

Deciphering Mechanisms of CO₂-Selective Recognition over Acetylene within Porous Materials

Published as part of *Chem & Bio Engineering virtual special issue "Advanced Separation Materials and Processes"*.

Zhaoqiang Zhang and Dan Zhao*

Cite This: *Chem Bio Eng.* 2024, 1, 366–380

Read Online

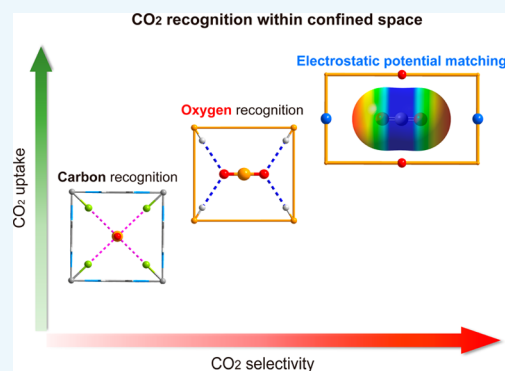
ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Reverse adsorption of carbon dioxide (CO₂) from acetylene (C₂H₂) presents both significant importance and formidable challenges, particularly in the context of carbon capture, energy efficiency, and environmental sustainability. In this Review, we delve into the burgeoning field of reverse CO₂/C₂H₂ adsorption and separation, underscoring the absence of a cohesive materials design strategy and a comprehensive understanding of the CO₂-selective capture mechanisms from C₂H₂, in contrast to the quite mature methodologies available for C₂H₂-selective adsorption. Focusing on porous materials, the latest advancements in CO₂-selective recognition mechanisms are highlighted. The review establishes that the efficacy of CO₂ recognition from C₂H₂ relies intricately on a myriad of factors, including pore architecture, framework flexibility, functional group interactions, and dynamic responsive behaviors under operating conditions. It is noted that achieving selectivity extends beyond physical sieving, necessitating meticulous adjustments in pore chemistry to exploit the subtle differences between CO₂ and C₂H₂. This comprehensive overview seeks to enhance the understanding of CO₂-selective recognition mechanisms, integrating essential insights crucial for the advancement of future materials. It also lays the groundwork for innovative porous materials in CO₂/C₂H₂ separation, addressing the pressing demand for more efficient molecular recognition within gas separation technologies.

KEYWORDS: Adsorption and separation, molecular recognition, reverse CO₂/acetylene separation, porous materials, host-guest interactions



1. INTRODUCTION

Acetylene (C₂H₂), the simplest alkyne, plays a vital role in the chemical industry, being fundamental for producing various chemicals (e.g., vinyl chloride, acrylic acid, and butanediol) and indispensable for gas welding and cutting.^{1–6} The global C₂H₂ market is projected to expand to USD 11.06 billion in 2023 with a robust compound annual growth rate (CAGR) of 8.7%. This growth trend is expected to continue, with an anticipated market size of USD 13.97 billion by 2027, at a CAGR of 6.0%.⁷ C₂H₂ is primarily produced from the steam cracking of hydrocarbons like petroleum or naphtha and through the partial combustion of methane, processes that inadvertently introduce CO₂ as an impurity, leading to a compromised quality of C₂H₂ that impedes its utility in downstream processes.^{8–13} Therefore, effective CO₂ removal is essential to ensure the high-grade quality of C₂H₂ necessary for creating high-value chemicals. The challenge in separating CO₂ from C₂H₂ lies in their closely aligned physical properties and molecular dimensions (Table 1), making traditional separation

Table 1. Physical-Chemical Properties of CO₂ and C₂H₂

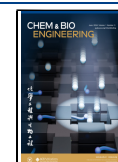
	CO ₂	C ₂ H ₂
Dynamic diameter (Å)	3.3	3.3
Dimension (Å ³)	3.2×3.3×5.4	3.3×3.5×5.7
Boiling point (K)	194.7	189.3
Quadrupole moments (×10 ⁻⁴⁰ C m ²)	-13.4	20.5
Dipole moment (D)	0	0
Critical temperature (K)	304.2	308.2
Polarizability (Å ³)	2.65	3.59

Received: February 19, 2024

Revised: May 3, 2024

Accepted: May 6, 2024

Published: May 13, 2024



methods like solvent extraction and cryogenic distillation not only energy-intensive but also environmentally burdensome, contributing to high carbon emissions and potential equipment corrosion.^{8–13} In alignment with global sustainability goals, there is a heightened demand for more eco-friendly and energy-conserving purification strategies for C_2H_2 . Adsorptive separation, utilizing porous adsorbents designed to selectively bind CO_2 , offers a streamlined and targeted approach to purifying C_2H_2 by effectively removing CO_2 contaminants. While this innovative strategy holds great promise, the pursuit of innovation and advancement of adsorbents that favor CO_2 over C_2H_2 remains a nascent and formidable challenge, yet it is an essential pursuit in the journey toward sustainable industrial processes.

Porous materials, especially metal-organic frameworks (MOFs) or porous coordination polymers (PCPs), offer unparalleled advantages in adsorption separation due to their customizable pore sizes, expansive surface areas, and the ability to tailor specific functional groups to target particular molecules.^{14–24} Compared to traditional adsorbents, MOFs constructed based on reticular chemistry and crystal engineering boast superior selectivity and greater uptake capacities, and often feature more robust regeneration capabilities, enabling more efficient separation processes for carbon capture and gas purification.^{25–35} In the scenario of C_2H_2 - CO_2 separation, significant strides have been made in the methodology of designing porous materials for C_2H_2 -selective capture.^{25–33,36–41} The electron-rich triple bond of C_2H_2 and its acidic H atoms make it particularly amenable to enhanced recognition when specific functional groups are integrated into the porous structure. C_2H_2 is mainly recognized through a variety of interactions, including hydrogen bonding, Lewis base interactions, and C_2H_2 -metal π -complexation or dipole- π interactions.^{25–33} However, the journey towards achieving equally efficient CO_2 -selective adsorption is still unfolding. The methodology to tune the porous materials, such as MOFs, zeolites, and hydrogen-bonded organic frameworks (HOFs), with the ability to preferentially recognize CO_2 over C_2H_2 , is still ambiguous.

Recently, there has been a surge in studies focusing on reverse CO_2/C_2H_2 adsorption and separation (Figure 1). Nevertheless, a conclusive and cohesive strategy for material design, coupled with a comprehensive understanding of the mechanisms dictating selective CO_2 capture from C_2H_2 , remains elusive. Therefore, a timely revelation of the CO_2 -selective recognition mechanisms within these materials is both critical and necessary. In this review, we endeavor to amalgamate the latest advancements in the context of reverse CO_2/C_2H_2 separation using porous materials, placing a particular emphasis on deciphering the mechanisms of CO_2 -selective recognition. The goal is to thoroughly understand the interplay between pore size and shape, the framework structures of the adsorbents, their potential sorption preferences, and the intrinsic recognition mechanisms of these porous materials. By doing so, we aspire to clarify the principles governing their selectivity and performance, ultimately offering an insightful blueprint to guide the development of future materials. Anticipating the progression, we posit that a judicious application of strategies tailored to appropriate scales may afford unprecedented precision in the orchestration of complex separation systems. Finally, some perspectives in the prospective trajectories are provided, which

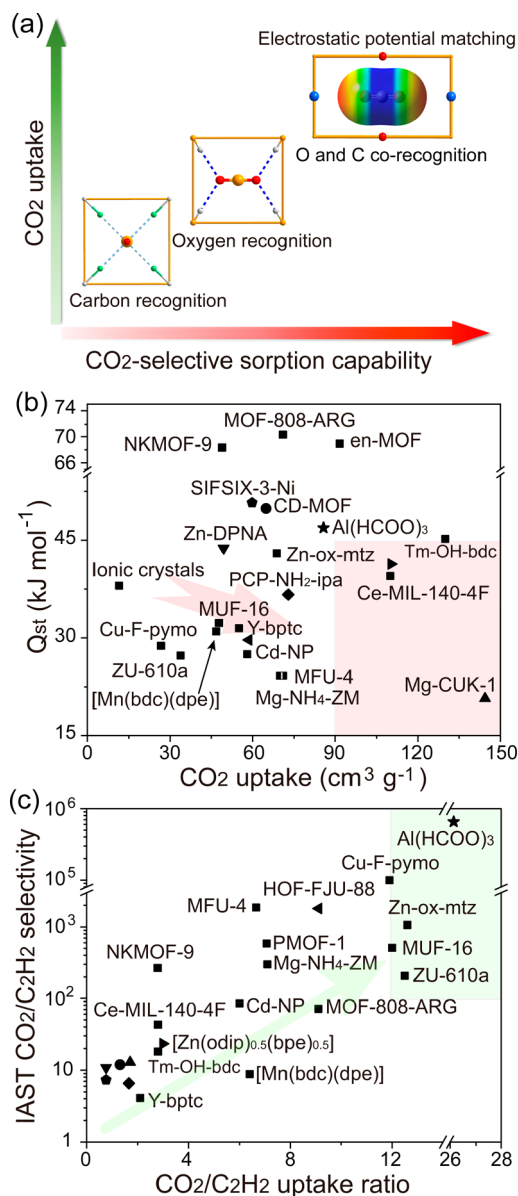


Figure 1. (a) CO_2 -selective recognition mechanism in physisorption. (b and c) Comparison of the CO_2 -selective sorption behavior over C_2H_2 on the state-of-the-art CO_2 -selective materials (Mg-CUK-1 at 233 K; [Mn(bdc)(dpe)] at 273 K; HOF-FJU-88 at 296 K; MFU-4 at 300 K; MUF-16 at 293 K; MOF-808-ARG at wet condition; PMOF-1 after irradiation and at 273 K).

might guide the path toward the future landscape of reverse CO_2/C_2H_2 separation technology.

2. THERMODYNAMIC ADSORPTION

Thermodynamic adsorption refers to the process where the selective uptake and binding of molecules to a surface or within a porous material are driven by energetically favorable interactions. This includes a variety of forces such as van der Waals interactions, hydrogen bonding, ionic or dipole interactions, and $\pi \cdots \pi$ interactions. Strategies to accomplish inverse separation of CO_2/C_2H_2 mixture by leveraging thermodynamic adsorption behaviors include binding site geometry control, adsorption site occupancy regulation, utilization of free metal sites, flexible behavior with gate-opening effect, and electrostatic potential matching. These

strategies aim to modify the adsorbent properties to favor CO₂ uptake and retention, thereby facilitating its inverse separation from C₂H₂ under specific conditions. Understanding the thermodynamics behind adsorption is critical for designing novel porous materials.

2.1. Binding Site Geometry Control. The geometry of binding sites within confined spaces, such as those in MOFs, zeolites, or other porous materials, is of great importance for the functionalization of porous materials, as it can determine how and what these sites can maximize the functionality.³ The spatial arrangement and accessibility of these sites are key factors that influence the selectivity and affinity of the confined space toward different guest molecules. This geometric configuration can be finely tuned to enhance the recognition and separation performance for targeted molecules, even achieving molecular sieving.

