.

2. CO₂-Selective Capture from CO₂/CH₄ Mixture

Natural gas, the main component of which is CH₄, is a clean energy source and a feedstock for bulk chemicals, for which the CO₂ concentration is required to be less than 2% for pipeline transportation and 50 ppm for liquefied natural gas [8,9]. Therefore, the separation of the CO₂/CH₄ mixture is an essential process for the industrial utilization of natural gas. However, CO₂ and CH₄ exhibit close polarizability (CH₄, $26.0 \times 10^{-25} \text{ cm}^3$; CO₂, $29.11 \times 10^{-25} \text{ cm}^3$) and kinetic diameters (CH₄, 3.76 Å; CO₂, 3.30 Å). By exploiting the slight differences in molecular size and polarizability, there are two solutions available using MOFs to trap CO₂ from CO₂/CH₄: (1) modulating the pore size/shape of MOFs for kinetic separation or molecular sieving and (2) constructing functional sites with enhanced CO₂ interactions, such as open metal sites (OMSs), quadrupole interaction sites, hydrogen bonding sites, Lewis basic sites, van der Waals interaction sites, etc. (Table 2).

Table 2. Representative MOFs for CO₂-selective capture from CO₂/CH₄ mixtures. *.

MOF	Functional Site	CO ₂ Capacity (mmol/g)	CO ₂ /CH ₄ Selectivity	Q _{st} for CO ₂ (kJ/mol)	Ref.
MOF-508b	quadrupole interactions	1.78 ^a	3–6 ^a	14.9	[33,34]
ZIF-78	Dipole–quadrupole interactions	2.32	10.6 ^b	—	[35]
Mg-MOF-74	open metal sites	8.61	8	73	[36]
MAF-66	uncoordinated N atoms	4.41	5.8	26	[37]
SIFSIX-1-Cu	SiF ₆ ²⁻	5.2	10.5	27	[38]
SIFSIX-2-Cu-i	SiF ₆ ²⁻	5.4	33	31.9	[39]
SIFSIX-3-Zn	SiF ₆ ²⁻	2.54	231	45	[39]
SYSU	narrow channels	3.11	4.7	28.2	[40]
NJU-Bai7	narrow channels	2.91	14.1 ^c	40.5	[40]
NJU-Bai8	uncoordinated N atoms	2.57	40.8 ^c	37.7	[40]

PEI-incorporated					
amine-MIL-101(Cr)	amine groups	3.6	931	— —	[41]
Qc-5-Cu-sql- β	molecular sieving	2.16 ^d	3300	36	[42]
SIFSIX-14-Cu-i	molecular sieving	4.71	46.7 ^e	37.7	[43]
NJU-Bai35	molecular sieving	3.125	11.6	33.37	[44]
dptz-CuTiF ₆	TiF ₆ ²⁻	4.52	— —	33.3	[28]
dptz-CuSiF ₆	SiF ₆ ²⁻	4.04	— —	38.2	[28]
TIFSIX-3-Ni	TiF ₆ ²⁻	2.213	158	50.0	[45]
NbOFFIVE-1-Ni	NbOF ₅ ²⁻	2.308	366	54.0	[45]
TIFSIX-2-Cu-i	TiF ₆ ²⁻	4.229	16	35.8	[45]
ZU-66	molecular sieving	4.56	136	35	[46]
IRH-3	uncoordinated N atoms	2.7	27	— —	[47]
In(aip) ₂	molecular sieving and —NH ₂ groups	1.27	1808	34.3	[48]
UTSA-280	molecular sieving	3.00	molecular sieving	42.9	[49]
UiO-66(N ₁₀ %-Zr)	uncoordinated N atoms and kinetic effect	2.1	326	35.7	[50]
MUF-16	N-H...O and C-H...O	2.13 ^d	6690 ^d	32.3	[51]
MUF-16 (Mn)	N-H...O and C-H...O	2.25 ^d	470 ^d	36.6	[51]
MUF-16 (Ni)	N-H...O and C-H...O	2.13 ^d	1220 ^d	37.3	[51]
Cu-F-pymo	molecular sieving	1.61 ^f	>10 ⁷	29.1	[52]
[Cu ₃ (μ ₃ -OH)(PCA) ₃]	open metal sites	2.93	15.9	31.5	[53]
[Zn(odip) _{0.5} (bpe) _{0.5}]	gate opening	5.3	376.0	42.3	[54]

* Unless otherwise specified, the capacity data were all recorded at 1 bar, 298 K; CO₂/CH₄ selectivity is the ideal adsorbed solution theory (IAST) selectivity for 50/50 (*v/v*) CO₂/CH₄ mixtures at 1 bar, 298 K; *Q_{st}* for CO₂ is the value at zero coverage; “— —” indicates that data were not found; ^a at 303 K; ^b Henry’s Law selectivity; ^c separation ratios at 273 K; ^d at 293 K; ^e calculated by the uptake ratio of CO₂/CH₄ at 1 bar; ^f calculated by (volumetric uptake)/(crystal density).

Bastin et al. presented the first example of the removal of CO₂ from a binary CO₂/CH₄ mixture by MOFs [33,34]. MOF-508 showed CO₂ uptake of 1.78 mmol/g and moderate selectivity in the range of 3–6 at 303 K, 1 bar. The very low adsorption enthalpy of 14.9 kJ/mol for CO₂ and 5.1 kJ/mol for CH₄ suggested that the CO₂ interaction with MOF-508 probably originated from quadrupole interaction and/or van der Waals interaction.

Due to the slight differences in molecular size between CO₂ and CH₄, some rigid MOF materials with molecular sieving effects achieved CO₂ capture from CO₂/CH₄ with high selectivity by reducing the aperture of MOFs so that only smaller CO₂ could diffuse into the pores, whereas larger CH₄ was completely excluded.

UTSA-280 is a typical rigid MOF with a molecular sieving effect [49,55]. The cross-sectional area of its 1D channel is approximately 14.4 Å², which is smaller than that of CH₄ (minimum: 15.1 Å²) but larger than that of CO₂ (minimum: 10.7 Å²). The CO₂ uptake capacity of UTSA-280 was 3.0 mmol/g at 1 atm, 298 K and the density of CO₂ in the pore channel was up to 733 g/L, which was comparable to the liquid CO₂ density of ~1.1 kg/L (236 K, 11.1 bar), indicating that the CO₂ molecules in UTSA-280 were tightly packed. However, the relatively high isosteric heat of adsorption (*Q_{st}*) of 42.9 kJ/mol was not favorable for material regeneration.

Another example of molecular sieving is Cu-F-pymo with dual functionality, exhibiting extremely high selectivity for CO₂ over CH₄ [52,56]. In Cu-F-pymo, Cu(II) atoms

are coordinated to four N atoms from four different ligands to form a 1D pore channel with a pore diameter of ~ 3.3 Å. The IAST selectivity was calculated to be ultra-high, at 10^7 for CO_2/CH_4 (v/v , 50/50) mixtures at 298 K and 1 bar. Grand canonical Monte Carlo (GCMC) simulation indicated that the binding affinity for CO_2 molecules was further enhanced by the pore channels functionalized with oxygen moieties through electrostatic and hydrogen bonding interactions. Furthermore, it could be easily synthesized in aqueous solution under ambient conditions. However, Cu-F-pymo showed a relatively low uptake capacity of 3.09 mmol/cm^3 (1.61 mmol/g) at 298 K and 1 bar due to the compact pore volume.

A higher CO_2 uptake achieved by molecular sieving adsorbent was achieved using SIFSIX-14-Cu-i [43]. SIFSIX-type MOFs are a typical kind of microporous MOF designed according to the isorecticular principle. These MOFs with 1D pores are composed of 2D metal-dipyridyl layers and SiF_6^{2-} -type anion pillars in pcu topology. The replacement of organic ligands with different molecule lengths and/or framework interpenetrations provides extensive adjustment of the pore diameter, and the presence of F atoms in the channel tends to provide high affinity for CO_2 [57]. The pore cavity of SIFSIX-14-Cu-i was embellished with a high density of SiF_6^{2-} anions and thus showed high CO_2 capacity (4.71 mmol/g) under ambient conditions.

Qc-5-Cu demonstrated a strategy of crystal engineering to tune pore size in MOFs (Figure 2) [42]. HQc (quinoline-5-carboxylic acid) and five kinds of metal ions were used to synthesize five different MOFs, Qc-5-M-dia (dia indicates a twofold and 3D diamondoid network) and Qc-5-Cu-sql- α (sql indicates a 2D square lattice network). Qc-5-Cu-sql- β was the desolvated phase of Qc-5-Cu-sql- α , with a contract cell volume of 1004.1 ± 0.1 to $908.0 \pm 0.1 \text{ Å}^3$ and a pore size of 3.8 to 3.3 Å. Such regulated channels of Qc-5-Cu-sql- β fit the kinetic diameter of CO_2 and could exclude methane molecules, leading to high selectivity (~ 3300) for CO_2 . Qc-5-Cu-sql- β also exhibited higher Q_{st} (36 kJ/mol) than its supramolecular isomer, Qc-5-Cu-dia (34 kJ/mol), and Qc-5-Ni-dia (32 kJ/mol). Molecular simulations of CO_2 adsorption revealed that the interaction sites were the H atoms in the Qc ligands, which could attract the negatively charged CO_2 oxygen atoms. In the modeled CO_2 -loaded structure, the distance between the O atoms and interaction sites was < 2.5 Å in Qc-5-Cu-sql- β but > 3.0 Å in Qc-5-Ni-dia, which explains the difference in their adsorption behavior and Q_{st} . However, the CO_2 capacity of the former was only 2.16 mmol/g at 293 K, 1 bar, which is negative for practical applications.

