

Cite this: *Chem. Sci.*, 2025, 16, 22732

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A cation gating–breathing synergetic mechanism in K-MER-2.0 zeolite enables unprecedented selective CO₂ separation from hydrocarbon gas streams

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The ubiquitous presence of CO₂ impurities in industrial hydrocarbon streams underscores the critical need for developing efficient CO₂-selective adsorbents. Herein, we synthesized a flexible K-MER-2.0 (a silica–alumina ratio of 2.0) zeolite without using an organic template, which demonstrates exceptional selective adsorption performance in CO₂/hydrocarbon systems, and in particular achieves the unprecedented reverse separation of CO₂/C₂H₂. K-MER exhibits a CO₂ adsorption capacity of 70.9 cm³ g⁻¹ under ambient conditions, accompanied by a remarkable CO₂/C₂H₂ uptake ratio (13.4). Breakthrough experiments conducted with a CO₂/C₂H₂ (50/50, v/v) mixture reveal that K-MER-2.0 delivers a high dynamic CO₂ adsorption capacity (65.1 cm³ g⁻¹) and separation factor (12.1), and in particular a high C₂H₂ yield of 1872 mmol kg⁻¹, establishing a benchmark for CO₂/C₂H₂ reverse separation. The rapid adsorption kinetics, excellent regeneration and robust moisture resistance of K-MER-2.0 further confirmed its application potential under harsh practical conditions. Mechanistic analyses, including CO₂/C₂H₂ adsorption isotherms, *in situ* CO₂ powder X-ray diffraction (PXRD) patterns and periodic density functional theory (DFT) calculations, reveal a unique CO₂-triggered cation gating–breathing synergetic mechanism in K-MER-2.0 zeolite. This stimulus-responsive mechanism facilitates selective framework expansion during CO₂ adsorption while preserving a constricted pore geometry that excludes C₂H₂. Such discriminative structural adaptability drives the record-breaking separation performance of the material. Additionally, the unique recognition ability for CO₂ endows K-MER-2.0 with good dynamic separation ability for binary mixtures of CO₂/hydrocarbons.

Received 6th May 2025

Accepted 12th October 2025

DOI: 10.1039/d5sc03281d

rsc.li/chemical-science

Introduction

The strategic significance of developing advanced CO₂/hydrocarbon separation technologies arises from two fundamental industrial considerations: (1) hydrocarbon gases (including C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and CH₄) serve as critical feedstocks and energy vectors, and (2) CO₂ invariably coexists in hydrocarbon product streams as a ubiquitous impurity.¹ C₂H₂/CO₂ separation represents one of the most challenging gas purification processes in petrochemical systems, primarily due to their nearly identical

molecular properties, including comparable polarities (33.3 × 10⁻²⁵ cm³ for C₂H₂ vs. 29.1 × 10⁻²⁵ cm³ for CO₂), similar kinetic diameters (3.3 Å for both), and overlapping adsorption affinities.^{2–4} Conventional industrial methods predominantly employ organic-solvent-based absorption systems and cryogenic distillation operations, which suffer from significant energy consumption.⁴ This has driven the increasing adoption of physisorption-based separation platforms that offer distinct advantages in energy efficiency (>30% reduction in energy consumption), rapid adsorption–desorption kinetics, and exceptional cycling stability.^{5–7} Notably, the energy efficiency of CO₂-selective adsorbents (CO₂/C₂H₂ reverse separation) increases by 40% compared to that of C₂H₂-selective alternatives (C₂H₂/CO₂ positive separation) in separation processes, highlighting the potential for sustainable hydrocarbon purification.¹ This advantage arises primarily from CO₂/C₂H₂ reverse separation, which facilitates the direct acquisition of pure C₂H₂ product while obviating the need for energy-intensive multistep desorption processes.