SIFSIX-3-Ni is a typical prototype material characterized by its specific spatial distribution of binding sites within the pore channels,⁴² which facilitates strong and selective interactions with CO₂ molecules over C₂H₂ (Figure 2). Its CO₂ selectivity

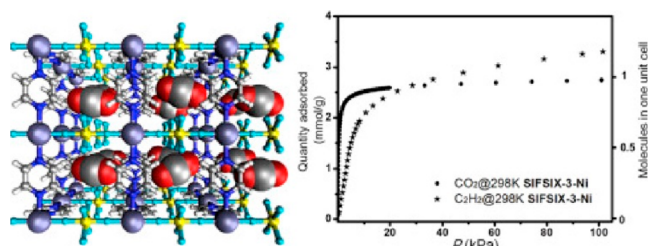


Figure 2. CO₂ binding configurations in SIFSIX-3-Ni (left), and CO₂ and C₂H₂ sorption isotherms (right) on SIFSIX-3-Ni at 298 K. Reproduced with permission from ref 42. Copyright 2016 Cell press.

is largely attributed to the narrow pore size and recognition site geometry, which are optimized to accommodate the shape and size of CO₂ molecules. The binding sites consist of four electronegative F atoms from four SiF₆²⁻ anion pillars that are spatially arranged to interact robustly with the electropositive C atom of CO₂, resulting in strong electrostatic attractions. Benefited from the particular spatial geometry of binding sites, isostructural materials such as NbOFFIVE-1-Ni,⁴³ GEFSIX-3-Ni,⁴⁴ and TIFSIX-3-Ni⁴⁴ with different inorganic anion-pillars also possess the capability for CO₂/C₂H₂ selective adsorption and separation. These anions create a high electrostatic

environment that enhances the selectivity towards CO₂, especially under lower pressures. However, there are two binding sites within this kind of framework, leading to a higher C₂H₂ capacity than that of CO₂ at high pressure. When used for CO₂/C₂H₂/He (5/10/85) separation, high-purity C₂H₂ (> 99.95) can be obtained with CO₂ captured. This work underscores the critical role of the specific spatial distribution of binding sites in selective adsorption mechanism within porous materials. From the interaction mode between CO₂ and SIFSIX-3-Ni, the selectivity arises from the confinement effects with a specific arrangement of multiple binding sites within SIFSIX-3-Ni material, which exhibits a small pore size that allows four anions to simultaneously interact with the carbon atom of CO₂. In contrast, selectivity towards C₂H₂ in other anion-pillared ultramicroporous materials stems from host-guest interactions between anions and hydrogen atoms on C₂H₂. However, other anion-pillared materials lack the specific pore environment found in SIFSIX-3-Ni, limiting CO₂ to interact with only one or two anions. Consequently, C₂H₂ demonstrates similar interactions within these materials, including hydrogen bonding between its hydrogen atoms and anions, as well as electrostatic interactions associated with the triple bond and carbon atoms of the C₂H₂ molecule. These combined interactions contribute to the anticipated selective sorption behavior of C₂H₂.

2.2. Adsorption Site Occupancy Regulation Suppressing C₂H₂ Adsorption. To control the accessibility of binding sites for targeted molecules, one can employ strategies such as designing the pore architecture to allow preferential adsorption of certain molecules and modifying the surface chemistry to enhance or deter interactions with specific chemical species. The approach can include modifying the size, shape, or chemical functionality of the adsorption sites to make them less conducive to C₂H₂ molecules while maintaining or enhancing the adsorption for CO₂.

Tm₂(OH-bdc)₂(μ₃-OH)₂(H₂O)₂ with coordinated H₂O on Tm metal sites demonstrates remarkable selectivity for CO₂ over C₂H₂.⁴⁵ This is due to the fact that within the confined spaces, the strategic positioning of aqua ligands and hydroxyl groups around its tetranuclear thulium centers extend into the pore centers, and this can foster strong O_{CO₂}⋯H₂O/OH interactions. Molecular simulation results confirm the critical importance of specific interactions stemming from residual H₂O and OH groups in CO₂ recognition. Upon full dehydration, the framework reveals open metal sites, resulting

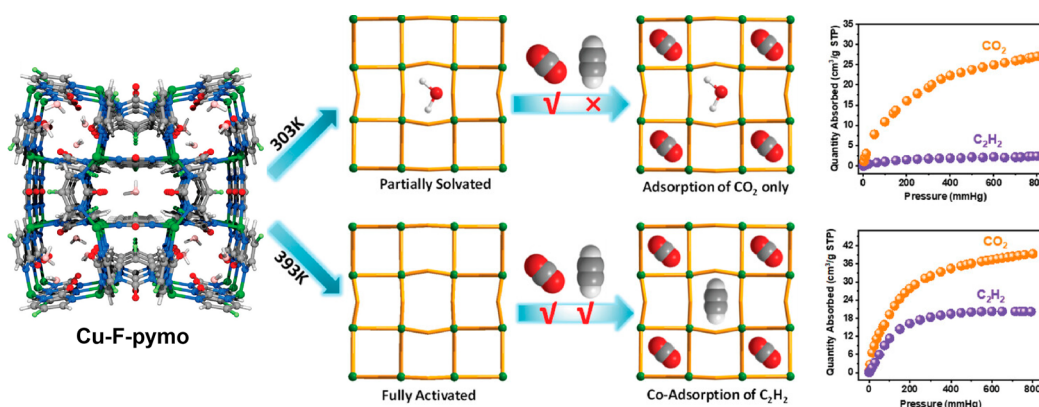


Figure 3. Schematic presentation of separation mechanism toward CO₂ and C₂H₂ in Cu-F-pymo under different activation conditions. Reproduced with permission from ref 46. Copyright 2021 Wiley-VCH.

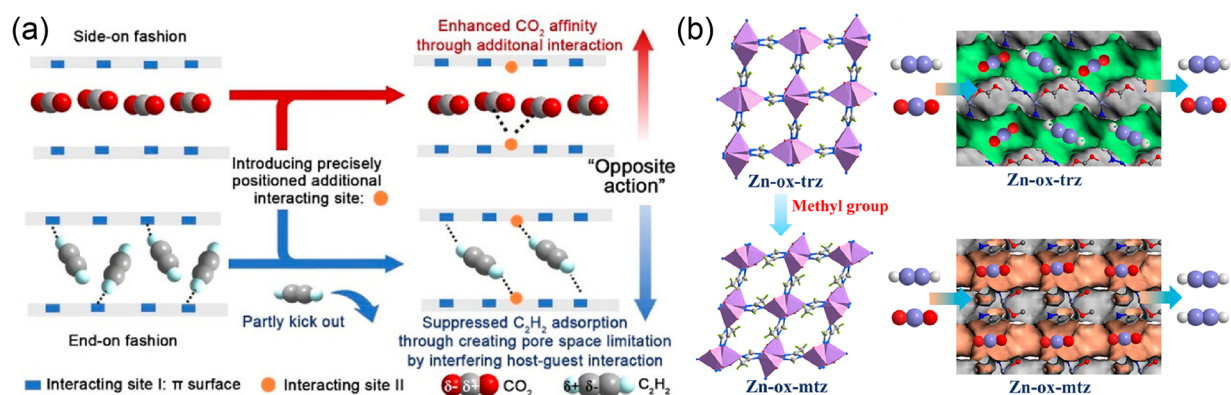


Figure 4. Schematic illustration of the “opposite action” strategy (a, Reproduced with permission from ref 47. Copyright 2021 Wiley-VCH) and immobilizing polar groups (b, Reproduced with permission from ref 49. Copyright 2023 American Chemical Society) within ultramicroporous materials for boosting CO₂/C₂H₂ selectivity.

in a substantial decrease in selectivity for CO₂ while enhancing C₂H₂ adsorption due to the robust interactions between open metal sites and C₂H₂. This suggests that residual solvent molecules can be harnessed to enhance gas adsorption and separation efficiency through host-guest interactions. Similarly, the partially desolvated Cu–F-pymo framework demonstrates an extraordinary selectivity for CO₂ with C₂H₂ rejected (Figure 3).⁴⁶ This inverse molecular sieving effect in partially desolvated Cu–F-pymo arises from residual water molecules within the framework that occupy C₂H₂-preferential sites, impeding C₂H₂ adsorption. Room temperature activation of the framework ensures the retention of these water molecules in the cavities and channels, optimizing the selective capture of CO₂. Further temperature elevation would lead to desorption of water and a decrease in selectivity. The separation efficacy of partially desolvated Cu–F-pymo for CO₂/C₂H₂ (50/50) mixtures was demonstrated by breakthrough experiments, and C₂H₂ can be immediately eluted from the fixed bed with a purity of 99.9%. This suggests that strategic control over residual water in the pore environment, aimed at mitigating C₂H₂ adsorption, is crucial for achieving efficient gas separation. However, implementing partial-activation strategies for selective gas adsorption and separation in industrial applications presents significant challenges. Firstly, achieving uniform activation across extensive batches is crucial. Secondly, maintaining precise control over temperature and humidity is vital for preserving materials’ performance. It is also important to ensure reproducibility, maintain materials stability under diverse operational conditions, and guarantee efficient regeneration of the materials. Furthermore, scaling the process from laboratory to industrial levels, ensuring economic viability against existing technologies, and addressing safety concerns related to specific operational conditions are critical considerations.

Unlike strategies that employ solvent water molecules to occupy the adsorption sites to suppress C₂H₂ adsorption, in the PCP-NH₂-bdc framework,⁴⁷ the incorporation of NH₂ groups strategically modifies the steric arrangement of the recognition sites, enhancing CO₂ affinity while concurrently inhibiting C₂H₂ adsorption due to space limitations and altered interaction sites (Figure 4a). Specifically, the NH₂ groups foster additional electrostatic interactions with CO₂, intensifying its adsorption while simultaneously obstructing the orientation and subsequent adsorption of C₂H₂ molecules at secondary binding sites through hydrogen bonding. This dual-

action mechanism, increasing CO₂ uptake and suppressing C₂H₂ adsorption, exemplifies an “opposite action” strategy within the constrained 1-D channel environment, demonstrating the delicate balance between enhanced functionality and spatial optimization in gas separation technologies.

Strategic integration of additional CO₂ recognition sites has also been successfully applied to Zn-ox-trz (also named CALF-20;⁴⁸ ox = oxalate; trz = 1,2,4-triazole). Zn-ox-trz inherently favors CO₂ adsorption over C₂H₂, yet the expansive pore spaces permit both gases to reach their ideal adsorption configurations, leading to low selectivity (Figure 4b).⁴⁹ To tackle this issue, Zn-ox-mtz (mtz = 3-methyl-1,2,4-triazole) was synthesized by incorporating methyl groups into the prototype Zn-ox-trz. This modification effectively decreases the pore size, allowing for a tighter fit, and introduces a positive charge to the pore surfaces (Figure 4b). The modified pore can enhance van der Waals interactions, courtesy of the –CH₃ groups, and electrostatic attraction towards CO₂, whose quadrupolar nature aligns with the modified framework polarity. This facilitates a selective pore environment that distinguishes and preferentially captures CO₂ with a remarkably high selectivity via multiple noncovalent interactions. In contrast, C₂H₂, bearing an opposing polarization compared to CO₂, faces electrostatic repulsion, leading to its exclusion. The adsorption and separation capabilities were assessed using single-component sorption isotherms and gas mixture breakthrough experiments. It was found that pure C₂H₂ could be effectively recovered by Zn-ox-mtz, achieving productivity of up to 2.66 mol kg^{−1} for an equimolar CO₂/C₂H₂ mixture.

Comprehensive knowledge of crystal engineering and framework chemistry is required to realize specific spatial geometry and chemical regulation of binding sites. This necessitates a thorough understanding of molecules’ intrinsic properties and their interactions with the pore chemistry of porous frameworks.

2.3. Free Metal Sites. Free metal sites refer to metal ions that have more than one coordination position available or that are more accessible due to their specific structures. This implies that the metal site is not just open but also has a certain degree of freedom in terms of movement or flexibility within the framework. Free metal sites within a confined space would endow the porous materials with the inverse CO₂/C₂H₂ adsorption and separation capability.

Different from open metal sites with C₂H₂-preferential sorption behavior, ionic crystals containing free potassium ions

can preferentially adsorb CO₂ with a unique two-step CO₂ isotherm, characterized by a significant hysteresis loop, indicative of a guest-induced phase transition.⁵⁰ This behavior is attributed to the strong interactions between CO₂ molecules and potassium ions, leading to a stepwise lattice expansion and high selectivity for CO₂ over C₂H₂. Computational studies combining Monte Carlo simulations and density functional theory (DFT) calculations have pinpointed the CO₂ binding sites to regions surrounded by organic ligands, where CO₂ molecules directly interact with potassium ions. This interaction underpins the structural flexibility and selectivity of ionic crystals towards CO₂.

NKMOF-9 with [Mn₈₆] nanocages showcases exceptional CO₂ adsorption selectivity driven by the cooperative interplay among pore structure, coordination interactions, and dipole–dipole interactions (Figure 5).⁵¹ Central to its design is a

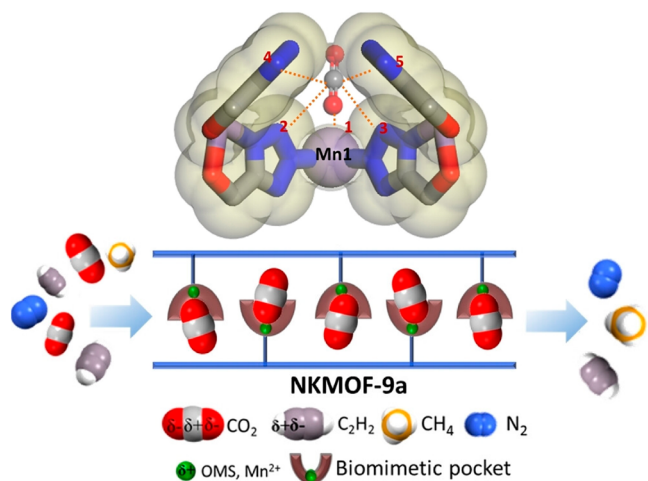


Figure 5. Schematic diagram of CO₂ capture mechanism in the biomimetic pocket of NKMOF-9. Reproduced with permission from ref 51. Copyright 2023 Wiley-VCH.