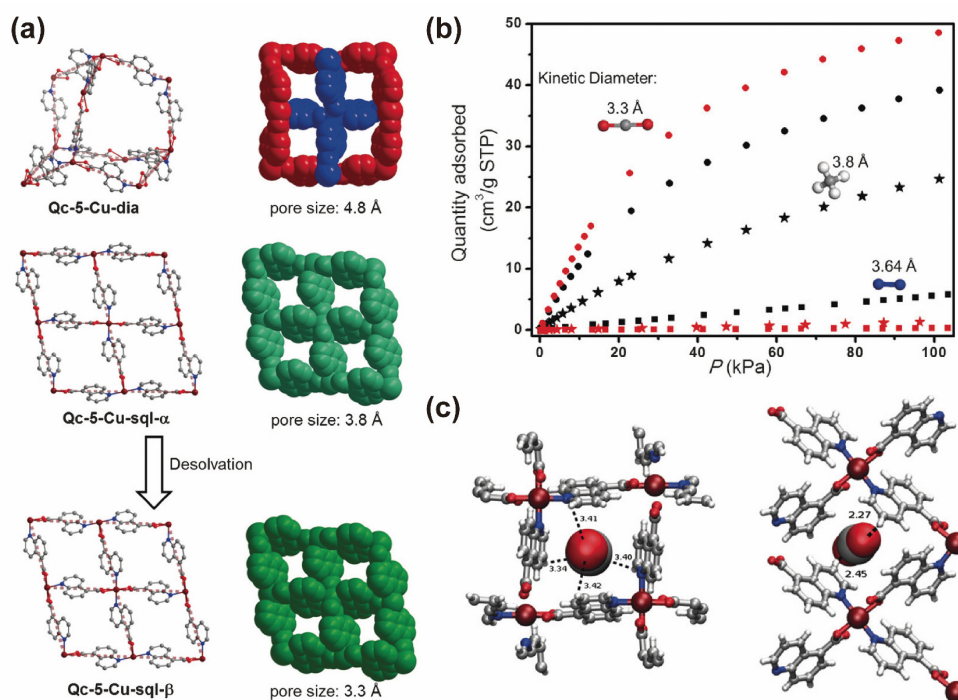


Figure 2. (a) Pore diameter tuning by supramolecular isomerism. (b) CO₂ (circle) and CH₄ (star) sorption isotherm for Qc-5-Cu-dia (black) and Qc-5-Cu-sql-β (red) at 293 K. (c) The binding sites in the CO₂-loaded Qc-5-Cu-dia (left) and Qc-5-Cu-sql-β (right). Color code: C (gray), H (white), Cu (brown), N (blue), O (red). Reproduced with permission from Chen et al., *Angewandte Chemie International Edition*; published by John Wiley and Sons, 2016 [42].

Jiang et al. found a new strategy to precisely tune the multinuclear clusters of MOFs via symmetry-upgrading isoreticular transformation and obtained MOFs with high CO₂ selectivity [44]. As a precursor, Cu(IN)₂ (termed FZU, IN = isonicotinic acid) with binuclear clusters was used for isoreticular transformation towards NJU-Bai34 and NJU-Bai35 with clusters of higher symmetry (Figure 3). The binuclear cluster of FZU offered certain structural flexibility, and the uncoordinated O atoms made it possible to incorporate additional metal ions and upgrade the symmetry of the inorganic clusters without changing connectivity. With an increase in the concentration of Cu²⁺ ions and the addition of water, acetonitrile and acetic acid, NJU-Bai34 was obtained from [Cu₄(μ₃-O)₂(COO)₄N₄O₂]. All Cu atoms in NJU-Bai34 were five-coordinated, and the remaining coordination sites were saturated by CH₃COO[−]. However, the coordination of CH₃COO[−] requires ((CH₃)₂NH₂)⁺ generated by DMF hydrolysis to neutralize the entire complex. Therefore, part of the pore channel is blocked by CH₃COO[−] and the counterions. To avoid this phenomenon, the reaction was conducted at 120 °C using DMF/H₂O as a solvent. The Cl atoms in copper chloride started to coordinate and shrunk the Cu clusters more than NJU-Bai34. After the symmetry of clusters was upgraded, the channels sizes of NJU-Bai35 were 3.6 × 3.6 Å² (along the *a* axis), 3.4 × 3.4 Å² (along the *b* axis) and 3.6 × 3.6 Å² (along the *c* axis) and perfectly fit the CO₂ molecules, which resulted in a higher CO₂ uptake capacity of 7.20 wt% than NJU-Bai34 and FZU at 298 K, 0.15 bar. Furthermore, NJU-Bai35 exhibited a high CO₂/CH₄ selectivity of 11.6 for an equimolar mixture at 298 K, 1 bar, mainly due to the molecular sieve effect, with a pore size of 3.6 × 3.6 Å². As a result, breakthrough curves further demonstrated that NJU-Bai35 has high potential for natural gas purification.

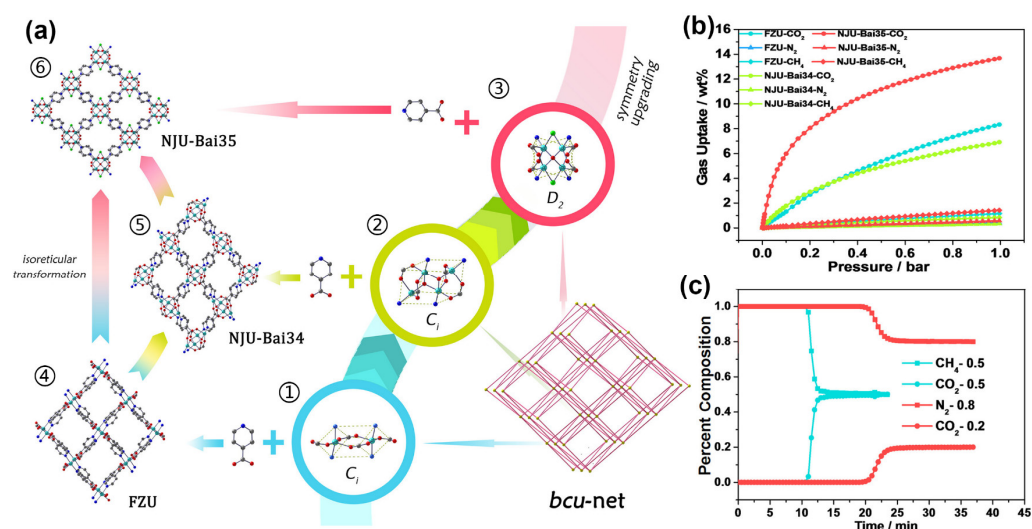


Figure 3. (a) Isoreticular transformation by symmetry-upgrading Cu clusters. Cu clusters and structures of FZU (1,4), NJU-Bai34 (2,5) and NJU-Bai35 (3,6). (b) CO₂ adsorption isotherms measured at 298 K. (c) Breakthrough curves of NJU-Bai35 at 298 K. Reproduced with permission from Jiang et al., Journal of the American Chemical Society; published by American Chemical Society, 2018 [44].

Despite the extremely high selectivity, the strategy of molecular sieving typically suffers from low capacity limited by the compact pore volume, which is not favorable for MOF applications. The discrepancy in polarizability and acidity inspired some researchers to construct functional sites such as OMSs and Lewis basic sites with enhanced CO₂ interactions.

The open magnesium sites in Mg-MOF-74 were discovered by Bao et al. with high affinity for CO₂ [36]. At 298 K and 1 atm, the uptake of CO₂ was as high as 8.61 mol/kg (37.8 wt.%), which is significantly higher than that of the general amine-treated adsorbents. Comparatively, the uptake of CH₄ was only 1.05 mol/kg (1.7 wt.%), and the Henry's Law selectivity for CO₂/CH₄ (50/50) was 8 at 298 K and 1 atm. Intense guest–framework interaction also induced an extremely high Q_{st} of 73 kJ/mol, which was not conducive to the regeneration of materials.

Amine functionalization is considered a feasible strategy to improve the CO₂ capture capacity of MOFs. PEI-incorporated amine-MIL-101(Cr) represented a polyethyleneimine-decorated MOF adsorbent [41]. After loading PEI, the structure of amine-MIL-101(Cr) was not degraded in scanning electron microscopy images; however, the pore size and polarity were affected as the PEI loading increased. Taking advantage of the porous characteristics of MIL-101(Cr) and Lewis basic –NH₂ groups, PEI-incorporated amine-MIL-101(Cr) showed a high CO₂ capacity of 3.6 mmol/g and an IAST selectivity of 931 for equimolar CO₂/CH₄ mixtures under 100 kPa, 298 K.

In(aip)₂ is a 2D stacked MOF composed of In clusters and 5-aminoisophthalic acid with abundant amine groups (–NH₂) in the channels, serving as hydrogen bonding sites and Bronsted basic sites to improve the interaction with CO₂ [48]. The Horvath–Kawazoe (HK) model determined the experimental average pore diameter of In(aip)₂ to be approximately 3.57 Å, which is between the molecular sizes of CH₄ and CO₂. A synergetic size-sieving effect and –NH₂ interaction sites resulted in an extremely high IAST selectivity of 1808 for CO₂/CH₄ (50/50, *v/v*) but limited uptake capacity of 1.27 mmol/g for CO₂ under ambient conditions.

Uncoordinated N donors as active sites could also enhance the CO₂ adsorption affinity and have been introduced into MOFs. Based on the MOF SYSU platform, two isoreticular MOFs, [Cu(L₂)·DMF] ∞ (NJU-Bai7) and [Cu(L₃)·DMF·H₂O] (NJU-Bai8), were created by altering the coordination sites of the ligands and adjusting the pore size while introducing uncoordinated nitrogen atoms to the inner surface (Figure 4) [40]. The

porosity and specific surface area of the three MOFs remained almost unchanged after channel narrowing and polarization. However, at low pressure (0.15 bar), NJU-Bai7 and NJU-Bai8 could adsorb 8.0 wt% and 5.4 wt% of CO₂ at 298 K, respectively—higher than the 3.6 wt% for SYSU. Both NJU-Bai7 and NJU-Bai8 showed much higher Q_{st} for CO₂ (40.5 and 37.7 kJ/mol, respectively) and separation ratios at 273 K (14.1 and 40.8, respectively) compared with the MOF SYSU platform, which may be attributed to the narrow channels, favoring the interaction with CO₂. In contrast, NJU-Bai8 showed stronger CO₂ recognition and higher CO₂/CH₄ selectivity than NJU-Bai7 because of unsaturated N atoms, which made it a better choice for trapping CO₂ from the CO₂/CH₄ mixture.