The key to achieving efficient CO₂/C₂H₂ reverse separation is the design and synthesis of advanced porous adsorbents. In the

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past decade, metal–organic frameworks (MOFs) have attracted considerable research interest for CO₂/C₂H₂ reverse separation, with notable examples including Zn-ox-mtz,⁸ MUF-16,⁹ PCP-NH₂-bdc,¹⁰ and PMOF-1.¹¹ However, their practical implementation in gas separation technologies has been constrained by persistently high synthesis costs and relatively poor stability.¹² This economic limitation has driven the increasing attention paid to zeolite-based materials, which offer distinct advantages in terms of cost-effectiveness, industrial scalability, structural stability, and high thermal/hydrothermal stability.⁴ Recent studies have demonstrated the potential of zeolites in this domain, exemplified by Sr/K-HEU achieving a dynamic CO₂/C₂H₂ separation factor of 48.0 and CO₂ dynamic uptake of 21.5 cm³ g⁻¹.¹³ Furthermore, Na-GIS(3.1) has shown selective CO₂ adsorption in CO₂/C₂H₂ mixtures, accompanied by a pure C₂H₂ yield of 100 mmol kg⁻¹.¹⁴ In addition, NaAlO₂@MOR(0.5) also exhibited a remarkable kinetic separation selectivity of 534.3.¹⁵ Among zeolitic materials, K-MER has emerged as particularly promising due to its flexible framework and unique adsorption mechanisms, particularly for CO₂/N₂ and CO₂/CH₄ mixed systems. *In situ* CO₂ variable-pressure synchrotron powder X-ray diffraction coupled with Rietveld refinement have revealed that K-MER exhibited a unique cation gating–breathing synergistic mechanism during CO₂ adsorption.^{16–19} This dual-action mechanism differs from the “trapdoor” effect observed in Sr/K-HEU,¹³ the monofunctional breathing behaviour of Na-GIS(3.1),¹⁴ and the kinetic separation of NaAlO₂@MOR(0.5).¹⁵ However, it has rarely been reported that the pore architecture of K-MER retains closure not only towards low-polar gases (N₂, CH₄) but also extends to high-polar hydrocarbons (*e.g.*, C₂H₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈). Despite this critical property, systematic investigation of the potential of K-MER for CO₂/hydrocarbon separation applications remains notably underexplored, creating a substantial gap in the understanding of its gas separation applications.

Herein, we report an organic-template-free synthesized K-MER-2.0 zeolite (a silica–alumina ratio of 2.0) that exhibits a remarkable CO₂ static adsorption capacity of 70.9 cm³ g⁻¹ at 298 K and 101 kPa, significantly outperforming its hydrocarbon adsorption capacities, and thereby demonstrating exceptional CO₂/hydrocarbon separation performance. This material achieves an ideal adsorbed solution theory (IAST) selectivity of 3056 for CO₂/C₂H₂ (50/50, v/v) mixtures. Notably, K-MER-2.0 enables the single-step purification of acetylene with a remarkably high C₂H₂ productivity of 1872 mmol kg⁻¹ in breakthrough experiments, eliminating the need for multi-stage desorption processes and serving as a benchmark for a zeolite-based adsorbent. Meanwhile, the dynamic adsorption capacity of CO₂ reached 65.1 cm³ g⁻¹, accompanied by a separation factor of 12.1. The material demonstrates rapid adsorption kinetics (1.7 min to reach CO₂ uptake of 43.7 mg g⁻¹), exceptional moisture tolerance (73.9% C₂H₂ production under 50% relative humidity), and a low regeneration temperature (353 K). Comparative analyses of CO₂/C₂H₂ adsorption isotherms, *in situ* CO₂ powder X-ray diffraction (PXRD) patterns, and periodic density functional theory (DFT) calculations reveal a unique CO₂-triggered cation gating–breathing synergetic mechanism.

This stimuli-responsive framework maintains a rigid structure for hydrocarbons while exhibiting CO₂-induced framework flexibility, enabling molecular discrimination through dynamic pore modulation. This work advances a fundamental understanding of cation-mediated framework flexibility and establishes a novel strategy for developing smart zeolite materials with selective framework-breathing and gate-opening functionalities for challenging gas separations.