[Mn₈O₁₂] cubic cluster core linked by tetrazolate anions to form extensive [Mn₈₆] nanocages. Dehydration of Mn-bound H₂O molecules triggers the formation of open metal sites in the cages, bolstering CO₂ affinity. The compact pocket featuring an Mn²⁺ site at the bottom possesses electronegative tetrazolyl rings that line its surface. Combined with the restricted pore window, these characteristics enable the favorable vertical orientation of the trapped CO₂ achieved

through strong Mn···O coordination and dipole–dipole interactions between the CO₂ and surrounding tetrazolyl rings (Figure 5). However, the structural configuration of the pocket would preclude C₂H₂ accommodation, thus allowing NKMOF-9 to selectively capture CO₂ in its uniquely tailored nanocages. When CO₂/C₂H₂ (1/2) mixtures with He serving as the carrier gas (85 % vol %) were passed through the packed column, C₂H₂ was first to be eluted, while CO₂ was retained for a longer duration.

2.4. Flexible Frameworks with Gate-Opening Effect.

Flexible or soft porous frameworks featuring reversible or non-reversible responsive behaviors towards external physical or chemical stimuli have demonstrated significant promise in the realm of gas adsorption and separation, particularly in the context of hydrocarbon separations.^{37,52–54} The flexibility is readily apparent through the distinct stepwise adsorption-desorption curve for target molecules, which is accompanied by the switchable structural dynamics. Benefiting from the specific flexibility, highly efficient reverse CO₂–C₂H₂ adsorption and separation can be realized. Among them, a common mechanism is observed, wherein CO₂ can effectively open narrow pores or gates through strong interactions, leading to high uptakes. However, C₂H₂ faces high energy barriers and cannot achieve the same result.

[Mn(bdc)(dpe)] (H₂bdc = 1,4-benzenedicarboxylic acid; dpe = 1,2-di(4-pyridyl)ethylene) with zero-dimensional pores displays a pronounced discriminatory gated effect, favoring the selective adsorption of CO₂ over C₂H₂ (Figure 6a).⁵⁵ The flexible gate in [Mn(bdc)(dpe)] is constrained by two phenylene rings, and the electrostatic potential established within the gate can effectively interact with the quadrupole moment of CO₂ when it adopts an end-on orientation. This interaction facilitates a gradual and smooth sorption process, causing CO₂ molecules to align parallel to the phenylene rings. Conversely, the optimal C₂H₂ sorption configuration situates C₂H₂ molecules perpendicular to phenylene rings, maximizing electrostatic interactions (C≡H···π). This C₂H₂ sorption configuration requires a high energy input to conquer the framework dynamics, resulting in the pore expansion for C₂H₂ sorption only at high pressures. In a similar vein, [Co(3,5-pdc)dpg]_n (3,5-pdc = 3,5-pyridinedicarboxylic acid; dpg = meso-α,β-di(4-pyridyl) glycol) features a densely interdigitated 2D layered structure characterized by a discriminative gate mechanism for CO₂ recognition (Figure 6b).⁵⁶ The gate is constrained by pyridyl rings, akin to what is observed in [Mn(bdc)(dpe)]. When exposed to CO₂ stimuli, the initially

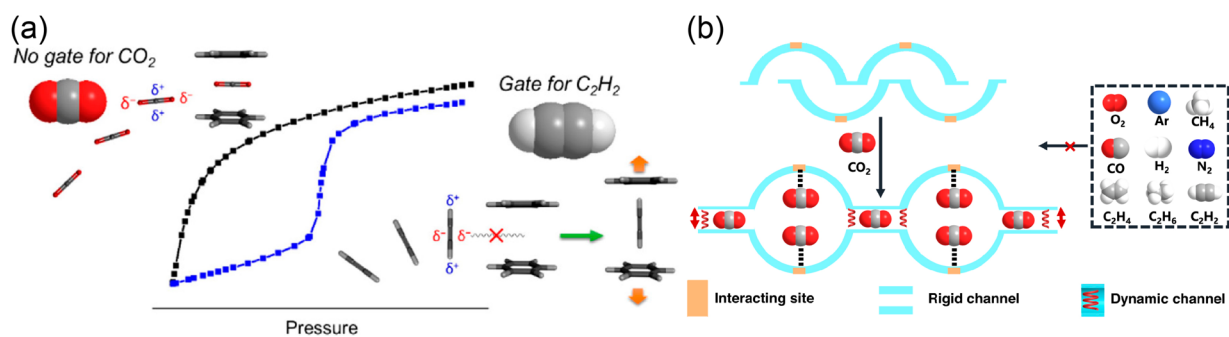


Figure 6. (a) CO₂ and C₂H₂ sorption mechanisms in [Mn(bdc)(dpe)]. Reproduced with permission from ref 55. Copyright 2016 American Chemical Society. (b) [Co(3,5-pdc)dpg]_n with restricted narrow corrugated channels with exclusive discrimination gating for CO₂ sorption. Reproduced with permission from ref 56. Copyright 2023 Springer Nature.

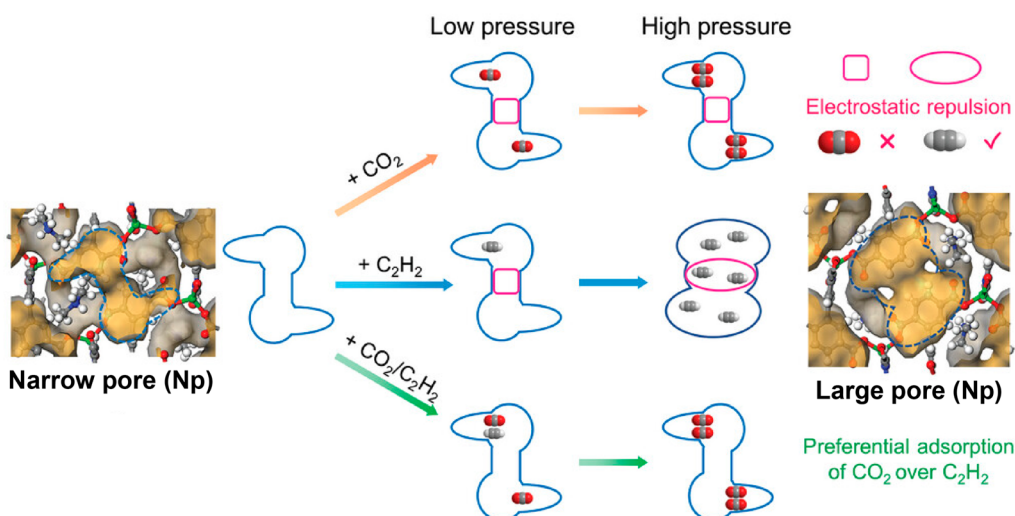


Figure 7. Discriminatory gate-opening effect in Zn-DPNA with loading and co-adsorption process toward CO₂ and C₂H₂. Reproduced with permission from ref 60. Copyright 2023 Wiley-VCH.

packed 2D interdigitated sublayers undergo distortion and displacement, transitioning into an open-phase structure. This transformation gives rise to 1D narrow-corrugated channels with large cavities ($7.2 \times 3.8 \text{ \AA}^2$) connected by ultrasmall windows ($3.8 \times 3.3 \text{ \AA}^2$). These dimensions are perfectly matched to accommodate CO₂, effectively sandwiching CO₂ between two pyrazine rings, and the narrow windows can facilitate CO₂ diffusion while blocking other gas molecules.

Materials featuring pyridyl or benzene rings confined gates exhibit regulated flexibility, enabling effective CO₂ recognition driven by the rotation of responsive linkers upon CO₂ adsorption. After a detailed analysis of structure-property relationships, it is evident that the hydrogen atoms bearing a positive charge on the pyridyl or benzene rings are responsible for the initially responsive gate-opening behavior. This characteristic, along with the narrow pore space, enables CO₂ molecules to form perpendicular interactions to the gates through O \cdots H interactions. Once aligned perpendicularly, the gates open, allowing CO₂ molecules to be securely trapped into the framework through $\pi\cdots\pi$ stacking interactions.

Another case is PMOF-1 ($[\text{Zn}_3(\text{CPB})_2(\text{BDC})_4(\text{OH})_2]$; CPB = 1-(4-carboxyphenyl)-4,4'-bipyridinium; BDC = 1,4-benzenedicarboxylate), which shows accessible pore windows controlled by H atoms from the linkers and μ_2 -bridging OH.⁵⁷ This characteristic equips PMOF-1 with the repulsion behavior for C₂H₂ but in favor of CO₂ adsorption and diffusion, leading to excellent inverse CO₂/C₂H₂ separation performance. When CO₂ was gradually loaded into PMOF-1, a sharp jump of sorption isotherm was observed. Additionally, the interannular dihedral of the bipyridinium groups tends to become more planar with CO₂ captured. CPB is photoactive, and the reduction of the 4,4'-bipyridinium group of CPB upon irradiation eliminates the gate-opening behavior for CO₂. This results in increased CO₂ uptake and decreased C₂H₂ adsorption. The key to enhancing CO₂ sorption lies in the inclusion of radical π moieties through the photoinduced electron-transfer (PIET) process, which increases interactions between CO₂ and framework while preserving the intrinsic electric field gradient. The decrease in C₂H₂ adsorption was achieved by weakening hydrogen bonds around C₂H₂, especially from carboxylate O atoms in the BDC ligand. It is reasonable to infer that structural regulation by PIET process

opens the “gate” in advance and eliminates the gate-opening effect. This work shows that introducing a radical to one π linker of the framework can enhance adsorption ability of the π molecule CO₂.

Unlike the above materials with flexible structures that selectively adsorb CO₂ while excluding C₂H₂, other materials can permit both CO₂ and C₂H₂ to enter the pore channels. However, only CO₂ can trigger switchable structural changes. Especially, in the case of Co(HL^{dc}) with different kinds of pore channels, CO₂ adsorption uniquely occurred in two distinct consecutive steps, forming a two-step isotherm loop.⁵⁸ By contrast, type-I profile for C₂H₂ was observed without any step-like features. The selective CO₂ sorption is believed to be due to the flexible entry points controlled by the rotatable pyridyl rings. Compared with C₂H₂, CO₂ can smoothly penetrate and subsequently initiate the gate-opening transition through strong CO₂-framework interactions, accompanied by gate-rotation transition and pore volume expansion from narrow pore (np) to large pore (lp). This resulted in a significantly higher adsorption capacity for CO₂ compared to C₂H₂. Likewise, $[\text{Zn}(\text{odip})_{0.5}(\text{bpe})_{0.5}(\text{CH}_3\text{OH})]$ (H₄odip = 5,5'-oxydiisophthalic acid; bpe = 1,2-bi(4-pyridyl)ethylene) with abundant accessible ether O sites within its channels also shows a flexible framework that preferentially responds to CO₂ in preference to hydrocarbons.⁵⁹ The ability to undergo a gate-opening process when interacting with CO₂, as opposed to hydrocarbons, imparted it with exceptional inverse CO₂/C₂H₂ separation capability. Molecular simulations suggested that the preferential and enhanced CO₂ adsorption was likely due to the multiple interactions between CO₂ molecules and the framework. However, from the structural point of view, the observed flexibility within this densely packed structure may arise from ligand rotations. These rotations, stimulated by the strong CO₂-framework interactions, would effectively increase the pore volume, thereby facilitating CO₂ diffusion and accommodating higher CO₂ adsorption capacity.