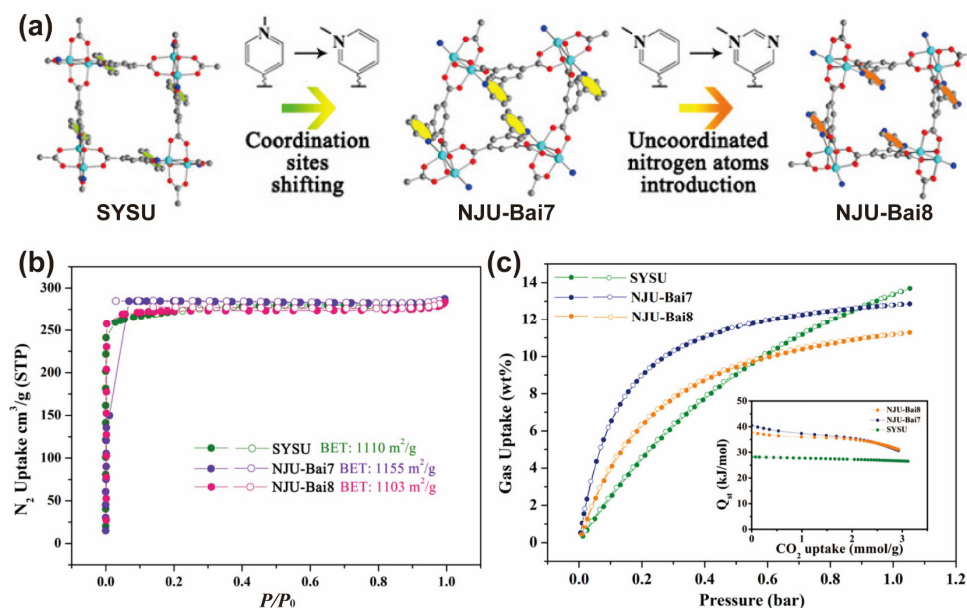


Figure 4. (a) Structure of SYSU (left), NJU-Bai7 (middle) and NJU-Bai8 (right). (b) N₂ sorption isotherms for SYSU, NJU-Bai7 and NJU-Bai8 at 77 K. (c) CO₂ sorption isotherms and CO₂ adsorption enthalpy (insert) for SYSU, NJU-Bai7 and NJU-Bai8 at 298 K. Reproduced with permission from Du et al., Journal of the American Chemical Society; published by American Chemical Society, 2013 [40].

IRHs(1–3) are three isorecticular lanthanide MOFs from cyamelurate linkers characterized by a large number of accessible N-donor sites [47]. Due to the abundant uncoordinated N on the hydrophilic pore walls, the interaction with CO₂ was enhanced, and CH₄ with nonpolar covalent bonds was excluded, facilitating the adsorption of CO₂ over CH₄. Through GCMC simulations, researchers found that no CH₄ was distributed around the metal center as a result of the existence of water molecules. The uptake of CO₂ and CH₄ in IRH-3 was 2.7 and 0.07 mmol/g, respectively, and the IAST selectivity for equimolar CO₂/CH₄ reached 27 at 298 K and 1 bar.

3-amino-1,2,4-triazole (Hatz) was used to produce a zeolite-like MOF, [Zn(atz)₂] (MAF-66), at room temperature with -NH₂ groups and uncoordinated triazolate nitrogen atoms in the channels [37]. MAF-66 exhibited a high CO₂ uptake capacity of 4.41 mol/kg, and the IAST selectivity for equimolar CO₂/CH₄ was 5.8 at 298 K and 1 bar. The Q_{st} of MAF-66 at zero coverage was 26.0 kJ/mol, which is significantly lower than those of PCPs based on OMSs. A low Q_{st} is beneficial to the adsorption–desorption cycle of the material.

UiO-66(N_{10%}-Zr) was designed through the in situ functionalization of node chemistry of UiO-66 with 2-aminobenzimidazole (2-AMI) by a novel microwave-assisted strategy [50]. The grafted 2-AMI on the nodes provided the N-containing five-membered heterocycle as an electron donor. Through electrostatic interactions, -NH₂ could act as a binding site for Lewis acidic CO₂ and produce a specific recognition effect. The stability

and hydrophobicity would also be enhanced because the benzene ring in 2-AMI modified the frameworks, making them inert. The node-engineered UiO-66(N_{10%}-Zr) showed excellent separation performance for CO₂/CH₄ through a synergetic equilibrium–kinetic effect. The CO₂ uptake was 2.1 mol/kg, and the IAST selectivity was up to 326 for a 50/50 CO₂/CH₄ mixture at 298 K, 1 atm—both higher than those of UiO-66. The Q_{st} of UiO-66(N_{10%}-Zr) was 35.7 kJ/mol, which is also higher than the Q_{st} of UiO-66 (22.0 kJ/mol), indicating that node-engineering contributed to the stronger affinity for CO₂.

The low-cost and water-stable SIFSIX-1-Cu [Cu(bpy)₂(SiF₆)] exhibited an extremely high capacity of 5.2 mmol/g for CO₂ at 298 K, 1 atm, and a high selectivity of 10.5 for an equimolar CO₂/CH₄ mixture [38]. Furthermore, the Q_{st} value for CO₂ was as low as 27 kJ/mol. SIFSIX-2-Cu and SIFSIX-2-Cu-i were both synthesized from the reaction of 4,4'-dipyridylacetylene (dpa) and CuSiF₆. SIFSIX-2-Cu-i was isostructural to SIFSIX-2-Cu but with double interpenetrated nets [39]. After interpenetrating, the pore size formed by SIFSIX-2-Cu-i was smaller than that of SIFSIX-2-Cu (13.05 Å), which was 5.15 Å. Similarly, SIFSIX-3-Zn was synthesized from the shorter pyrazine and thus resulted in smaller pore size of 3.84 Å (Figure 5). Owing to its optimal pore size, the electropositive carbon atoms of CO₂ molecules could closely interact with the fluorine atoms of SiF₆^{2−} and provided a benchmark IAST selectivity of 231 for a 50/50 CO₂/CH₄ mixture. This research demonstrates the successful control of pore size according to the isorecticular principle. Together with the favorable electrostatic interactions provided by the inorganic anion array, the SIFSIX series MOFs are capable of a synergetic equilibrium–kinetic effect, allowing for the separation of CO₂ mixtures, with the potential for high selectivity, recoverability and moisture stability.

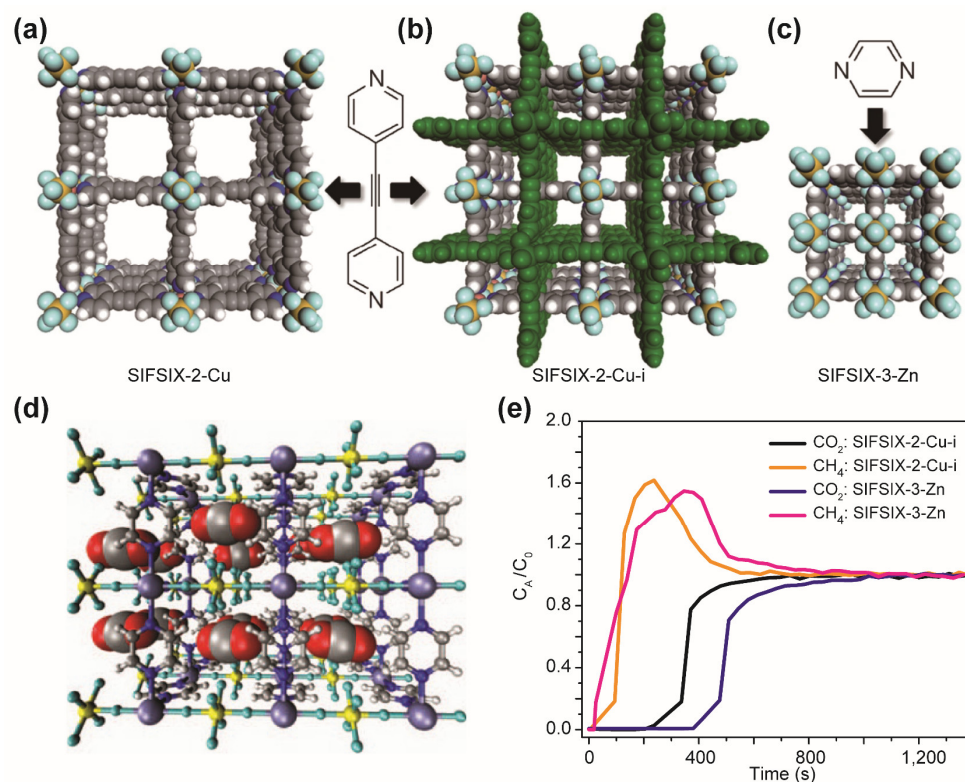


Figure 5. (a–c) Schematic diagram of the frameworks of SIFSIX-2-Cu (a), SIFSIX-2-Cu-i (b) and SIFSIX-3-Zn (c). Color code: Si (yellow), C (gray), F (light blue), N (blue), H (white). For clarity, the green structure indicates the interpenetrated network. (d) Structure diagram of interactions between the CO₂ molecules and SiF₆^{2−}. Color code: C (gray), F (green), N (blue), Si (yellow), O (red), H (white), Zn (purple). (e) Breakthrough curves for a CO₂/CH₄ (50/50) mixture for SIFSIX-2-Cu-i and SIFSIX-3-Zn at 298 K, 1 atm. Reproduced with permission from Nugent et al., Nature; published by Springer Nature, 2013 [39].