Results and discussion

Characterizations of K-MER-2.0 zeolites

Utilizing KOH as the exclusive alkaline medium, K-MER-2.0 zeolite was successfully synthesized in an organic-template-free system. The powder X-ray diffraction (PXRD) pattern of as-synthesized K-MER-2.0 zeolite was almost consistent with a simulated one of MER-type zeolite, except for the distinctive diffraction peaks at 26.0° and 29.7° (Fig. 1a), which were induced by symmetry reduction from the *Immm* space group (no. 71) of a typical MER framework to a lower-symmetry *Pnmm* space group (no. 58), rather than arising from phase impurities.^{20,21} Scanning/transmission electron microscopy (SEM/TEM) images showed the as-synthesized K-MER-2.0 zeolite existed in the form of micron-sized rod-like aggregations (Fig. S1, S2 and Table S1). The coordination environment of framework elements was elucidated through ²⁹Si/²⁷Al solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) analysis (Fig. 1b and S3). Four distinct strong signals at –91, –96, –101, and –107 ppm in the ²⁹Si MAS NMR spectrum were attributed to Si(OSi)₄ (Q₄), Si(OSi)₃(OAl) (Q₄), Si(OSi)₂(OAl)₂ (Q₄), and Si(OSi)(OAl)₃ (Q₄), respectively, indicating the good crystallization of K-MER-2.0. The ²⁷Al solid-state MAS NMR spectrum demonstrated that the aluminum species in the as-synthesized K-MER-2.0 existed exclusively in a tetrahedral coordination state (60.5 ppm) without the presence of extra-framework aluminum species (0 ppm). Complementary ¹³C solid-state CP/MAS NMR spectrum (Fig. 1c) and thermogravimetric analysis (Fig. S4) confirmed no residual oxalic acid in the as-synthesized K-MER-2.0 zeolite. These findings suggest that oxalic acid functions primarily as a pH modulator and mineralizer complexing agent (with K⁺), rather than acting as a structure-directing template.²² Elemental mapping *via* TEM-EDS (Fig. 1d–h) further verified the homogeneous distribution of K⁺ within the pore channels. To investigate cation effects on structural stability and gas adsorption properties, ion-exchanged derivatives (Li-MER-2.0, Na-MER-2.0, and Cs-MER-2.0) were prepared from K-MER-2.0 through cation exchange followed by calcination (Fig. 1a and Table S1). Na-MER-2.0 maintained both MER topology and crystallinity comparable to the parent K-MER-2.0, while Cs-MER-2.0 exhibited minor framework degradation during the ion exchange process. In contrast, Li-MER-2.0 showed significant attenuation in PXRD peak intensity, attributed to the insufficient framework stabilization by smaller Li⁺ ions in the flexible MER architecture.^{17,18} Consequently, subsequent analyses focused on the more stable Na-MER-2.0, K-MER-2.0, and Cs-MER-2.0 variants. Meanwhile, for Na-MER-2.0 and Cs-MER-2.0, SEM images confirmed the