The three-dimensional framework, $(\text{Me}_2\text{NH}_2)[\text{Zn}(\text{DPNA})]$ (H₃DPNA = 5-(2',5'-dicarboxylphenyl)nicotinic acid) features cages along its channels, reinforced by Me₂NH₂⁺ ions (Figure 7).⁶⁰ Zn-DPNA exhibits a discriminatory gate-opening effect for C₂H₂ while maintaining a typical type-I isotherm for CO₂, reflecting stronger interactions between CO₂ and Zn-DPNA

(Figure 7). At low pressures, the initial adsorption of C_2H_2 occurs gradually, suggesting restricted pore accessibility. This is succeeded by a significant gate-opening effect, resulting in a stepped increase in C_2H_2 uptake. Notably, the C_2H_2 saturation capacity surpasses that of CO_2 . Molecular simulations suggested that CO_2 would form strong electrostatic bonds—mainly hydrogen bonds—with $Me_2NH_2^+$ ions, thus immobilizing these ions and the surrounding hydrogen-bond network and inhibiting the framework dynamics. Electrostatic potential analyses in np and lp phases, before and after C_2H_2 adsorption, revealed that the restricted space around the four hydrogen atoms located between the two DPNA $^{3-}$ linkers and the $Me_2NH_2^+$ ions exhibited a pronounced positive potential, aligning well with the quadrupole moment of C_2H_2 , thus facilitating its further diffusion and uptake. CO_2 , however, was repelled and thus unable to enter these restricted spaces. When CO_2 and C_2H_2 enter the np together, due to the higher affinity for CO_2 , CO_2 will be preferentially adsorbed, and negligible C_2H_2 uptake can be found.

Despite significant progress in the development of flexible frameworks for gas adsorption, the discovery of most flexible porous frameworks has been largely serendipitous, and their true separation capabilities for gas mixtures have not been fully verified. Predicting switchable features and deliberately engineering new flexible MOFs remains a formidable task in materials science. Molecular simulations, which are pivotal for probing the flexibility of these frameworks, may not always reveal the true underlying mechanisms due to the intricacies of host-guest interactions and the inherent complexity of the framework structures. These complexities can lead to unreliable conclusions regarding the behavior of the materials. Moreover, in situ characterization, particularly during the adsorption process, is critical for a deeper understanding of flexible behavior. Such real-time characterization techniques can provide valuable insights into the dynamic structural changes that occur upon guest molecule adsorption, which are often critical to the material's functionality. Considering these challenges, future developments in advanced simulation methods, sophisticated in situ characterization techniques, especially during the adsorption process, and systematic design principles are highly demanded. These areas are critical for propelling the field forward and realizing the full potential of flexible porous materials in applications such as gas storage and separation.

2.5. Electrostatic Potential Matching. The intrinsic difference between CO_2 and C_2H_2 is rooted in their respective molecular configurations and the consequent electrostatic profiles. Exploiting these intrinsic differences, materials with suitable pore architecture and electrostatic potential can be engineered for the specific and efficient recognition and capture of CO_2 via an electrostatic potential matching mechanism, thereby enabling the effective purification of C_2H_2 .

The MUF-16 framework demonstrates CO_2 -selective adsorption due to its pore dimensions being precisely tuned to the size of CO_2 , fostering multiple non-covalent interactions that envelop the guest molecules.⁶¹ Furthermore, the favorable selectivity is amplified by the complementary relationship between the electric quadrupole of CO_2 and the polarized surface of the MUF-16 pores, which aligns and orients the CO_2 molecules efficiently within the channels (Figure 8a). Conversely, the reversed quadrupole moment of other gases like C_2H_2 led to their electrostatic repulsion, enhancing CO_2 selectivity due to the contrasting electrostatic potential.

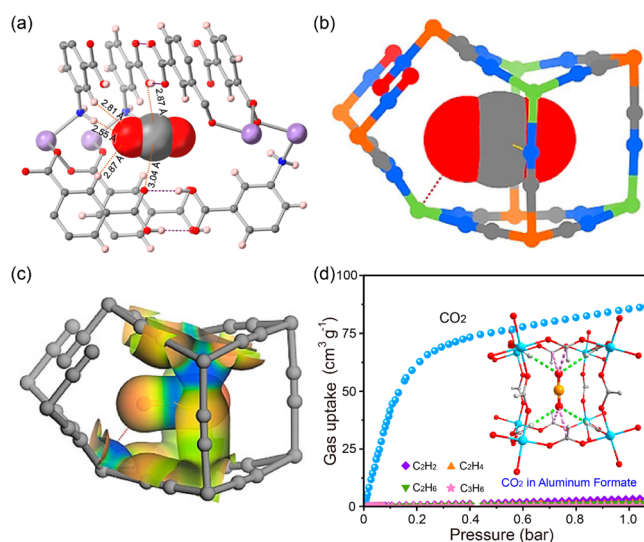


Figure 8. (a) The binding configuration of CO_2 molecules in MUF-16. Reproduced with permission from ref 61. Copyright 2021 Springer Nature. (b and c) CO_2 -loaded Cd-NP structure obtained by neutron diffraction and electrostatic potential (ESP) of CO_2 -loaded Cd-NP. Reproduced with permission from ref 62. Copyright 2021 Wiley-VCH. (d) CO_2 recognition mechanism and sorption isotherms of CO_2 and hydrocarbons of $Al(HCOO)_3$. Reproduced with permission from ref 63. Copyright 2023 American Chemical Society.

Analogously, selective adsorption of CO_2 over C_2H_2 is achieved in Cd-NP (cadmium nitroprusside) through a confinement effect within a complementary electrostatic potential that facilitates molecular quadrupole moment recognition (Figure 8b).⁶² The precise electrostatic compatibility of CO_2 with the pore structure allows for a head-on orientation towards the Cd centers (Figure 8b) and enhanced host-guest interactions (Figure 8c). In contrast, the pore environment proves electrostatically unsuitable for C_2H_2 adsorption.

The above CO_2 selective recognition mechanism demonstrates the importance of the confinement effect in appropriate pores and electrostatic potential complementarity of the pore surface in optimizing gas recognition and separation performance. Inspired by the intrinsic difference in electron distributions, the electropositive hydrogen-confined pore cavities of aluminum formate, $Al(HCOO)_3$, present it as an excellent candidate for the separation of CO_2 from hydrocarbon mixtures, particularly for CO_2/C_2H_2 separations.⁶³ These pore cavities confined by H atoms are distinguished by their electropositive surfaces and meticulously calibrated dimensions, creating an idealized pore chemistry that exclusively resonates with CO_2 molecules, leveraging molecular quadrupole moment recognition and specific O recognition mechanism (Figure 8d). This deliberate design of pore interactions ensured that other hydrocarbons were consistently and effectively excluded from adsorption. The exceptional ability to selectively capture CO_2 from mixtures containing C_2H_2 and hydrocarbons was demonstrated through breakthrough experiments. This selective recognition and high separation efficiency result from both the pore sieving and confinement effects and the electrostatically complementary nature of the pore surface.

HOF-FJU-88, a two-dimensional HOF featuring a pore size of approximately 7.6 Å, where bilayers exhibit slipped AA stacking facilitated by weak $\pi \cdots \pi$ interactions between pyrazole

units.⁶⁴ This configuration allows for the selective adsorption of CO₂ molecules, which are stabilized within the 2D layers by multiple weak hydrogen bonds to three neighboring hydrogen atoms from pyrazole rings. The adsorption capacity is enhanced through the alignment of electrostatic potential. Specifically, the positive electrostatic potential of the carbon atom in CO₂ matches the negative potential of the nitrogen atom in the pyridine ring from an adjacent layer, thereby creating complementary electrostatic potential cavities. This intricate arrangement, however, prevents the perpendicular intercalation of C₂H₂ molecules due to spatial and electrostatic constraints. The selective adsorption mechanism comes from the electrostatic potential matching between the negative electrostatic potential of CO₂ oxygen atoms and the positive potential of hydrogen atoms on the pyrazole, also indicative of the O recognition mechanism critical for CO₂ capture.

Constructing pore chemistry within limited channels can selectively match the electrostatic potential of CO₂ by tuning electron distributions in porous materials. The introduction of a Ce(IV) ion featuring a low-energy vacant 4f orbital, coupled with tetrafluoroterephthalate ligands containing electron-withdrawing fluorine atoms, provides the opportunity to adjust electron distribution within ultramicroporous Ce(IV)-MIL-140-4F via ligand-to-metal charge transfer interactions.⁴⁴ This behavior gives rise to an optimal pore environment surrounded by four F atoms that perfectly match CO₂ via the F...C interactions, yielding significant selectivity over C₂H₂. This is indicated by the results from single-component CO₂ and C₂H₂ adsorption and breakthrough experiments for CO₂/C₂H₂ mixtures. In contrast, the Zr(IV) analogue, Zr(IV)-MIL-140-4F, only displays a conventional C₂H₂-selective adsorption behavior. This opens new avenues to tune the pore chemistry in porous materials.

Overall, in the case of gases with similar molecular sizes and shapes, the electric properties of the pore surface and the pore structure provide an alternative approach to molecular recognition. The appropriate pore size and the confined effect are instrumental in maximizing interactions with the preferred guest molecules, optimizing the sieving effect for gas separation. These insights are anticipated to inform the future rational design of ultramicroporous materials for complex gas separation tasks.

3. PACKING OF GUEST MOLECULES

Unlike thermodynamic adsorption, which can be elucidated through molecular simulations, our comprehension of guest-guest interactions within confined nanopores remains limited despite the crucial role these interactions play in determining molecular selectivity and capacity.^{65–69} The complexity of the challenge stems from the inherent difficulty in directly predicting, observing, or comprehending these interactions and guest clusters within confined nanovoids. Therefore, in situ characterization techniques are usually essential to advance our knowledge in this area.

Recently, the temperature-dependent modulation of guest-cluster geometries for the normal and inverse selective adsorption and separation of CO₂ and C₂H₂ has been reported within robust ultramicroporous CUK-1 (Figure 9).⁷⁰ At ambient temperature, CO₂ and C₂H₂ exhibit intersecting isotherms. The well-packed one-dimensional CO₂ chains featuring T-shaped dimers resulted in higher crystallographic occupancy and enhanced CO₂ capacity. However, the stronger host-guest interactions between C₂H₂ and the framework led

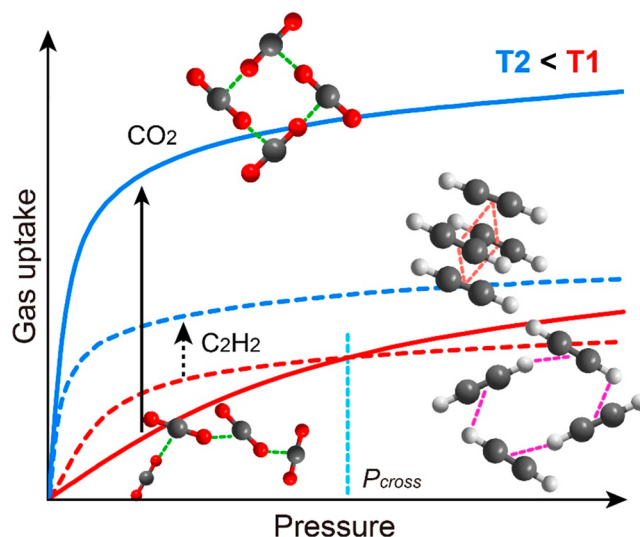


Figure 9. Schematic representation of the temperature-dependent guest-cluster packing geometries for the normal and inverse adsorption behavior. Reproduced with permission from ref 70. Copyright 2023 Springer Nature.

to a preference for C₂H₂ adsorption over CO₂. Upon lowering the temperature, CO₂ clusters would rearrange into head-to-center quasi-T-shaped tetramer configurations and exhibit significantly stronger host-guest interactions with CUK-1. On the other hand, the tetramer clusters of C₂H₂—originally packed through multiple $\pi_{C_2H_2} \cdots H_{C_2H_2}$ interactions—underwent a transformation to be packed via $\pi_{C_2H_2} \cdots \pi_{C_2H_2}$ interactions, with only slight changes in their packing density. This rearrangement in the packing geometry of the guest clusters gives rise to a pronounced increase in CO₂ capacity at lower pressures, outperforming that of C₂H₂ and leading to a reversal in sorption preference. Notably, the final CO₂ packing density approaches the density of dry ice with a calculated value of 1.40 g cm⁻³. Temperature-dependent sorption reverse was also found in SNU-334; however, the reason was not evaluated.⁷¹ This observation of temperature-induced guest-guest packing geometry rearrangement within a porous material is unprecedented and marks a significant milestone in the field of gas adsorption and separation.