For the mixture system of CO₂ and CH₄, CO₂ has a smaller molecular size and is more acidic and can therefore be easily separated by the strategy of molecular sieving and construction of strong CO₂ binding sites. It should be noted that although ultra-high selectivity can be achieved using a molecular sieving mechanism, the narrowed pore channels often tend to result in low adsorption capacity. Therefore, future studies should investigate the construction of pore structures with large cavities connected by narrow pore channels, potentially maintaining a large adsorption capacity while sieving at a narrow entrance with high selectivity.

3. CO₂-Selective Capture from CO₂/C₂H₂ Mixture

C₂H₂ is an important fuel for the welding industry and an essential feedstock used to fabricate petrochemical products. Among the gas mixtures of acetylene, the separation of C₂H₂/CO₂ is the most important and challenging due to the ultra-high similarity of these compounds in molecular size, shape and boiling points (Table 1). Moreover, most of reported MOF materials interact more strongly with C₂H₂ than CO₂, as the hydrogens and π -electrons on C₂H₂ are highly polarizable and acidic and usually interact with acid–base interaction sites. Such C₂H₂ selectivity is called “normal selectivity” and suffers from two energy-intensive steps of adsorption and desorption to obtain pure C₂H₂ gas [58–66]. CO₂ capture from C₂H₂/CO₂ in one step is more energy-efficient for purification of C₂H₂, saving approximately 40% energy by eliminating other complex post-regeneration operations [22]. Therefore, ideal physisorbents should preferentially capture the trace CO₂ from the gas mixture rather than C₂H₂ (“inverse selectivity”) to further reduce the energy consumption of C₂H₂/CO₂ separation [25,67,68].

In the past few years, various benchmark MOFs have been demonstrated to exhibit “inverse selectivity” for CO₂/C₂H₂ separation, as shown in Table 3. Owing to their very close kinetic diameters, it is difficult to separate CO₂/C₂H₂ with the molecular sieve mechanism. Generally, the following strategies are utilized: (1) exploiting the structural flexibility or phase transition induced by different gas molecules, (2) optimizing pore chemistry through different electrostatic interactions or thermodynamic affinity and (3) constructing kinetic diffusivity differences through precise pore geometry.

Table 3. Representative MOFs for CO₂-selective capture from CO₂/C₂H₂ mixture. *.

MOF	Functional Site	CO ₂ Capacity (mmol/g)	CO ₂ /C ₂ H ₂ Selectivity	Q _{st} for CO ₂ (kJ/mol)	Ref.
Co(HL ^{dc})	gate opening	10.69 ^a	1.7 ^{a,b}	—	[69]
[Mn(bdc)(dpe)]	gate opening	2.17 ^c	8.8 ^c	29.5	[70]
SIFSIX-3-Ni	SiF ₆ ²⁻	2.7	7.69 ^d	50.9	[71]
CD-MOF-1	uncoordinated primary hydroxyl groups	2.87	6.6 ^d	41.0	[72]
CD-MOF-2	uncoordinated primary hydroxyl groups	2.65	16 ^d	67.2	[72]
[Tm ₂ (OH-bdc)] (1a)	OH groups	5.83	17.5 ^d	45.2	[73]
[Tm ₂ (OH-bdc)] (1a')	OH groups	6.21	1.65 ^d	32.7	[73]
PCP-NH ₂ -bdc	amino group	3.03	4.4	34.57	[74]
PCP-NH ₂ -ipa	amino group	3.21	6.4	36.6	[74]
Cd-NP	electrostatic potential	2.59	85	27.7	[75]
Ce ^{IV} -MIL-140-4F	electrostatic potential	2.24	9.5	39.5	[76]
Cu-F-pymo	electrostatic potential	1.19	10 ⁵	28.8	[77]
[Zn(atz)(BDC-Cl ₄) _{0.5}] _n	electrostatic potential	0.94 ^{f,g}	2.4 ^f	32.7	[78]
PMOF-1(irra)	electrostatic potential	2.38 ^c	694 ^c	—	[79]
MUF-16	electrostatic potential	2.13 ^e	510 ^e	32.3	[51]

MUF-16(Mn)	electrostatic potential	2.25 ^e	31 ^e	36.6	[51]
MUF-16(Ni)	electrostatic potential	2.13 ^e	46 ^e	37.3	[51]
en-MOF	amine groups	4.8	—	71.2	[80]
nmen-MOF	amine groups	4.55	—	62.3	[80]
een-MOF	amine groups	4.9	—	68.8	[80]
ZU-610a	kinetic sieving	1.51	207	27.3	[81]
SU-101(Bi)	carbonyl oxygen atoms	2.4	5.5	30.5	[82]
SU-101(Al)	carbonyl oxygen atoms	2.37	15.5	31.3	[82]
SU-101(In)	carbonyl oxygen atoms	2.46	6.2	28.3	[82]
SU-101(Ga)	carbonyl oxygen atoms	1.79	11.1	27.7	[82]
[Zn(odip) _{0.5} (bpe) _{0.5}]	Gate Opening	5.3	13.2	42.3	[54]

* Unless otherwise specified, the capacity data were all recorded at 1 bar, 298 K; CO₂/C₂H₂ selectivity is IAST selectivity for 50/50 (*v/v*) CO₂/C₂H₂ mixtures at 1 bar, 298 K; *Q_{st}* for CO₂ is the value at zero coverage; “—” indicates that data were not found; ^a at 195 K; ^b calculated by uptake ratio; ^c at 273 K; ^d selectivity for CO₂/C₂H₂ (1/2, *v/v*); ^e at 293 K; ^f at 285 K; ^g calculated by (volumetric uptake)/(crystal density).

It has been reported that some flexible MOFs can achieve efficient separation of highly challenging gas mixtures by mechanisms such as guest-induced “gate opening”. The structural flexibility and/or phase transition of flexible MOFs leads to an abrupt increment in uptake amount at a critical pressure, i.e., a “step” adsorption isotherm [83–87].

[Co(HL^{dc})] is a dynamic bifunctional MOF with inverse CO₂/C₂H₂ selectivity [69]. The framework flexibility of [Co(HL^{dc})] is provided by the dangling carboxylic groups and electron-donating nitrogen centers on the channel surface, showing gated adsorption for CO₂ instead of C₂H₂. At 195 K, symmetric CO₂ molecules with a permanent quadrupole moment can interact with the MOF frameworks and lead to the rotation of pyridyl rings, opening the “gate”. However, C₂H₂ could not trigger a similar “gate” rotation because the adsorption temperature (195 K) was higher than its boiling point (189 K), and therefore, more C₂H₂ uptake was required. The CO₂ uptake capacity was 10.69 mol/kg at 195 K, 1 bar, and the CO₂/C₂H₂ uptake ratio was 1.7.

Another flexible MOF with inverse CO₂/C₂H₂ selectivity is [Mn(bdc)(dpe)] [70]. Its small zero-dimensional pores showed gated adsorption for C₂H₂ instead of CO₂ due to their opposite quadrupole moments, resulting in different CH– π and π – π interactions. The adsorption isotherm of C₂H₂ showed a gated behavior at a gate-opening pressure (*P_{go}*) of 1.45 kPa at 195 K, whereas CO₂ did not. The CO₂ uptake amount was 2.17 mmol/g at 273 K, 100 kPa, and the IAST selectivity for CO₂/C₂H₂ (*v/v*, 50/50) gas mixture varied from 8.8 to 13, indicating the excellent potential for CO₂ capture from a CO₂/C₂H₂ mixture. In situ X-ray diffraction (XRD) and density functional theory (DFT) calculations illustrate that due to the opposite quadrupole moment, the electrostatic potential of the pore leads to repulsion with C₂H₂ in an end-on orientation, requiring more structural transformation energy to adapt to C₂H₂ with a side-on orientation (Figure 6).