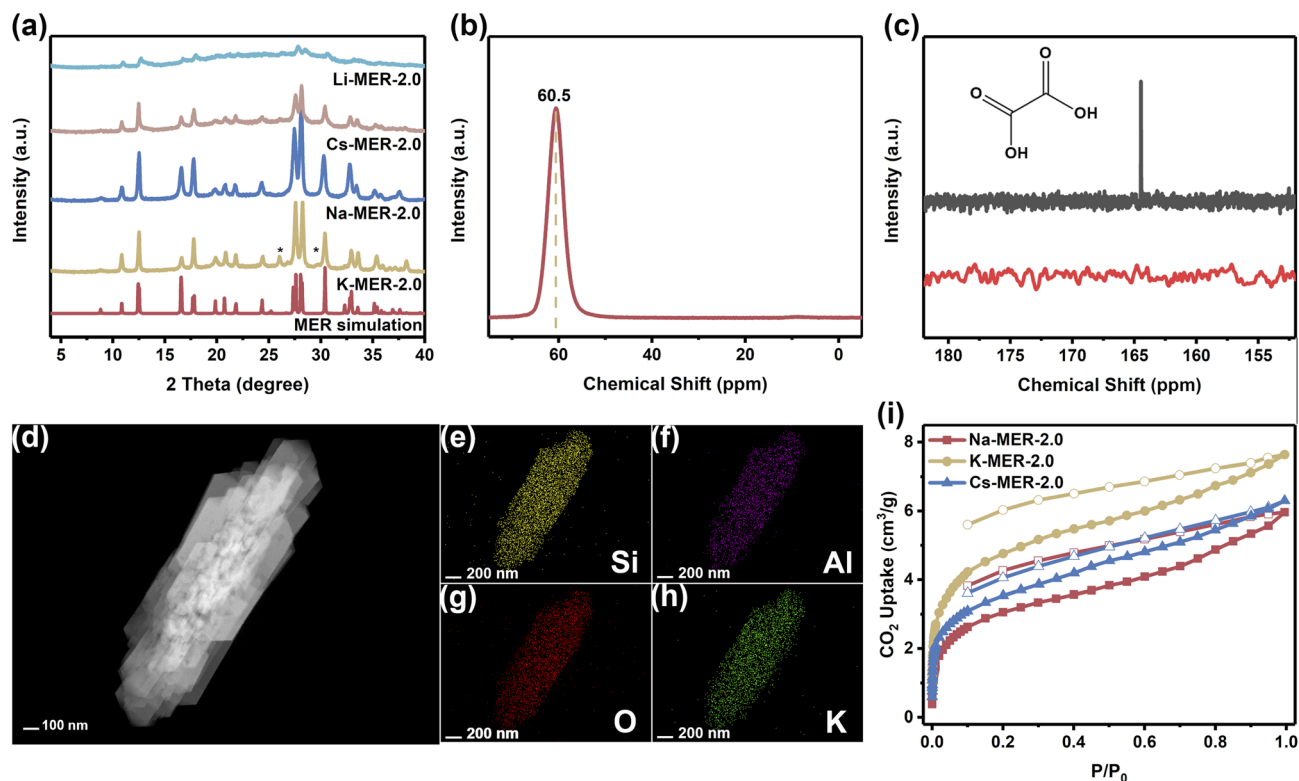


Fig. 1 (a) The simulated PXRD pattern of MER zeolite and experimental patterns of K-MER-2.0, Na-MER-2.0, Cs-MER-2.0, and Li-MER-2.0. (b) The solid-state ^{27}Al MAS NMR spectrum of K-MER-2.0. (c) The liquid-state ^{13}C NMR spectrum of oxalic acid dissolved in D_2O (top curve, black) and the solid-state ^{13}C MAS NMR spectrum of the as-synthesized K-MER-2.0 after washing with deionized water (bottom curve, red). (d) An TEM image of K-MER-2.0. (e–h) Elemental mapping via TEM-EDS of K-MER-2.0 for Si (e), Al (f), O (g), and K (h). (i) The CO_2 adsorption isotherms of Na-MER-2.0, K-MER-2.0, and Cs-MER-2.0 at 195 K.

preservation of morphological features during ion exchange (Fig. S5), and ^{27}Al solid-state MAS NMR spectra confirmed the absence of extra-framework Al species (Fig. S6 and S7).

It is well known that the adsorption capacity of porous materials is critically influenced by their specific surface area and pore volume.²³ However, the adsorption isotherms of N_2 ($d = 0.36$ nm) at 77 K and Ar ($d = 0.34$ nm) at 87 K revealed that only a few N_2 and Ar molecules could be adsorbed into the micropores of K-MER-2.0, Na-MER-2.0, and Cs-MER-2.0 (Fig. S8 and S9). This observation suggests that the flexible framework of K-MER-2.0 maintains a contracted configuration under nitrogen or argon atmospheres.¹⁶ To further investigate this size exclusion effect, we conducted CO_2 ($d = 0.33$ nm) adsorption measurements at 195 K. Surprisingly, despite its smaller kinetic diameter, the CO_2 adsorption amounts of all three MER-type zeolites were still less than $8 \text{ cm}^3 \text{ g}^{-1}$ (Fig. 1i). We propose that this anomalous exclusion behavior stems primarily from the suppressed thermal motion of charge-balancing cations within the zeolite pores at cryogenic temperatures. The reduced cation vibration elevates the energy barrier for cation migration, effectively maintaining a rigid pore structure that prevents gas molecule penetration. This phenomenon aligns with the temperature-dependent adsorption behavior observed in LTA-type zeolites, which adsorb N_2 at room temperature but exhibit non-adsorbent characteristics at 77 K.²⁴