4. CHEMISORPTION

Chemisorption, distinct from physical adsorption, utilizes the acidic properties of CO₂ for its selective reversible capture by forming chemical bonds. This process is commonly used for extracting CO₂ from emissions like flue gases, employing aqueous amine solutions. The interaction between amino groups and CO₂ predominantly occurs through Lewis acid–base reactions, wherein the amino groups serve as nucleophiles that donate electron pairs to the electrophilic carbon atom of CO₂. This specific interaction mechanism facilitates the selective capture of CO₂, as the amino groups in amine solutions or functionalized materials exhibit a stronger affinity for CO₂ compared to other gases. This affinity is primarily due to the formation of carbamates or bicarbonate complexes, which provides a targeted approach for CO₂ separation.⁷²

Inspired by this, the attachment of alkyldiamines to coordinatively unsaturated metal sites lining the pores of selected MOFs has also been demonstrated as a simple methodology for increasing low-pressure CO₂ adsorption

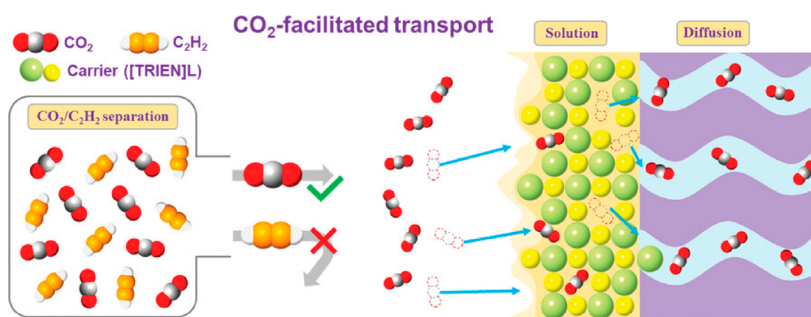


Figure 10. Schematic illustration of the proposed BUCT-C19 composite and its separation process. Reproduced with permission from ref 76. Copyright 2023 Wiley-VCH.

selectivity and capacity. For example, the diamine- $\text{Mg}_2(\text{dobpdc})$ demonstrates effective CO_2 capture capabilities at low pressures, attributed to a distinct CO_2 insertion mechanism arising from its unique chemisorption properties.⁷³ When CO_2 penetrated into the pore channels, the amines would grasp CO_2 by reorganizing the amines into well-ordered chains of ammonium carbamate. This specific chemisorptive recognition via strong acid–base interactions for CO_2 gives rise to diamine- $\text{Mg}_2(\text{dobpdc})$ with CO_2 preferential sorption ability over C_2H_2 . Similarly, MOF-808-ARG, obtained by anchoring L-arginine (ARG) on MOF-808, shows preferential CO_2 sorption over C_2H_2 due to the chemisorption of amino groups for CO_2 .⁷⁴ Moreover, the alkalinity of ARG would be enhanced by moisture to further facilitate its affinity toward acidic CO_2 . Due to the moisture-boosted effect, both static adsorption capacity and dynamic adsorption capacity of CO_2 were increased, while C_2H_2 sorption was significantly suppressed. The moisture-boosted CO_2 adsorption mechanism is that water can change the CO_2 adsorption behavior of MOF-808-ARG, from the formation of carbamate at dry conditions to bicarbonate at wet conditions where the formation of the latter one is both thermodynamically and kinetically favored.

Similar to the reversible chemisorption between CO_2 and amino groups in specific molecules, the amino-rich functionalized ionic liquids (ILs) were also reported to be good solvents for CO_2 adsorption or absorption via the chemical reaction.⁷⁵ Benefiting from this, BUCT-C19, which was constructed with a CO_2 -facilitated transport layer (an amino-rich functionalized ILs) on ZIF-8, shows CO_2 -selective sorption over C_2H_2 (Figure 10).⁷⁶ The IL shows an excellent solubility for CO_2 via the reversible chemical absorption, realizing the efficient recognition and solution of CO_2 in the composite while excluding C_2H_2 . Multi-scale simulations revealed that the preferential retention of CO_2 compared to C_2H_2 can be attributed to the CO_2 -facilitated transport layer composed of ILs in BUCT-C19, operating via a solution-diffusion mechanism. This mechanism, albeit with a focus on chemisorption, mirrors the adsorption or absorption processes observed in porous liquids and membrane-based separations. However, the respective contributions of chemisorption and physisorption to CO_2 capture were not evaluated. Furthermore, the amount of ILs loaded onto ZIF-8 was not provided either. The composites formed by porous materials and ILs have presented great potential in different applications. However, the reusability and regeneration of composites are still long-term challenges that should be addressed in industrial applications.

Apart from chemisorption involving amino groups for CO_2 capture, chemisorption can also occur when utilizing basic hydroxyl groups and/or anions as sorption sites in porous materials by forming carbonate or bicarbonate. Typically, cyclodextrin-based frameworks, known as CD-MOFs, are characterized by their hydrophilic nature due to the presence of free primary and secondary hydroxyl groups on the external surface of the cyclodextrin cavities.⁷⁷ The uncoordinated hydroxyl groups within the ligand possess weak nucleophilic properties, enabling them to engage in reversible interactions with CO_2 . Moreover, hydroxyl anions act as the primary binding sites. The basicity of these anions within the porous channels tends to surpass that of the hydroxyl groups on cyclodextrin, leading to stronger interactions between hydroxyl anions and CO_2 . Consequently, this chemisorption process may not be entirely reversible, leading to a slight reduction in separation performance. The chemisorption process enhances the CO_2 capture performance of CD-MOFs in comparison to C_2H_2 .

Chemisorption can enhance the selective adsorption of CO_2 due to the specific formation of chemical bonds. However, the regeneration process would require a higher energy input compared to physical adsorption to release the adsorbed CO_2 and refresh the material for further use. When evaluating pressure swing adsorption (PSA) and temperature swing adsorption (TSA) in this context, each method offers distinct advantages and challenges for CO_2 capture. PSA, which operates by varying pressure, is more suited to physical adsorption processes and is generally less energy-intensive during regeneration. In contrast, TSA, which relies on temperature changes to regenerate the adsorbent, is particularly effective for systems dominated by chemisorption. While TSA can offer higher selectivity and capacity for CO_2 capture, it also necessitates adsorbents with exceptional thermal stability and anti-oxidation properties. Thermal stability is crucial because the adsorbents must withstand repeated thermal cycling without degradation, ensuring long-term operation without loss of efficacy. Moreover, the anti-oxidation characteristic of the adsorbents used in TSA processes, especially those functionalized with amino groups, becomes particularly important as oxidative degradation can significantly reduce the lifespan and performance of the adsorbents. Therefore, materials used in TSA must be designed to resist oxidation at the high temperatures required for chemisorption regeneration, maintaining their structure and functionality over many cycles. This emphasizes the need for specialized materials that can meet these stringent requirements, highlighting the trade-offs between the efficiency of CO_2 capture

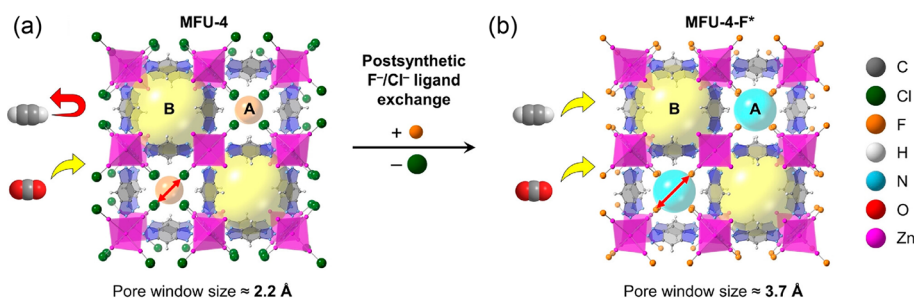


Figure 11. MFU-4 (a) and MFU-4-F (b) with transparent spheres representing the cavities of A- and B-type pores showing different CO₂/C₂H₂ adsorption and separation behaviors. Reproduced with permission from ref 79. Copyright 2023 Wiley-VCH.

via chemisorption and the operational demands of the regeneration process.

5. KINETIC SEPARATION

Adjusting preferential binding sites within porous materials can induce thermodynamic adsorption, effective even when pore sizes are larger than the molecular size of adsorbates. Kinetic separation, in contrast, is achieved by fine-tuning pore sizes to closely match those of the gas molecules in question. Molecules with faster diffusion rates tend to occupy the pores initially, and subsequent interactions with the host material facilitate the selective retention of these rapidly moving molecules while allowing slower ones to pass through. This separation method is predicated on the differential diffusion rates of the guest molecules. However, it is worth noting that such kinetic separation is highly sensitive to variations in temperature and pressure.

ZU-610a, with contracted pore size achieved through heat treatment of ZU-610, demonstrates CO₂-selective adsorption over C₂H₂ through a kinetically controlled adsorption and diffusion process.⁷⁸ Notably, C₂H₂ requires a much longer time to reach sorption equilibrium in both ZU-610a and ZU-610, indicating higher diffusion barriers for C₂H₂. The preference for C₂H₂ sorption in ZU-610 is primarily governed by thermodynamic effects. While it is suggested that the pore size effect plays a significant role in the kinetic separation of CO₂ from C₂H₂ in ZU-610a, a closer examination of the crystal structures of ZU-610 and ZU-610a reveals that sulfonic anions are buried within the corners of the pore channels viewed from *c*-direction. The anions cannot be in direct contact with guest molecules. In contrast, the positively charged hydrogen atoms that line the pore surfaces and confine the pore channels should be the main facilitators of CO₂ sorption, as they attract CO₂ while repelling C₂H₂ diffusion.

In contrast to the pore windows confined by positively charged atoms, the excellent inverse CO₂/C₂H₂ separation via kinetic sieving mechanism was also reported by using MFU-4 (Zn₅Cl₄(bbta)₃; bbta = benzo-1,2,4,5-bistriazolate) with negative Cl atoms confined pore channels (Figure 11a).⁷⁹ The diffusion of C₂H₂ is notably reduced in MFU-4-F with a pore size of 3.7 Å, achieved through the substitution of Cl atoms with F atoms in MFU-4 (Figure 11b). This finally gives rise to MFU-4-F with normal C₂H₂-selective sorption behavior. In MUF-4, though C₂H₂ can potentially approach the pores vertically via H···Cl interactions, the pore window (2.2 Å) and diameter (3.9 Å) are too small to accommodate C₂H₂, especially given the triple bond in C₂H₂, which is strongly repelled by four Cl atoms. In contrast, CO₂ with the positively charged carbon center would enter the pores in parallel driven

by strong C_{co2}(δ+)···Cl(δ-) interactions, resulting in high CO₂ diffusivity. The expanded pore apertures in MFU-4-F create sufficient space for C₂H₂ to be adsorbed through H···F interactions. This research underscores the critical importance of having confined spaces in close proximity to guest molecules as a prerequisite for achieving or fine-tuning kinetic diffusion behaviors.

A similar concept of negative-atom-controlled pore windows has also been observed in an *ε*-Keggin polyoxometalate (POM)-based zeolitic octahedral metal oxide.⁸⁰ This kind of materials allows for precise tuning of micropore sizes at a subatomic level by altering the cations and linkers (where metal ions serve as the linkers). The cavities of these materials are surrounded by ten POM units, each connected by linkers. The pore windows, with a diameter of ca. 3 Å, are formed by six oxygen atoms. Using Mg-NH₄-ZM (Mg²⁺-exchanged ammonium zinc molybdate) as an example, molecular simulations and the experimental isosteric heat of adsorption suggest that this material exhibits almost indistinguishable thermodynamic affinities for CO₂ and C₂H₂, implying that the separation of CO₂/C₂H₂ is not primarily governed by electrostatic interactions between the molecules and the frameworks. Based on the simulated adsorption transition states, there are six close repulsive interactions for C of C₂H₂ from the O atoms on the pore windows, whereas fewer repulsive interactions occur for CO₂. Furthermore, the much lower activation energy for CO₂ indicates CO₂ can pass through the pore windows easily, while C₂H₂ is more strongly repelled. However, it is worth noting that the kinetic sorption behaviors of CO₂ and C₂H₂ on this material have not been investigated experimentally.

Currently, engineering this kind of kinetic selectivity in porous materials for gas separation is an area with limited precedent and poses a significant challenge. A fundamental challenge is the lack of a comprehensive understanding of the kinetic mechanisms at play. This includes the rate at which CO₂ and C₂H₂ molecules are adsorbed and desorbed on various adsorbents.