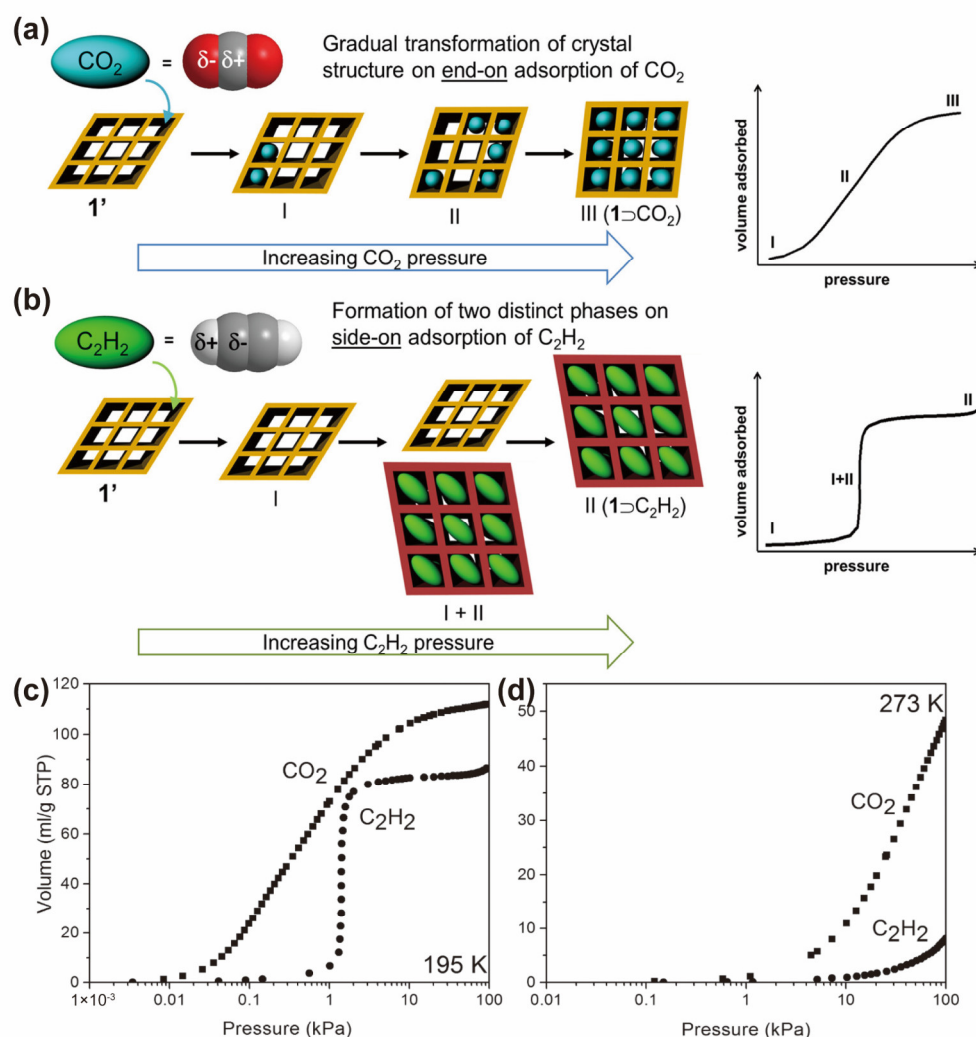


Figure 6. (a,b) Potential adsorption mechanism of [Mn(bdc)(dpe)] for CO₂ (a) and C₂H₂ (b) at 195 K. (c,d) Adsorption isotherms of [Mn(bdc)(dpe)] for CO₂ and C₂H₂ at 195 (c) and 273 K (d). Reproduced with permission from Foo et al., Journal of the American Chemical Society; published by American Chemical Society, 2016 [70].

The opposite quadrupole moments of CO₂ (-13.4×10^{-40} C m²) and C₂H₂ ($+20.5 \times 10^{-40}$ C m²) have enlightened researchers to adjust the pore environment with inverse electrostatic potential (ESP) or precise steric arrangement of interaction sites on the pore surface, which is more favorable for CO₂ adsorption and leads to inverse CO₂/C₂H₂ separation [74].

Cd[Fe(CN)₅NO] (Cd-NP) is an ultra-microporous MOF constructed by 3.2 Å pore channels connecting ellipsoidal cavities, which are analogous to the molecular shapes of CO₂ and C₂H₂ [75]. The ESP of the pore surface mapped by DFT calculations shows a positive potential (α) around the Cd center, a positive potential (β) on the N atom of nitrosyl and a negative potential (γ) near the N atom of cyanide. Therefore, the ESP of the pore surface was complementary to CO₂ rather than C₂H₂. Cd-NP provided a high CO₂ capacity of 2.59 mol/kg and an IAST selectivity of 85 for an equimolar CO₂/C₂H₂ gas mixture at 298 K, 1 atm. The calculated Q_{st} for CO₂ at near-zero coverage was 27.7 kJ/mol, which supported the viability of regeneration under mild conditions.

Zhang et al. proposed that metal nodes in a highly oxidized state can attract electrons from the ligands, generating a pore surface with more polarities that preferentially recognize CO₂ molecules [76]. Therefore, they synthesized Ce^{IV}-MIL-140-4F from tetrafluoro terephthalate and Ce^{IV} with unoccupied 4f orbitals. Ce^{IV}-MIL-140-4F provided

an optimal pore environment to specifically trap CO₂ via strong host–guest interactions, whereas the isostructural Zr^{IV}-MIL-140-4F exhibited normal C₂H₂ selectivity over CO₂. The ESP distributions illustrate that there are two different electron regions at the edge of the channel of the two MIL-140-4F MOFs (electron-rich region I and electron-poor region II). (Figure 7). Compared with Zr^{IV}-MIL-140-4F, the electron cloud density of Ce^{IV}-MIL-140-4F was higher at site I, and the potential was more positive at site II. In situ PXRD and in situ FTIR spectra indicate that CO₂ was perfectly located on site I of Ce^{IV}-MIL-140-4F and bound by four fluorine atoms with strong F...C=O interactions. In contrast, DFT calculations indicate that C₂H₂ was located on site II of Ce^{IV}-MIL-140-4F with weaker ≡C–H...F interactions. The different binding configurations of CO₂ and C₂H₂ in Ce^{IV}-MIL-140-4F resulted in a superior CO₂ capacity of 110.3 cm³/cm³ (2.24 mmol/g) and an excellent separation selectivity of ~9.5 for 50/50 CO₂/C₂H₂ mixtures at 298 K, 100 kPa. Furthermore, the *Q*_{st} for CO₂ and C₂H₂ on Ce^{IV}-MIL-140-4F was 39.5 and 27.4 kJ/mol, respectively, showing stronger affinity to CO₂ than C₂H₂.

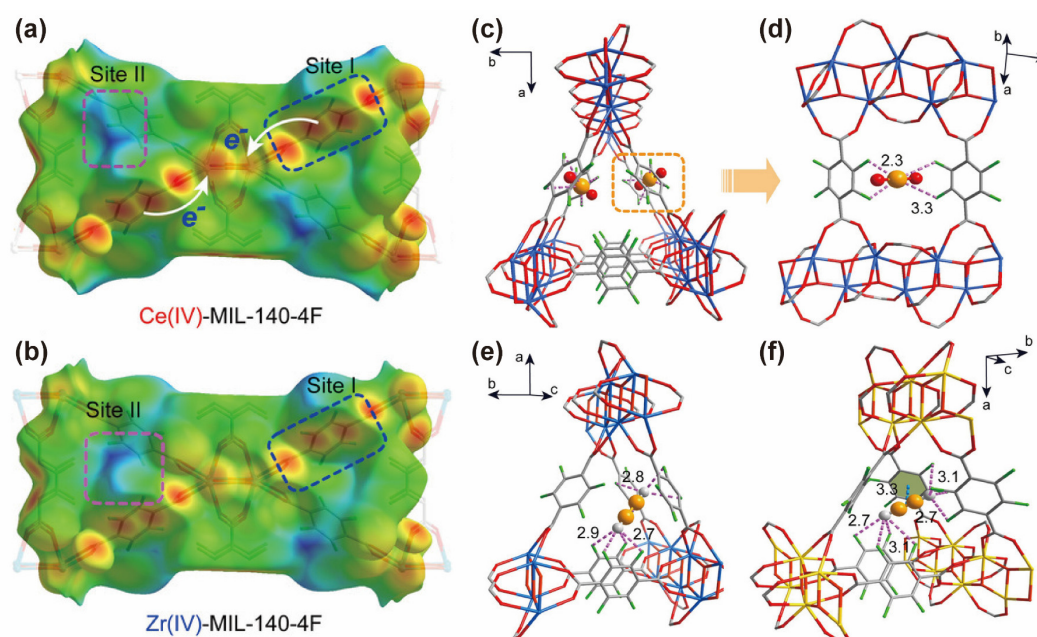


Figure 7. (a,b) The Hirshfeld surface with *d_e* (ESP) in Ce^{IV}-MIL-140-4F (a) and Zr^{IV}-MIL-140-4F (b) (gradient color from red to blue indicates changes in electron density from high to low). (c,d) Structure of CO₂-loaded Ce^{IV}-MIL-140-4F and the interaction between CO₂ and F atoms. (e,f) The binding sites of C₂H₂ in Ce^{IV}-MIL-140-4F (e) and Zr^{IV}-MIL-140-4F (f). Reproduced with permission from Zhang et al., *Angewandte Chemie International Edition*; published by John Wiley and Sons, 2021 [76].

Cu-F-pymo was constructed by Shi et al. from 5-fluoropyrimidin-2-olate for inverse CO₂ selectivity [77]. They found that residual solvent molecules under different conditions could provide sites for gas molecules to realize high separation performance. GCMC simulation and DFT were used to calculate ESP, revealing that CO₂ and C₂H₂ molecules were preferentially adsorbed in different pores but the C₂H₂-preferential pore A was occupied by residual water molecules. CO₂ could still be collected with three molecules per unit cell. At 1 atm, 298 K, the partly dehydrated Cu-F-pymo exhibited a CO₂ adsorption capacity of 1.19 mmol/g and benchmark CO₂/C₂H₂ selectivity of over 10⁵ for the equimolar CO₂/C₂H₂ mixture.

[Zn(atz)(BDC-Cl₄)_{0.5}]_n is a 3D pillared-layer ultra-microporous MOF constructed with electronegative Cl atoms embedded in the pore surface for inverse CO₂/C₂H₂ separation [78]. [Zn(atz)(BDC-Cl₄)_{0.5}]_n showed an adsorption selectivity of 2.4 for a CO₂/C₂H₂ (50/50) mixture at 285 K and 100 kPa and a *Q*_{st} of 32.7 kJ/mol for CO₂. The CO₂-

selectivity resulted from a match between the pore surface adorned with Cl atoms and the quadrupole moment of CO₂. However, [Zn(atz)(BDC-Cl₄)_{0.5}]_n could only adsorb CO₂ with a capacity of 34.6 cm³/cm³ (0.94 mol/kg) at 285 K, 1 bar.

Cai et al. proposed a photoinduced electron-transfer (PIET) strategy to modulate the electrostatic gradient of MOFs for selective adsorption of CO₂ over C₂H₂ [79]. Researchers found that the intrinsic electric field gradients of zwitterions were favorable for selective CO₂ adsorption and that the radical π moieties generated by photoelectron transfer had strong affinity for the π systems of CO₂. During the PIET process, electrons were transferred from the oxygen-containing carboxylic acid ligand to the zwitterion, which would not change the electric field gradient of the material and prevent a decrease in CO₂ adsorption. However, after the loss of one electron, the O atom could not form H-C $\equiv$ C-H $\cdots$ O hydrogen bonds with C₂H₂ easily, reducing the adsorption of C₂H₂ (Figure 8). Based on this strategy, the authors synthesized PMOF-1, which achieved a CO₂ uptake of 47.5 cm³/g before irradiation and 53.3 cm³/g after irradiation for 1 h at 273 K and 100 kPa. The uptake ratio was also enhanced from 5.0 to 7.1. Notably, the IAST selectivity for an equimolar CO₂/C₂H₂ mixture reached 694 at 273 K, 1 bar, which was superior to any other porous material reported for inverse CO₂ adsorption over C₂H₂.