Compared to the CO_2 adsorption isotherm observed at 195 K, the K-MER-2.0 zeolite demonstrated significantly enhanced CO_2 adsorption performance at 298 K with a remarkable adsorption capacity of $70.9 \text{ cm}^3 \text{ g}^{-1}$ at 101 kPa and a steep adsorption curve within the low-pressure region (1 kPa: $37.8 \text{ cm}^3 \text{ g}^{-1}$, 10 kPa: $52.6 \text{ cm}^3 \text{ g}^{-1}$) (Fig. 2a and Table S2). The quasi-reversible nature of CO_2 adsorption was confirmed by the nearly overlapping adsorption–desorption isotherms. Simultaneously, a critical structural transition was identified at 0.4 kPa (298 K), marked by an inflection point in the CO_2 adsorption curve and a subsequent sharp increase in adsorption capacity (Fig. S10). This phenomenon indicates a pressure-induced framework transformation from a contracted to an expanded state in the K-MER-2.0 structure, which has been observed in PHI topology molecular sieves.²⁵ In stark contrast, K-MER-2.0 displayed ultra-low adsorption capacities for various hydrocarbon gases at 298 K and 101 kPa, with uptakes of $5.3 \text{ cm}^3 \text{ g}^{-1}$ for C_2H_2 , $1.3 \text{ cm}^3 \text{ g}^{-1}$ for C_2H_4 , $0.6 \text{ cm}^3 \text{ g}^{-1}$ for C_2H_6 , $2.7 \text{ cm}^3 \text{ g}^{-1}$ for C_3H_6 , $3.3 \text{ cm}^3 \text{ g}^{-1}$ for C_3H_8 , and $0.04 \text{ cm}^3 \text{ g}^{-1}$ for CH_4 (Fig. 2a and Table S2). The ultra-low adsorption capacities and the absence of inflection points in these hydrocarbon isotherms suggest that the framework maintains its contracted conformation during hydrocarbon gas adsorption. This salient adsorption selectivity establishes K-MER-2.0 as an exceptional molecular sieve material for CO_2 /hydrocarbon separation, with impressive adsorption capacity ratios at 298 K and 101 kPa: 13.4 ($\text{CO}_2/\text{C}_2\text{H}_2$), 54.5