6. THERMODYNAMIC-KINETIC SYNERGISTIC SEPARATION

Leveraging the synergistic effects of thermodynamics and kinetics in adsorptive separation offers unparalleled selectivity and efficiency, enabling rapid and specific molecular separation while conserving energy.^{81–84} This dual approach not only optimizes the process by reducing operational costs and enhancing throughput but also aligns with environmental sustainability goals, particularly in applications like carbon

Table 2. Summary of Adsorption Performance of CO₂-Selective Materials

Materials	CO ₂ uptake (cm ³ g ⁻¹)	C ₂ H ₂ uptake (cm ³ g ⁻¹)	Temp (K)	CO ₂ /C ₂ H ₂ uptake ratio	IAST selectivity	Ref
SIFSIX-3-Ni	60.5	73.9	298	0.8	7.5	42
Tm-OH-bdc	130.6	47	298	2.8	18.2	45
Cu-F-pymo	26.6	2.3	298	11.6	>10 ⁵	46
PCP-NH ₂ -ipa	72	43.7	298	1.66	6.4	47
Zn-ox-mtz	68.8	5.5	298	12.6	1046.9	49
NKMOF-9	46.4	2.8	298	16.8	241.9	51
[Mn(bdc)(dpe)]	46.8	7.3	273	6.4	8.8	55
PMOF-1	53.3	7.5	273	7.1	694	57
[Zn(odip) _{0.5} (bpe) _{0.5} (CH ₃ OH)]	118.7	29.8	298	3	13.2	59
Zn-DPNA	52.7	62	298		11.9 ^a	60
MUF-16	47.8	4.0	298	12	510	61
Cd-NP	58.0	9.7	298	6.0	85	62
Al(HCOO) ₃	86.2	3.3	298	26.1	6.5×10 ⁵	63
HOF-FJU-88	59.6	6.28	296	9.5	1894	64
Ce(IV)-MIL-140-4F	110.3	41.5	298	2.7	44	44
Co-CUK-1	170	119	233		9.5	70
MOF-808-ARG ^b	71	7.8	298		71	74
BUCT-C19	40.3	6.7	298		10700	76
CD-MOF-2	59.6	45.5	298	1.3	12.8	77
ZU-610a	33.8	2.7	298	12.5	207	78
MFU-4	71		300		3363 ^c	79
Mg-NH ₄ -ZM	70	9.9	298		16.1	80
Y-bptc	55	26.2	298	2.1	4.1	85

^aAt low pressure. ^bAt wet condition for CO₂/C₂H₂ (1/2). ^cKinetic selectivity

capture. It represents a sophisticated, adaptable solution that can meet a wide array of industrial separation challenges.

The Y-bptc framework demonstrates an effective separation of CO₂/C₂H₂ through synergistic thermodynamic and kinetic effects.⁸⁵ Its distinct cage-like structure, composed of small interconnecting windows, possesses a high adsorption affinity for CO₂ while simultaneously hindering the adsorptive diffusion of C₂H₂. The CO₂ molecules were selectively adsorbed primarily due to the specific interaction with μ₃-OH groups that facilitate H···O interactions for CO₂. This interaction with strategically sized windows in the cage-like structure ensures both thermodynamic affinity and kinetic accessibility for CO₂. This favorable combination leads to selective and preferential CO₂ adsorption, effectively impeding C₂H₂ diffusion and ultimately enhancing separation efficiency, as evidenced by breakthrough experiments with C₂H₂ productivity of 1.52 mmol g⁻¹ obtained (purity higher than 99%). However, the influence of cations within the pore channels on this selective adsorption behavior has not been fully explored.

Implementing this equilibrium-kinetic synergetic effect for separation is challenging and usually extends beyond the scope of crystal engineering. It requires an interdisciplinary approach that combines insights from materials science, surface chemistry, molecular dynamics, and even computational modeling to understand and manipulate the complex interactions at play within adsorbent materials. Designing systems that effectively utilize both thermodynamic and kinetic principles for selective adsorption demands a nuanced understanding of molecular behavior in confined spaces, as well as the ability to engineer specific surface properties and pore architectures at the nanoscale.

The adsorption performance of CO₂-selective materials is summarized in Table 2. This table clearly presents the adsorption and separation performance of various materials.

7. CONCLUSION AND OUTLOOK

In summary, we have systematically examined the intricate landscape of CO₂-selective recognition mechanisms in the context of CO₂/C₂H₂ reverse adsorption using porous materials. Our in-depth analysis highlights that the efficiency of CO₂ recognition from C₂H₂ is contingent upon a complex interplay of factors, including pore size and shape, framework flexibility, functional group interactions, and the dynamic behavior of adsorbents under operational conditions. It is evident that achieving selectivity is not merely a function of the physical sieving effect but rather a result of the precise tuning of adsorbent properties, especially the pore chemistry, to leverage the subtle differences in the physicochemical properties of CO₂ and C₂H₂. This underscores the critical need for a deeper dissection and comprehension of the mechanisms behind CO₂-selective recognition within these materials. The nuanced understanding of molecular interactions provided by current studies illuminates the pathway toward designing advanced porous materials for molecular recognition.

Looking forward, the field is poised on the cusp of significant breakthroughs, with potential advancements predicated on several key areas:

- 1) The creation of novel materials, especially those featuring adaptable pore environments and augmented chemical functionalities to improve CO₂ affinity, is of paramount importance and highly demanded. However, the state of the field has not yet fully converged on an optimal set of design principles for such advancements. This indicates a substantial gap between existing capabilities and the desired targets for CO₂ adsorption efficacy.
- 2) The exploration of molecular recognition mechanisms holds substantial significance for guiding the development of new materials through artificial intelligence (AI)

and machine learning. However, it is challenging to harness AI and deep learning to discover novel separation and recognition mechanisms. These advanced computational approaches require extensive datasets and a deep understanding of material interactions, which are often complex and not fully understood. In the context of CO₂/C₂H₂ reverse adsorption and separation, the integration of AI and deep learning could be transformative, potentially accelerating the design of porous materials with precise pore structures and functionalities tailored for specific gas separations. Nonetheless, the intricacy of gas adsorption processes and the subtle interplay of molecular interactions present substantial hurdles. To bridge the gap between the current state of porous materials design and the potential offered by AI and deep learning, a concerted effort to compile high-quality, detailed datasets are essential.

- 3) As environmental considerations become increasingly paramount, the development of materials capable of operating under humid conditions or harsh conditions—conditions that closely mirror industrial settings—without compromising selectivity or capacity becomes imperative. Yet, the assessment of such materials for CO₂/C₂H₂ reverse adsorption separation under these realistic conditions remains incomplete and warrants a more thorough investigation. A multi-disciplinary approach that bridges the gap between laboratory research and industrial needs is critical for the successful implementation of these technologies in real-world applications.
- 4) Combining kinetic separation techniques with other technologies, such as membrane separation,⁸⁶ has the potential to offer a fertile ground for innovation in industrial-scale separations. However, this integration hinges on a comprehensive understanding of the kinetic adsorption separation behavior, an area where current knowledge remains incomplete. At present, efforts are needed to deepen our grasp of the dynamic interactions and adsorption rates of different gases, particularly in complex mixtures like CO₂/C₂H₂. Addressing this knowledge gap is essential for effectively merging kinetic separation with complementary technologies and achieving optimal performance in gas separation applications.
- 5) The equilibrium between performance and energy for regeneration and cost remains and needs a critical focus for ongoing research. Enhancing this balance is essential for advancing carbon capture and gas separation technologies that are both environmentally and economically sustainable.
- 6) Bridging the gap to commercialization. The journey from laboratory discovery to commercial application embodies numerous challenges that must be addressed to realize the potential of new adsorbent materials. These challenges include scalability, shaping, cost-effectiveness, durability, and resistance to contaminants. Acknowledging these hurdles is crucial, as it sets a realistic framework for future research. Strategies for overcoming these obstacles should involve interdisciplinary collaboration, integrating insights from chemistry, materials science, engineering, and economics. By outlining a roadmap that considers these multidisciplinary

nary approaches, we can better align research objectives with the practical requirements of industry applications.

- 7) Understanding market needs and industry pull. A critical aspect of transitioning from research to real-world applications is understanding the market demand and industry pull for new technologies. This involves conducting thorough market analysis and engaging with industry stakeholders to gauge the interest and potential scale of adoption for new adsorbent materials. Evidence of industry demand and an assessment of the market size and potential economic impact would significantly bolster the case for further development and investment in these materials. Highlighting the role of these materials in addressing the urgent needs for energy efficiency and environmental sustainability could serve as a compelling motivator for both research and industry sectors.

The future where the development of advanced novel porous materials for inverse CO₂/C₂H₂ separation, carbon capture, and other hydrocarbon separations is propelled by a synergy between empirical evidence and computational modeling, leading to a new generation of adsorbents with unprecedented selectivities and operational efficiencies. The challenges ahead are not trivial, but with continued interdisciplinary collaboration and ingenuity, the design of materials for CO₂/C₂H₂ separation and even other hydrocarbon separations will no doubt achieve new heights, playing a pivotal role in addressing the urgent demands of energy efficiency and environmental sustainability.

■ AUTHOR INFORMATION

Corresponding Author

Dan Zhao – Department of Chemical and Biomolecular Engineering, National University of Singapore, 117585, Singapore; orcid.org/0000-0002-4427-2150; Email: chezhao@nus.edu.sg

Author

Zhaoqiang Zhang – Department of Chemical and Biomolecular Engineering, National University of Singapore, 117585, Singapore; State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China; orcid.org/0000-0002-9172-2871

Complete contact information is available at: <https://pubs.acs.org/10.1021/cbe.4c00035>

Notes

The authors declare no competing financial interest.

Biographies

Zhaoqiang Zhang obtained his Ph.D. in Chemical Engineering from Zhejiang University under the supervision of Prof. Huabin Xing in 2019. Then, he joined Prof. Dan Zhao's group at the National University of Singapore for postdoctoral research. In 2024, he embarked on a new journey as an independent Principal Investigator at the School of Chemistry and Chemical Engineering, Nanjing University. His research focuses on developing advanced porous materials for applications in adsorptive separation and low-carbon chemical engineering technologies.

Dan Zhao obtained his Ph.D. in inorganic chemistry under the supervision of Prof. Hong-Cai Joe Zhou at Texas A&M University in 2010. After finishing his postdoctoral training at Argonne National

Laboratory, he joined the Department of Chemical & Biomolecular Engineering at the National University of Singapore in July 2012 as an assistant professor and was promoted to associate professor with tenure in July 2018. His research interests include advanced porous materials and membranes with applications in clean energy and environmental sustainability.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education - Singapore (MOE2019-T2-1-093, MOE-T2EP10122-0002), the Energy Market Authority of Singapore (EMA-EP009-SEGC-020), the Agency for Science, Technology and Research (U2102d2004, U2102d2012), and the National Research Foundation Singapore (NRF-CRP26-2021RS-0002, NRF-NRF108-2022-0008).