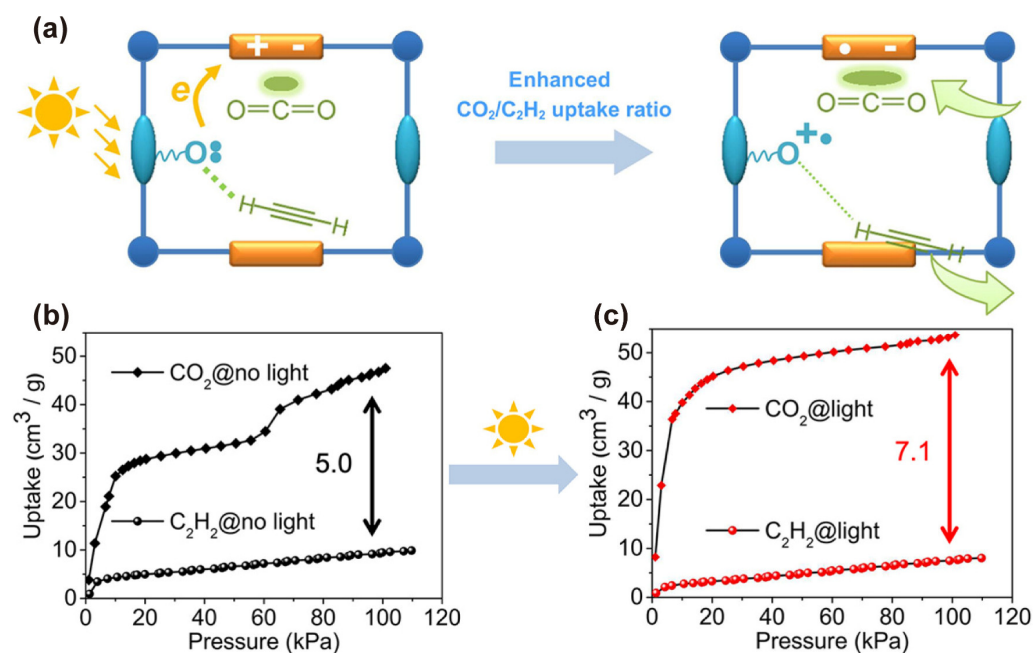


Figure 8. (a) PIET strategy for improving the uptake ratio of CO₂/C₂H₂. (b,c) Adsorption isotherms of C₂H₂ and CO₂ before (b) and after (c) irradiation at 273 K. Reproduced with permission from Cai et al., *Angewandte Chemie International Edition*; published by John Wiley and Sons, 2021 [79].

Pore chemistry can also be optimized through a precise steric arrangement of interaction sites for favorable CO₂ adsorption on the pore surface. Gu et al. demonstrated the strategy of “opposite action” in MOFs, realizing the CO₂ selective adsorption and separation of CO₂/C₂H₂ under ambient temperature and pressure [74]. They synthesized two isostructural MOFs, PCP-NH₂-bdc and PCP-NH₂-ipa, from meso- α,β -di(4-pyridyl) glycol (dpg), terephthalic acid (bdc) and isophthalic acid (ipa). Owing to the different electronic structures of CO₂ and C₂H₂, they tended to exhibit different binding orientations when adsorbed in microporous channels. Therefore, the precise encoding of interaction sites (-NH₂) parallel to the CO₂ binding site in the channel could enhance the CO₂-framework interaction without significantly changing the adsorption orientation of the CO₂ molecules. On the contrary, the additional interaction sites could impact the adsorption orientation of C₂H₂ and combine with the spatial restriction of the 1D confined channel to inhibit C₂H₂ adsorption at other sites, ultimately achieving high CO₂/C₂H₂

selectivity of more than 4.4 (Figure 9). PCP-NH₂-bdc and PCP-NH₂-ipa exhibited remarkably high CO₂ uptake of 3.03 and 3.21 mmol/g, respectively. The Q_{st} at zero coverage of CO₂ for PCP-NH₂-bdc and PCP-NH₂-ipa was reduced to 34.57 and 36.6 kJ/mol, respectively, indicating reduced energy consumption for regeneration and recycling.

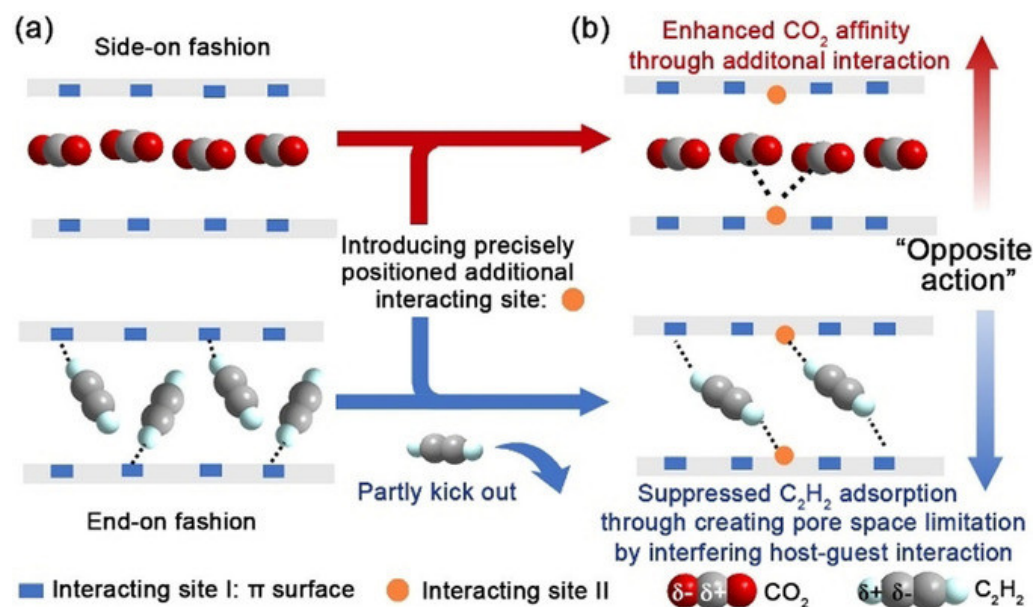


Figure 9. Schematic diagram of the “opposite action” strategy to improve CO₂ selectivity. (a) Different orientations of CO₂ and C₂H₂ into the channel. (b) Precise steric arrangement of interaction sites providing an enhanced CO₂–framework interactions and inhibiting C₂H₂ adsorption. Reproduced with permission from Gu et al., *Angewandte Chemie International Edition*; published by John Wiley and Sons, 2021 [74].

SIFSIX-type MOFs were reported to provide high affinity for CO₂ via extensive adjustable pore size and electron-rich F atoms on the channel surface [57]. For instance, in SIFSIX-3-Ni, each CO₂ molecule was located near four F atoms of four SiF₆^{2−} anions with a short distance of ~ 2.75 Å between C and F [71]. SIFSIX-3-Ni exhibited a high CO₂/C₂H₂ capacity of 2.5/2.0 mmol/g at 298 K, 0.1 bar, and a selectivity of 7.69 for CO₂/C₂H₂ (2/1; v/v) at 298 K, 1.0 bar. However, with a comparable pore environment, the analogous TIFSIX-2-Cu-i could only provide normal C₂H₂ selectivity over CO₂. The inverse “yin-yang” behavior in two analogous MOFs was explained by the different geometry of host–guest binding sites.

Thulium(iii)-based MOFs embellished with -OH groups and H₂O [Tm₂(OH-bdc)] with partly and fully dehydrated phases were termed **1a** and **1a'**, respectively [73]. With its optimized pore size and pore surface modified with -OH groups that could interact reversibly with CO₂ through hydrogen bonding, **1a** showed a high CO₂ capacity of 5.83 mol/kg and an IAST selectivity of 17.5 for CO₂/C₂H₂ (1/2, v/v) at 100 kPa, 298 K. The Q_{st} of CO₂ on **1a** was 45.2 kJ/mol, which is significantly higher than the Q_{st} of C₂H₂ (17.8 kJ/mol), showing its strong affinity for CO₂. The completely dehydrated phase **1a'** with both hydroxyl groups and open metal sites also provided a CO₂ capacity of 6.21 mmol/g but lower selectivity of only 1.65 under the same conditions.

Recently, a new kinetic sieving strategy for C₂H₂/CO₂ separation was demonstrated by ZU-610a with sulfonic anion pillars [81]. ZU-610a was obtained by heat treatment of ZU-610. The pore size was reduced from 3.8 Å and 4.7 Å to 3.2 Å and 4.1 Å after heat treatment, but the topology remained unchanged. Interestingly, after shrinking the pore size, the C₂H₂-selectivity of ZU-610 was reversed to the CO₂ selectivity of ZU-610a, due to the separation process, which transformed thermodynamic control into kinetic control. Kinetic adsorption studies revealed that CO₂ achieved equilibrium after ~ 10 min on Zu-

610 and Zu-610a. However, C_2H_2 did not reach equilibrium until 70 min (Figure 10). The absorption of CO_2 on Zu-610a was reduced slightly (1.51 mmol/g) due to pore shrinking, but the capacity of C_2H_2 fell drastically from 3.22 to 0.12 mmol/g at 100 kPa, 298 K. Profiting from kinetic sieving, ZU-610a showed a selectivity of up to 207 for an equimolar CO_2/C_2H_2 mixture, which is higher than that of many benchmark MOFs. Moreover, comparing the Q_{st} of CO_2 with other MOFs, ZU-610a showed the lowest Q_{st} of 27.3 kJ/mol, indicating its extremely low regeneration energy. Kinetic studies of MOFs for CO_2/C_2H_2 separation have been less reported, and this research offered recommendations for the design of MOFs for separation systems with comparable molecular dimensions.