REFERENCES

- (1) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. Highly controlled acetylene accommodation in a metal-organic microporous material. *Nature* **2005**, *436*, 238–241.
- (2) Zhang, J.; Chen, X. Optimized acetylene/carbon dioxide sorption in a dynamic porous crystal. *J. Am. Chem. Soc.* **2009**, *131*, 5516–5521.
- (3) Adil, K.; Belmabkhout, Y.; Pillai, R. S.; Cadiau, A.; Bhatt, P. M.; Assen, A. H.; Maurin, G.; Eddaoudi, M. Gas/vapour separation using ultra-microporous metal-organic frameworks: Insights into the structure/separation relationship. *Chem. Soc. Rev.* **2017**, *46*, 3402–3430.
- (4) Bao, Z.; Chang, G.; Xing, H.; Krishna, R.; Ren, Q.; Chen, B. Potential of microporous metal-organic frameworks for separation of hydrocarbon mixtures. *Energy Environ. Sci.* **2016**, *9*, 3612–3641.
- (5) Li, H.; Li, L.; Lin, R. B.; Zhou, W.; Zhang, Z.; Xiang, S.; Chen, B. Porous metal-organic frameworks for gas storage and separation: Status and challenges. *EnergyChem.* **2019**, *1*, No. 100006.
- (6) Li, J. R.; Sculley, J.; Zhou, H. C. Metal-organic frameworks for separations. *Chem. Rev.* **2012**, *112*, 869–932.
- (7) The Business Research Company. *Acetylene global market report 2023*; Dublin, 2023.
- (8) Han, X.; Yang, S. Molecular mechanisms behind acetylene adsorption and selectivity in functional porous materials. *Angew. Chem. Int. Ed.* **2023**, *62*, No. e202218274.
- (9) Wang, X.; Liu, H.; Li, Y.; Yang, X.; Gao, F.; Wang, X.; Kang, Z.; Fan, W.; Sun, D. Metal-organic frameworks for C₂H₂/CO₂ separation: Recent development. *Coord. Chem. Rev.* **2023**, *482*, No. 215093.
- (10) Ye, Y.; Xian, S.; Cui, H.; Tan, K.; Gong, L.; Liang, B.; Pham, T.; Pandey, H.; Krishna, R.; Lan, P. C.; Forrest, K. A.; Space, B.; Thonhauser, T.; Li, J.; Ma, S. Metal-organic framework based hydrogen-bonding nanotrap for efficient acetylene storage and separation. *J. Am. Chem. Soc.* **2022**, *144*, 1681–1689.
- (11) Mukherjee, S.; Sensharma, D.; Chen, K. J.; Zaworotko, M. J. Crystal engineering of porous coordination networks to enable separation of C₂ hydrocarbons. *Chem. Commun.* **2020**, *56*, 10419–10441.
- (12) Fu, X. P.; Wang, Y. L.; Liu, Q. Y. Metal-organic frameworks for C₂H₂/CO₂ separation. *Dalton Trans.* **2020**, *49*, 16598–16607.
- (13) Pei, J.; Shao, K.; Wang, J. X.; Wen, H. M.; Yang, Y.; Cui, Y.; Krishna, R.; Li, B.; Qian, G. A chemically stable hofmann-type metal-organic framework with sandwich-like binding sites for benchmark acetylene capture. *Adv. Mater.* **2020**, *32*, No. e1908275.
- (14) Ebadi Amooghini, A.; Sanaeepour, H.; Luque, R.; Garcia, H.; Chen, B. Fluorinated metal-organic frameworks for gas separation. *Chem. Soc. Rev.* **2022**, *51*, 7427–7508.
- (15) Zhang, Z. Q.; Peh, S. B.; Kang, C.; Chai, K.; Zhao, D. Metal-organic frameworks for C₆–C₈ hydrocarbon separations. *Energy-Chem.* **2021**, *3* (4), No. 100057.
- (16) Zeng, H.; Xie, M.; Wang, T.; Wei, R. J.; Xie, X. J.; Zhao, Y.; Lu, W.; Li, D. Orthogonal-array dynamic molecular sieving of propylene/propane mixtures. *Nature* **2021**, *595* (7868), 542–548.
- (17) Wang, S.; Reinsch, H.; Heymans, N.; Wahiduzzaman, M.; Martineau-Corcoss, C.; De Weireld, G.; Maurin, G.; Serre, C. Toward a rational design of titanium metal-organic frameworks. *Matter* **2020**, *2*, 440–450.
- (18) Schoedel, A.; Li, M.; Li, D.; O’Keeffe, M.; Yaghi, O. M. Structures of metal-organic frameworks with rod secondary building units. *Chem. Rev.* **2016**, *116*, 12466–12535.
- (19) Yuan, S.; Feng, L.; Wang, K.; Pang, J.; Bosch, M.; Lollar, C.; Sun, Y.; Qin, J.; Yang, X.; Zhang, P.; Wang, Q.; Zou, L.; Zhang, Y.; Zhang, L.; Fang, Y.; Li, J.; Zhou, H. C. Stable metal-organic frameworks: Design, synthesis, and applications. *Adv. Mater.* **2018**, *30*, No. e1704303.
- (20) Wang, Z.; Zhang, S.; Chen, Y.; Zhang, Z.; Ma, S. Covalent organic frameworks for separation applications. *Chem. Soc. Rev.* **2020**, *49*, 708–735.
- (21) Zhang, Z.; Ye, Y.; Xiang, S.; Chen, B. Exploring multifunctional hydrogen-bonded organic framework materials. *Acc. Chem. Res.* **2022**, *55*, 3752–3766.
- (22) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341*, No. 1230444.
- (23) Trickett, C. A.; Helal, A.; Al-Maythaly, B. A.; Yamani, Z. H.; Cordova, K. E.; Yaghi, O. M. The chemistry of metal-organic frameworks for CO₂ capture, regeneration and conversion. *Nat. Rev. Mater.* **2017**, *2*, 17045.
- (24) Chen, K. J.; Madden, D. G.; Mukherjee, S.; Pham, T.; Forrest, K. A.; Kumar, A.; Space, B.; Kong, J.; Zhang, Q.; Zaworotko, M. Synergistic sorbent separation for one-step ethylene purification from a four-component mixture. *Science* **2019**, *366*, 241–246.
- (25) Zhou, D.; Zhang, X.; Mo, Z.; Xu, Y.; Tian, X.; Li, Y.; Chen, X.; Zhang, J. Adsorptive separation of carbon dioxide: From conventional porous materials to metal-organic frameworks. *EnergyChem.* **2019**, *1*, No. 100016.
- (26) Barnett, B. R.; Gonzalez, M. I.; Long, J. R. Recent progress towards light hydrocarbon separations using metal-organic frameworks. *Trends Chem.* **2019**, *1*, 159–171.
- (27) Cui, X.; Chen, K.; Xing, H.; Yang, Q.; Krishna, R.; Bao, Z.; Wu, H.; Zhou, W.; Dong, X.; Han, Y.; Li, B.; Ren, Q.; Zaworotko, M.; Chen, B. Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene. *Science* **2016**, *353*, 141–144.
- (28) O’Keeffe, M.; Yaghi, O. M. Deconstructing the crystal structures of metal-organic frameworks and related materials into their underlying nets. *Chem. Rev.* **2012**, *112*, 675–702.
- (29) Wang, H.; Liu, Y.; Li, J. Designer metal-organic frameworks for size-exclusion-based hydrocarbon separations: Progress and challenges. *Adv. Mater.* **2020**, *32*, No. e2002603.
- (30) Zhang, Z.; Ding, Q.; Cui, J.; Cui, X.; Xing, H. Fine-tuning pore dimension in hybrid ultramicroporous materials boosting simultaneous trapping of trace alkynes from alkenes. *Small* **2020**, *16*, No. e2005360.
- (31) Zhang, Z.; Yang, Q.; Cui, X.; Yang, L.; Bao, Z.; Ren, Q.; Xing, H. Sorting of C₄ olefins with interpenetrated hybrid ultramicroporous materials by combining molecular recognition and size-sieving. *Angew. Chem. Int. Ed.* **2017**, *56*, 16282–16287.
- (32) He, C. T.; Ye, Z. M.; Xu, Y. T.; Zhou, D. D.; Zhou, H. L.; Chen, D.; Zhang, J. P.; Chen, X. M. Hyperfine adjustment of flexible pore-surface pockets enables smart recognition of gas size and quadrupole moment. *Chem. Sci.* **2017**, *8*, 7560–7565.
- (33) Liao, P. Q.; Huang, N. Y.; Zhang, W. X.; Zhang, J. P.; Chen, X. M. Controlling guest conformation for efficient purification of butadiene. *Science* **2017**, *356*, 1193–1196.
- (34) Wu, E.; Gu, X. W.; Liu, D.; Zhang, X.; Wu, H.; Zhou, W.; Qian, G.; Li, B. Incorporation of multiple supramolecular binding sites into a robust MOF for benchmark one-step ethylene purification. *Nat. Commun.* **2023**, *14*, 6146.

- (35) Zeng, H.; Xie, X. J.; Wang, T.; Xie, M.; Wang, Y.; Wei, R. J.; Lu, W.; Li, D. Dynamic molecular pockets on one-dimensional channels for splitting ethylene from C₂–C₄ alkynes. *Nat. Chem. Eng.* **2024**, *1*, 108–115.
- (36) Liu, X.; Zhang, P.; Xiong, H.; Zhang, Y.; Wu, K.; Liu, J.; Krishna, R.; Chen, J.; Chen, S.; Zeng, Z.; Deng, S.; Wang, J. Engineering pore environments of sulfate-pillared metal-organic framework for efficient C₂H₂/CO₂ separation with record selectivity. *Adv. Mater.* **2023**, *35*, No. e2210415.
- (37) Zheng, F.; Chen, R.; Ding, Z.; Liu, Y.; Zhang, Z.; Yang, Q.; Yang, Y.; Ren, Q.; Bao, Z. Interlayer symmetry control in flexible-robust layered metal-organic frameworks for highly efficient C₂H₂/CO₂ separation. *J. Am. Chem. Soc.* **2023**, *145*, 19903–19911.
- (38) Wang, J. W.; Fan, S. C.; Li, H. P.; Bu, X.; Xue, Y. Y.; Zhai, Q. G. De-linker-enabled exceptional volumetric acetylene storage capacity and benchmark C₂H₂/C₂H₄ and C₂H₂/CO₂ separations in metal-organic frameworks. *Angew. Chem. Int. Ed.* **2023**, *62*, No. e202217839.
- (39) Yang, S.; Xing, B.; Wang, L.; Zhou, L.; Zhang, F.; Li, Y.; Hu, T. L. Boosting acetylene packing density within an isoreticular metal-organic framework for efficient C₂H₂/CO₂ separation. *Chem. Bio Eng.* **2024**, *1*, 245.
- (40) Yang, Y.; Zhang, H.; Yuan, Z.; Wang, J. Q.; Xiang, F.; Chen, L.; Wei, F.; Xiang, S.; Chen, B.; Zhang, Z. An ultramicroporous hydrogen-bonded organic framework exhibiting high C₂H₂/CO₂ separation. *Angew. Chem. Int. Ed.* **2022**, *61*, No. e202207579.
- (41) Wang, T.; Lin, E.; Peng, Y. L.; Chen, Y.; Cheng, P.; Zhang, Z. Rational design and synthesis of ultramicroporous metal-organic frameworks for gas separation. *Coord. Chem. Rev.* **2020**, *423*, No. 213485.
- (42) Chen, K. J.; Scott, H. S.; Madden, D. G.; Pham, T.; Kumar, A.; Bajpai, A.; Lusi, M.; Forrest, K. A.; Space, B.; Perry, J. J.; Zaworotko, M. J. Benchmark C₂H₂/CO₂ and CO₂/C₂H₂ separation by two closely related hybrid ultramicroporous materials. *Chem.* **2016**, *1*, 753–765.
- (43) Belmabkhout, Y.; Zhang, Z.; Adil, K.; Bhatt, P. M.; Cadiau, A.; Solovyeva, V.; Xing, H.; Eddaoudi, M. Hydrocarbon recovery using ultra-microporous fluorinated MOF platform with and without uncoordinated metal sites: I-Structure properties relationships for C₂H₂/C₂H₄ and CO₂/C₂H₂ separation. *Chem. Eng. J.* **2019**, *359*, 32–36.
- (44) Zhang, Z.; Peh, S. B.; Krishna, R.; Kang, C.; Chai, K.; Wang, Y.; Shi, D.; Zhao, D. Optimal pore chemistry in an ultramicroporous metal-organic framework for benchmark inverse CO₂/C₂H₂ separation. *Angew. Chem. Int. Ed.* **2021**, *60*, 17198–17204.
- (45) Ma, D.; Li, Z.; Zhu, J.; Zhou, Y.; Chen, L.; Mai, X.; Liufu, M.; Wu, Y.; Li, Y. Inverse and highly selective separation of CO₂/C₂H₂ on a thulium-organic framework. *J. Mater. Chem. A* **2020**, *8*, 11933–11937.
- (46) Shi, Y.; Xie, Y.; Cui, H.; Ye, Y.; Wu, H.; Zhou, W.; Arman, H.; Lin, R. B.; Chen, B. Highly selective adsorption of carbon dioxide over acetylene in an ultramicroporous metal-organic framework. *Adv. Mater.* **2021**, *33*, No. 2105880.
- (47) Gu, Y.; Zheng, J. J.; Otake, K. I.; Shivanna, M.; Sakaki, S.; Yoshino, H.; Ohba, M.; Kawaguchi, S.; Wang, Y.; Li, F.; Kitagawa, S. Host-guest interaction modulation in porous coordination polymers for inverse selective CO₂/C₂H₂ separation. *Angew. Chem. Int. Ed.* **2021**, *60*, 11688–11694.
- (48) Wang, X.; Zhao, T.; Cai, Y.; Zheng, Y.; Chen, Y.; Gao, J. Reversed CO₂/C₂H₂ separation with ultrahigh carbon dioxide adsorption capacity in Zn-based pillared metal-organic frameworks. *J. Solid State Chem.* **2023**, *327*, No. 124280.
- (49) Yang, S. Q.; Krishna, R.; Chen, H.; Li, L.; Zhou, L.; An, Y. F.; Zhang, F. Y.; Zhang, Q.; Zhang, Y. H.; Li, W.; Hu, T. L.; Bu, X. H. Immobilization of the polar group into an ultramicroporous metal-organic framework enabling benchmark inverse selective CO₂/C₂H₂ separation with record C₂H₂ production. *J. Am. Chem. Soc.* **2023**, *145*, 13901–13911.
- (50) Eguchi, R.; Uchida, S.; Mizuno, N. Inverse and high CO₂/C₂H₂ sorption selectivity in flexible organic-inorganic ionic crystals. *Angew. Chem. Int. Ed.* **2012**, *51*, 1635–1639.
- (51) Geng, S.; Xu, H.; Cao, C. S.; Pham, T.; Zhao, B.; Zhang, Z. Bioinspired design of a giant [Mn₃₆] nanocage-based metal-organic framework with specific CO₂ binding pockets for highly selective CO₂ separation. *Angew. Chem. Int. Ed.* **2023**, *62*, No. e202305390.
- (52) Krause, S.; Hosono, N.; Kitagawa, S. Chemistry of soft porous crystals: Structural dynamics and gas adsorption properties. *Angew. Chem. Int. Ed.* **2020**, *59*, 15325–15341.
- (53) Elsaidi, S. K.; Mohamed, M. H.; Banerjee, D.; Thallapally, P. K. Flexibility in metal-organic frameworks: A fundamental understanding. *Coord. Chem. Rev.* **2018**, *358*, 125–152.
- (54) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible metal-organic frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062–6096.
- (55) Foo, M. L.; Matsuda, R.; Hijikata, Y.; Krishna, R.; Sato, H.; Horike, S.; Hori, A.; Duan, J.; Sato, Y.; Kubota, Y.; Takata, M.; Kitagawa, S. An adsorbate discriminatory gate effect in a flexible porous coordination polymer for selective adsorption of CO₂ over C₂H₂. *J. Am. Chem. Soc.* **2016**, *138*, 3022–3030.
- (56) Gu, Y.; Zheng, J. J.; Otake, K. I.; Sakaki, S.; Ashitani, H.; Kubota, Y.; Kawaguchi, S.; Yao, M. S.; Wang, P.; Wang, Y.; Li, F.; Kitagawa, S. Soft corrugated channel with synergistic exclusive discrimination gating for CO₂ recognition in gas mixture. *Nat. Commun.* **2023**, *14*, 4245.
- (57) Cai, L. Z.; Yao, Z. Z.; Lin, S. J.; Wang, M. S.; Guo, G. C. Photoinduced electron-transfer (PIET) strategy for selective adsorption of CO₂ over C₂H₂ in a MOF. *Angew. Chem. Int. Ed.* **2021**, *60*, 18223–18230.
- (58) Yang, W.; Davies, A.; Lin, X.; Suyetin, M.; Matsuda, R.; Blake, A.; Wilson, C.; Lewis, W.; Parker, J.; Tang, C.; George, M.; Hubberstey, P.; Kitagawa, S.; Sakamoto, H.; Bichoutskaia, E.; Champness, N.; Yang, S.; Schröder, M. Selective CO₂ uptake and inverse CO₂/C₂H₂ selectivity in a dynamic bifunctional metal-organic framework. *Chem. Sci.* **2012**, *3*, 2993–2999.
- (59) Ma, L.; Wang, G.; Hou, L.; Zhu, Z.; Wang, Y. Efficient one-step purification of C1 and C2 hydrocarbons over CO₂ in a new CO₂-Selective MOF with a gate-opening effect. *ACS Appl. Mater. Interfaces* **2022**, *14*, 26858–26865.
- (60) Wang, W.; Wang, G.; Zhang, B.; Li, X.; Hou, L.; Yang, Q.; Liu, B. Discriminatory gate-opening effect in a flexible metal-organic framework for inverse CO₂/C₂H₂ separation. *Small* **2023**, *19*, No. 202302975.
- (61) Qazvini, O. T.; Babarao, R.; Telfer, S. G. Selective capture of carbon dioxide from hydrocarbons using a metal-organic framework. *Nat. Commun.* **2021**, *12*, 197.
- (62) Xie, Y.; Cui, H.; Wu, H.; Lin, R. B.; Zhou, W.; Chen, B. Electrostatically driven selective adsorption of carbon dioxide over acetylene in an ultramicroporous material. *Angew. Chem. Int. Ed.* **2021**, *60*, 9604–9609.
- (63) Zhang, Z.; Deng, Z.; Evans, H. A.; Mullangi, D.; Kang, C.; Peh, S. B.; Wang, Y.; Brown, C. M.; Wang, J.; Canepa, P.; Cheetham, A. K.; Zhao, D. Exclusive recognition of CO₂ from hydrocarbons by aluminum formate with hydrogen-confined pore cavities. *J. Am. Chem. Soc.* **2023**, *145*, 11643–11649.
- (64) Li, Y.; Wang, X.; Zhang, H.; He, L.; Huang, J.; Wei, W.; Yuan, Z.; Xiong, Z.; Chen, H.; Xiang, S.; Chen, B.; Zhang, Z. A microporous hydrogen bonded organic framework for highly selective separation of carbon dioxide over acetylene. *Angew. Chem. Int. Ed.* **2023**, *62*, No. e202311419.
- (65) Lehn, J. M. Supramolecular chemistry: Where from? Where to? *Chem. Soc. Rev.* **2017**, *46*, 2378–2379.
- (66) Ma, Y.; Matsuda, R.; Sato, H.; Hijikata, Y.; Li, L.; Kusaka, S.; Foo, M.; Xue, F.; Akiyama, G.; Yuan, R.; Kitagawa, S. A convenient strategy for designing a soft nanospace: An atomic exchange in a ligand with isostructural frameworks. *J. Am. Chem. Soc.* **2015**, *137*, 15825–15832.

- (67) Gong, W.; Cui, H.; Xie, Y.; Li, Y.; Tang, X.; Liu, Y.; Cui, Y.; Chen, B. Efficient C₂H₂/CO₂ separation in ultramicroporous metal-organic frameworks with record C₂H₂ storage density. *J. Am. Chem. Soc.* **2021**, *143*, 14869–14876.
- (68) Huang, Z.; Chai, K.; Kang, C.; Krishna, R.; Zhang, Z. Commensurate stacking within confined ultramicropores boosting acetylene storage capacity and separation efficiency. *Nano Res.* **2023**, *16*, 7742–7748.
- (69) Wang, S.; Lee, J.; Wahiduzzaman, M.; Park, J.; Muschi, M.; Martineau-Corcus, C.; Tissot, A.; Cho, K.; Marrot, J.; Shepard, W.; Maurin, G.; Chang, J.; Serre, C. A robust large-pore zirconium carboxylate metal–organic framework for energy-efficient water-sorption-driven refrigeration. *Nat. Energy* **2018**, *3*, 985–993.
- (70) Zhang, Z.; Chen, Y.; Chai, K.; Kang, C.; Peh, S. B.; Li, H.; Ren, J.; Shi, X.; Han, X.; Dejoie, C.; Day, S. J.; Yang, S.; Zhao, D. Temperature-dependent rearrangement of gas molecules in ultramicroporous materials for tunable adsorption of CO₂ and C₂H₂. *Nat. Commun.* **2023**, *14*, 3789.
- (71) Yu, J.; Zhang, J.; Zhang, P.; Wang, Y.; Li, S.; Zhai, Q. Controllable inverse C₂H₂/CO₂ separation in ultra-stable Zn-organic frameworks for efficient removal of trace CO₂ from acetylene. *J. Mater. Chem. A* **2022**, *10*, 23630–23638.
- (72) Kim, E. J.; Siegelman, R. L.; Jiang, H. Z. H.; Forse, A. C.; Lee, J.-H.; Martell, J. D.; Milner, P. J.; Falkowski, J. M.; Neaton, J. B.; Reimer, J. A.; Weston, S. C.; Long, J. R. Cooperative carbon capture and steam regeneration with tetraamine-appended metal-organic frameworks. *Science* **2020**, *369*, 392–396.
- (73) Choi, D.; Kim, D.; Kang, D.; Kang, M.; Chae, Y.; Hong, C. Highly selective CO₂ separation from a CO₂/C₂H₂ mixture using a diamine-appended metal–organic framework. *J. Mater. Chem. A* **2021**, *9*, 21424–21428.
- (74) Zhu, H.; Xue, W.; Huang, H.; Chen, L.; Liu, H.; Zhong, C. Water boosted CO₂/C₂H₂ separation in L-arginine functionalized metal–organic framework. *Nano Res.* **2023**, *16*, 6113–6119.
- (75) Zeng, S.; Zhang, X.; Bai, L.; Zhang, X.; Wang, H.; Wang, J.; Bao, D.; Li, M.; Liu, X.; Zhang, S. Ionic-liquid-based CO₂ capture systems: Structure, interaction and process. *Chem. Rev.* **2017**, *117*, 9625–9673.
- (76) Yang, J.; Tong, M.; Han, G.; Chang, M.; Yan, T.; Ying, Y.; Yang, Q.; Liu, D. Solubility-boosted molecular sieving-based separation for purification of acetylene in core–shell IL@MOF composites. *Adv. Funct. Mater.* **2023**, *33*, No. 2213743.
- (77) Li, L.; Wang, J.; Zhang, Z.; Yang, Q.; Yang, Y.; Su, B.; Bao, Z.; Ren, Q. Inverse adsorption separation of CO₂/C₂H₂ mixture in cyclodextrin-based metal-organic frameworks. *ACS Appl. Mater. Interfaces* **2019**, *11*, 2543–2550.
- (78) Cui, J.; Qiu, Z.; Yang, L.; Zhang, Z.; Cui, X.; Xing, H. Kinetic-sieving of carbon dioxide from acetylene through a novel sulfonic ultramicroporous material. *Angew. Chem. Int. Ed.* **2022**, *61*, No. e202208756.
- (79) Liu, Q.; Cho, S. G.; Hilliard, J.; Wang, T. Y.; Chien, S. C.; Lin, L. C.; Co, A. C.; Wade, C. R. Inverse CO₂/C₂H₂ separation with MFU-4 and selectivity reversal via postsynthetic ligand exchange. *Angew. Chem. Int. Ed.* **2023**, *62*, No. e202218854.
- (80) Ma, B.; Li, D.; Zhu, Q.; Li, Y.; Ueda, W.; Zhang, Z. A zeolitic octahedral metal oxide with ultra-microporosity for inverse CO₂/C₂H₂ separation at high temperature and humidity. *Angew. Chem. Int. Ed.* **2022**, *61*, No. e202209121.
- (81) Ding, Q.; Zhang, Z.; Yu, C.; Zhang, P.; Wang, J.; Cui, X.; He, C. H.; Deng, S.; Xing, H. Exploiting equilibrium-kinetic synergetic effect for separation of ethylene and ethane in a microporous metal-organic framework. *Sci. Adv.* **2020**, *6*, No. eaaz4322.
- (82) Ding, Q.; Zhang, Z. Q.; Yu, C.; Zhang, P.; Wang, J.; Kong, L.; Cui, X.; He, C.; Deng, S.; Xing, H. Separation of propylene and propane with a microporous metal–organic framework via equilibrium-kinetic synergetic effect. *AIChE J.* **2021**, *67*, No. e17094.
- (83) Chen, Y.; Wu, H.; Yu, L.; Tu, S.; Wu, Y.; Li, Z.; Xia, Q. Separation of propylene and propane with pillar-layer metal–organic frameworks by exploiting thermodynamic-kinetic synergetic effect. *Chem. Eng. J.* **2022**, *431*, No. 133284.
- (84) Zhang, Z.; Ding, Q.; Cui, X.; Jiang, X. M.; Xing, H. Fine-tuning and selective-binding within an anion-functionalized ultramicroporous metal-organic framework for efficient olefin/paraffin separation. *ACS Appl. Mater. Interfaces* **2020**, *12*, 40229–40235.
- (85) He, C.; Zhang, P.; Wang, Y.; Zhang, Y.; Hu, T.; Li, L.; Li, J. Thermodynamic and kinetic synergetic separation of CO₂/C₂H₂ in an ultramicroporous metal-organic framework. *Sep. Purif. Technol.* **2023**, *304*, No. 122318.
- (86) Anjekar, N. D.; Hinkle, K. R.; Talu, O.; Fu, Q.; Nair, S.; Yang, S. Unexpected high CO₂ over C₂H₂ separation performance by high-silica CHA zeolite membranes. *J. Membr. Sci.* **2023**, *683*, No. 121853.