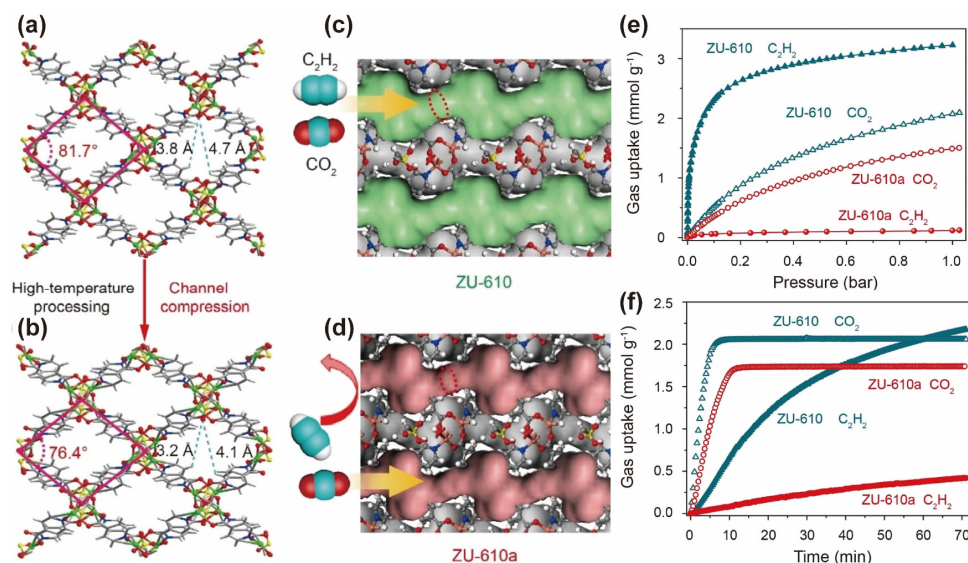


Figure 10. (a,b) The structures and rhombic channel of ZU-610 (a) and ZU-610a (b). (c,d) The 1D channel of ZU-610 (c) and ZU-610a (d). (e) Sorption isotherms of C_2H_2 and CO_2 . (f) Gas adsorption of C_2H_2 and CO_2 versus time at 298 K, 1 bar. Reproduced with permission from Cui et al., *Angewandte Chemie International Edition*; published by John Wiley and Sons, 2022 [81].

Overall, C_2H_2 is the most similar substance to CO_2 in terms of physical properties. The challenge of directly capturing CO_2 instead of C_2H_2 from CO_2/C_2H_2 is to avoid stronger electrostatic interactions between C_2H_2 and the adsorbent. The separation by exploiting the flexibility of MOFs is fascinating but less predictable, making it difficult to develop design principles. Optimizing the pore chemistry through different electrostatic interactions or thermodynamic affinity will be more opportune.

4. CO_2 -Selective Capture from Other Binary Light Hydrocarbon Mixtures

High-purity ethylene (C_2H_4) and ethane (C_2H_6) are important raw materials to produce plastics, rubber and other industrial chemicals but always contain contaminants such as CO_2 , which is corrosive to gas pipelines and can affect the conversion of products. In addition, C_2H_4 and C_2H_6 can form maximum pressure azeotrope with CO_2 , which is a barrier to CO_2 removal by distillation [88,89]. Compared to C_2H_2 , however, the kinetic diameter and polarizability of C_2H_4 and C_2H_6 differ more from CO_2 ; therefore, many MOFs could exploit these differences for highly efficient separation.

Horike et al. reported an early study of a dense coordination framework $[Zn(5NO_2-ip)(dpe)]$ in 2012 [90]. $[Zn(5NO_2-ip)(dpe)]$ showed the inherent structural flexibility and CO_2 preference over C_2H_4 and C_2H_6 under ambient conditions in single-component and mixed gas-flow experiments. For C_2H_6 , the observed adsorption amount could be neglected (less than 10 cm³/g at 273 K, 8 bar). For C_2H_4 , the adsorption isotherm represented a gate-opening behavior. At 298 K, the pressure at which adsorption begins was 720 kPa, whereas the total uptake was only 32 mL/g at 800 kPa. For CO_2 , however,

the adsorption capacity reached 31 mL/g at 298 K and 101 kPa with a type I isotherm. Breakthrough curves were measured for a mixture of C₂H₄/CO₂ (80/20, *v/v*) at 298 K, with outlet C₂H₄ purity of almost 100%, exhibiting the significant separation property of CO₂ over C₂H₄.

In a subsequent study, a family of rare earth MOFs (named RE-PCP) were designed with various flexibility from an acrylamide-modified ligand for CO₂/C₂H₆ and CO₂/C₂H₄ separation [88]. At 195 K, Y-PCP and Ho-PCP showed fully reversible type I isotherms for CO₂ and C₂H₄ with higher CO₂ capacity than C₂H₄. However, the adsorption of CO₂ in La-PCP showed a “gate opening” phenomenon, and at around 80 kPa, the second uptake occurred. In contrast, even at pressures up to 100 kPa, there was almost no absorption for C₂H₄ or C₂H₆ in La-PCP. The total CO₂ uptake by La-PCP was approximately 34 mL/g at 273 K, 150 kPa, whereas the adsorption of C₂H₄ and C₂H₆ was almost absent before 150 kPa, indicating that La-PCP is a potential candidate for CO₂ capture from CO₂/C₂H₄ and CO₂/C₂H₆ mixtures.

Qc-5-Cu has been demonstrated to be efficient in CO₂/C₂H₄ separation, with high thermal and water stability [91]. The pore diameter of Qc-5-Cu was estimated to be approximately 3.3 Å, which is similar to the molecular dimensions of CO₂ (3.3 Å) but smaller than those of C₂H₄ (4.16 Å). Thus, Qc-5-Cu could molecularly sieve CO₂ from C₂H₄ to achieve a high selectivity of 39.95 for a CO₂/C₂H₄ (*v/v*, 1:99) mixture. The saturation capacity of CO₂ also reached 2.48 mmol/g. The *Q_{st}* value for CO₂ and C₂H₄ was calculated to be 36.2 kJ/mol and 23.1 kJ/mol, respectively, indicating the higher CO₂ adsorption intensity. However, these results are considerably lower than those of MOFs with OMSs, leading to lower regeneration energy costs.

[Co(pysa)(H₂O)]_n (YAU-7) was synthesized from H₂pysa (2-(pyrid-4'-yl)-benzimidazole-5-carboxylic acid) with superior separation performance for CO₂, C₂H₂ and C₂H₄ [92]. Among these four gases, YAU-7 was found to be most favorable for the adsorption of CO₂. Importantly, YAU-7 had a high selectivity of 36.8, 80.7 and 31.6 for CO₂/CH₄, CO₂/C₂H₂ and CO₂/C₂H₄ (*v/v*, 50/50) mixtures at 298 K and 100 kPa, respectively. However, its CO₂ capacity was only 1.53 mmol/g under 298 K, 100 kPa.

The SU-101(M) series MOFs, which comprise Bi, In, Ga and Al, have a small pore size of approximately 6.8 Å and an abundance of carbonyl oxygen atoms in the channel, which could act as Lewis basic sites to bind acidic CO₂ [82]. Each metal center in SU-101(M) was coordinated to one coordinated H₂O molecule. Compared to the fully activated phase SU-101(M)-a, which did not contain coordinated H₂O, the presence of coordinated H₂O in SU-101(M) strengthened the interaction between the C atom in CO₂ and carbonyl O with more electrons, whereas it weakened interactions with both C₂H₂ and C₂H₄. Therefore, SU-101(M) showed a high CO₂ capacity of 40.2~53.7 mL/g (1.79~2.4 mmol/g) and a high selectivity of 5.5~15.5. The *Q_{st}* values of CO₂ were also obviously larger than those of C₂H₂ and C₂H₄.

The kinetic diameters and polarizabilities of C₂H₄ and C₂H₆ differ more from those of CO₂ compared to C₂H₂, which is why many MOFs can efficiently separate CO₂ based on these differences. Future research should focus on further increasing the adsorption capacity of CO₂ and reducing the energy consumption for regeneration. Moreover, the efficient capture of CO₂ from multiple C₁-C₂ mixtures is also very attractive.

In addition to C₁ and C₂ components, gaseous light hydrocarbons also include C₃ and C₄ components, such as propylene (C₃H₆), propane (C₃H₈), butene (C₄H₈), etc. Their physical properties differ more significantly from those of CO₂, which are easier to separate. Therefore, CO₂ capture from C₃ and C₄ mixtures has not attracted much attention from researchers and is outside the scope of this review.

5. CO₂-Selective Capture from Multicomponent Light Hydrocarbon Mixtures

Porous materials capable of recognizing CO₂ with high selectivity and specificity from a more complex system have always been a goal pursued by researchers; therefore,

attention needs to be paid to the development of MOFs that capture CO₂ from multiple components.

Some MOFs with CO₂/C₂H₂ inverse selectivity mentioned in Section 2 can also exhibit a higher capacity for CO₂ than some other light hydrocarbons. For instance, Cd-NP was reported to selectively adsorb CO₂ over C₂H₂ through optimization of the ESP of the pore surface; moreover, with a narrow pore size of 3.2 Å, it did not adsorb larger molecules at all, such as C₂H₄ and C₂H₆ [75]. The presence of coordinated H₂O in SU-101(M) strengthened the CO₂ adsorption but reduced both C₂H₂ and C₂H₄ adsorption. Taking SU-101(Al) as an example, the equimolar CO₂/C₂H₂ and CO₂/C₂H₄ selectivities were 15.5 and 8.3 at 298 K 100 kPa, respectively, showing the potential of SU-101(Al) for CO₂ capture from C₂H₂ and C₂H₄.

[Zn(odip)_{0.5}(bpe)_{0.5}] is a flexible MOF with a gate-opening effect for efficient purification of C₁-C₂ hydrocarbons and CO₂ capture [54]. At 298 K, a gate-opening behavior for CO₂ was clearly observed. The adsorption of CO₂ first rapidly reached 55.0 mL/g at 20.7 kPa and then suddenly increased to 118.7 mL/g (5.30 mmol/g) until 100 kPa. For C₁ and C₂ hydrocarbons, no clear gate-adsorption behaviors occurred, but lower adsorption was observed at all temperatures. Owing to the gate-opening behavior for CO₂, the selectivities for equimolar mixtures of [Zn(odip)_{0.5}(bpe)_{0.5}] were 376.0 for CO₂/CH₄, 13.2 for CO₂/C₂H₂, 26.2 for CO₂/C₂H₄ and 27.9 for CO₂/C₂H₆ at 298 K, 100 kPa.

However, practical multicomponent breakthrough experiments to demonstrate separation performance are lacking in these studies. Qazvini et al. provided MUF-16-M (M = Co, Mn, Ni)-type MOFs from 5-aminoisophthalic acid (H₂aip) [51]. The pore chemistry of MUF-16-M was precisely designed with complementary size (3.6 × 7.6 Å) and electrostatic potential to CO₂. Single-crystal XRD and DFT calculations indicated that the O atoms of CO₂ could form N-H...O and C-H...O hydrogen bonds with the -NH₂ and phenyl groups, whereas the electropositive C atom contacted the O atom from the two uncoordinated carboxyl groups. The adsorption of N₂O with similar size and electrostatic distribution on MUF-16 confirmed this binding mode. The uptake capacities of MUF-16 were 47.78 mL/g for CO₂, 1.20 mL/g for CH₄, 3.99 mL/g for C₂H₂, 3.17 mL/g for C₂H₄, 3.06 mL/g for C₂H₆, 5.35 mL/g for C₃H₆ and 4.82 mL/g for C₃H₈. For equimolar CO₂/CH₄ and CO₂/C₂H₂ mixtures, the selectivities were as high as 6690 and 510 at 293 K and 1 atm, respectively. MUF-16 successfully captured CO₂ from CO₂/CH₄/C₂H₆/C₃H₈ (15/80/4/1) mixtures at 1.1 bar in a breakthrough experiment with steep elution profiles (Figure 11). On account of these features, MUF-16 is a promising physical adsorbent for direct capture of CO₂ from multicomponent light hydrocarbon mixtures.

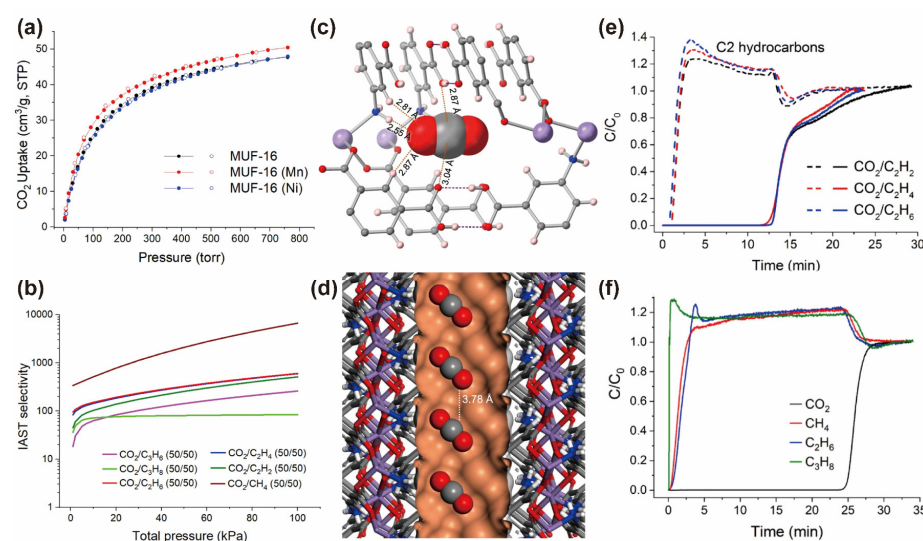


Figure 11. (a) The adsorption/desorption isotherms for CO₂ at 293 K. (b) IAST selectivities of MUF-16 for different mixtures (50/50) at 293 K. (c,d) The adsorption sites (c) and arrangement (d) of

adsorbed CO₂ molecules in MUF-16(Mn). Color codes: Mn, lilac; N, blue; O, red; C, gray; H, light pink or white; pore surface, orange. (e,f) Breakthrough experiment curves for CO₂/C₂ (50/50) (e) and CO₂/CH₄/C₂H₆/C₃H₈ (15/80/4/1) (f) at 293 K and 1.1 bar for MUF-16. Reproduced with permission from Qazvini et al., Nature Communications; published by Springer Nature, 2021 [51].

The study of CO₂ capture from multiple hydrocarbon mixtures is still at the beginning stage, and it is expected to be a hot research topic, as it is very difficult but urgently needed. Finely tuning the pore chemistry or developing flexible MOFs with gate-opening behavior for CO₂ represent very promising strategies. We expect more valuable research to explore how to specifically recognize CO₂ and extend it to other CO₂ mixture systems.

6. Outlook

Capturing CO₂ from various gas mixtures is a necessary prerequisite for subsequent CO₂ reduction, conversion, utilization or storage technologies. From this perspective, the issue of CO₂ capture has been recognized as one of the major challenges of the 21st century. With further understanding of the pore chemistry, structural flexibility and host–guest interaction of MOFs, additional progress has been made in the field of CO₂ capture from light hydrocarbon mixtures. In situ characterization and theoretical computational studies have revealed the mechanisms of selective CO₂ recognition behavior at the molecular level, providing an important impetus for the development of MOFs.

Although MOF chemistry has recently made considerable progress, there are several aspects of practical applications that remain challenging and deserve further exploration in the future:

- (1) Elimination of the trade-off between CO₂ uptake capacity and selectivity. This problem is more evident in CO₂ capture from CO₂/C₂H₂ mixtures, as they are extremely close in nature. To develop optimal MOFs combining high CO₂ selectivity and high capacity, in the future, researchers should focus on (a) designing flexible MOFs that can transform structures to accommodate target gas to substantially improve selectivity; (b) hyperfine control of pore size, shape and environment through reticular chemistry or crystal engineering strategies; and (c) developing MOF composites or grading combination strategies to compensate for the shortcomings of individual pristine MOFs.
- (2) CO₂-selective capture at trace concentrations. The CO₂/hydrocarbon ratios used for experiments in most studies are 1/1, 1/2 or 1/9, whereas the initial concentration of CO₂ in real hydrocarbon mixtures is typically much lower (<5%). It is extremely challenging to maintain superior selective adsorption for CO₂ at such low concentrations. In this regard, flexible MOFs with gate-opening effects for CO₂ at low pressure are highly promising.
- (3) CO₂ selective adsorption from multicomponent hydrocarbon mixtures. Porous materials capable of recognizing CO₂ in more complex systems with high selectivity and specificity are extremely challenging but sought-after for material design. A grading combination of multiple MOFs or integration of pores with multiple properties into one MOF platform may be effective approaches.
- (4) Combination of desirable separation performance with broader performance for practical applications, such as high thermal/water/mechanical stability and low regeneration energy. Compared to conventional porous materials, MOF materials have more suitable ultra-microporous-level channels for CO₂ molecules, high designability and the potential to capture CO₂ from more complex systems. However, many MOFs are not as stable as porous carbon materials in terms of moisture stability and thermal stability. The introduction of open metal sites should be avoided, owing to their typically high activation temperature, regeneration energy consumption and poor water stability. An increasing number of researchers are

employing strategies such as the construction of robust coordination geometries to build stable MOF materials.

- (5) Further reduction in economic and energy costs (from precursors, solvents, synthesis temperatures, activation conditions, etc.). Unaffordable raw materials and severe synthesis or activation conditions have become one of the most challenging issues in scaling MOFs up for practical applications.
- (6) Large-scale synthesis and industrialization. Taking technology from the laboratory to industrialization is always a challenge. A good adsorbent material should be synthesized on a large scale with high purity; however, this is rarely achieved in MOF studies. Making use of non-toxic metal ions, low-cost sustainable organic linkers and solvent-recoverable or solvent-free reactions may be beneficial in industrialization.
- (7) Introducing the design strategy of MOFs into other porous materials and other gas separation applications. For instance, in reticular chemistry, COFs and HOFs feature organic frameworks similar to that of MOFs and can therefore be developed by introducing design strategies for MOFs. On the other hand, air is a complex gas mixture with a CO₂ concentration of only 0.04%. If MOFs for CO₂ capture from light hydrocarbons can be extended to direct CO₂ capture from air, considerable ecological and economic benefits can be realized.

Overall, it should be acknowledged that MOFs have shown tremendous potential for applications in the direct CO₂-selective capture and purification of light hydrocarbons, owing to their high designability. Their implementation on a large scale offers the potential for significant environmental and economic benefits. Although there are still some challenging problems, we have confidence that with the persistent efforts of researchers working in this popular field, additional progress will be made in developing CO₂-selective MOFs for light hydrocarbon purification.

Author Contributions: Conceptualization, Y.G. and H.H.; writing—original draft preparation, H.H.; writing—review and editing, Y.G., L.W., X.Z. and H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (2022YFE0110500), the National Natural Science Foundation of China (21906120), the Shanghai Pujiang Program (NO. 21PJ1412600) and the Fundamental Research Funds for the Central Universities of China (22120220153).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work was supported by the National Key Research and Development Program of China (2022YFE0110500), the National Natural Science Foundation of China (21906120), the Shanghai Pujiang Program (NO.21PJ1412600) and the Fundamental Research Funds for the Central Universities of China (22120220153).

Conflicts of Interest: The authors declare no conflict of interest.

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