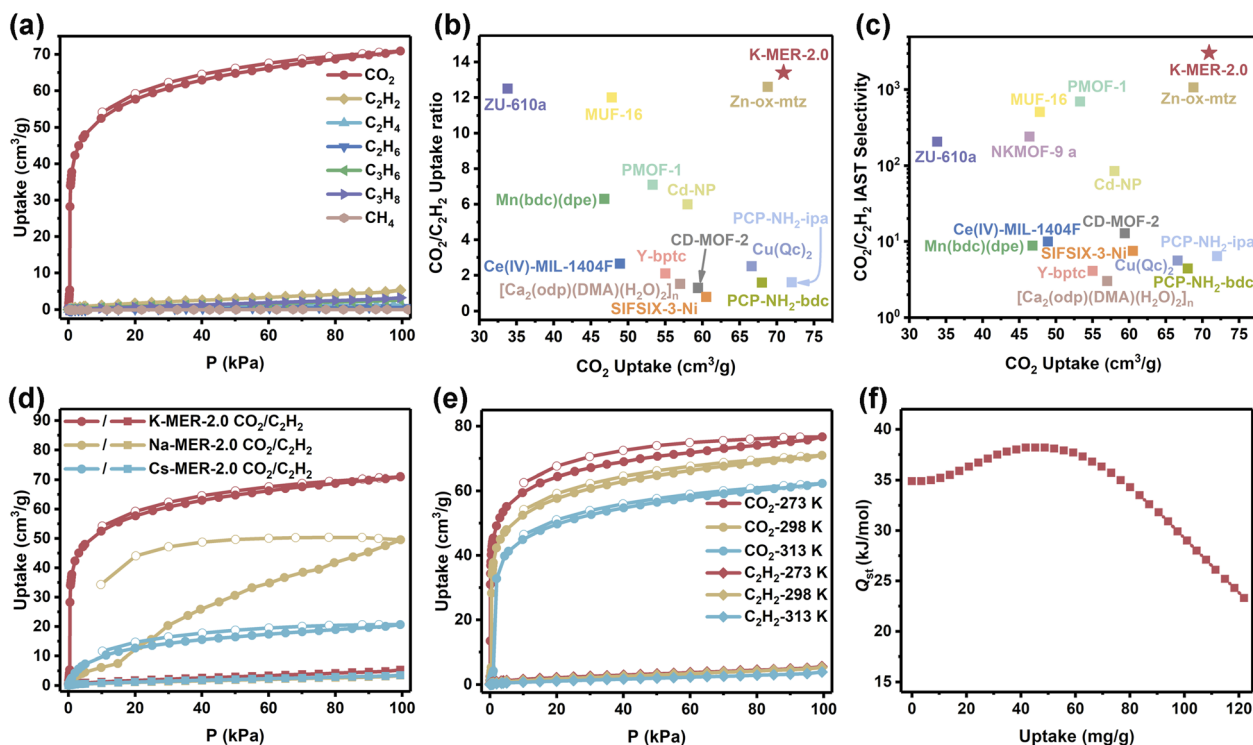


Fig. 2 A comparison of static adsorption performance. (a) Static sorption curves of CO_2 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , and CH_4 for K-MER-2.0 at 298 K. (b) A comparison of the $\text{CO}_2/\text{C}_2\text{H}_2$ uptake ratio and CO_2 uptake of state-of-the-art materials (101 kPa, 298 K). (c) A comparison of $\text{CO}_2/\text{C}_2\text{H}_2$ (50/50, v/v) IAST selectivity and CO_2 uptake (101 kPa, 298 K) of state-of-the-art materials. (d) Static sorption curves of CO_2 and C_2H_2 for Na-MER-2.0, K-MER-2.0, and Cs-MER-2.0 at 298 K. (e) Static sorption curves of CO_2 and C_2H_2 for K-MER-2.0 at 273, 298 and 313 K. (f) CO_2 adsorption enthalpies (Q_{st}) of K-MER-2.0.

($\text{CO}_2/\text{C}_2\text{H}_4$), 118.2 ($\text{CO}_2/\text{C}_2\text{H}_6$), 26.3 ($\text{CO}_2/\text{C}_3\text{H}_6$), 21.3 ($\text{CO}_2/\text{C}_3\text{H}_8$), and 1772.5 (CO_2/CH_4) (Table S2).

It is well established that among various hydrocarbons, C_2H_2 exhibits physicochemical properties and a kinetic diameter most closely resembling those of CO_2 .^{4,12} The high adsorption capacity ratio of $\text{CO}_2/\text{C}_2\text{H}_2$ indicates that the K-MER-2.0 zeolite is particularly suitable for selective CO_2 capture from the $\text{CO}_2/\text{C}_2\text{H}_2$ separation system to produce pure C_2H_2 . Remarkably, K-MER-2.0 demonstrated exceptional separation efficiency with an IAST selectivity of 3056 for the $\text{CO}_2/\text{C}_2\text{H}_2$ (50/50, v/v) system (Fig. S11). As shown in Fig. 2b, c and Table S4, K-MER-2.0 exhibited superior performance metrics in reverse $\text{CO}_2/\text{C}_2\text{H}_2$ separation: CO_2 uptake ($70.9 \text{ cm}^3 \text{ g}^{-1}$), uptake ratio (13.4), and IAST selectivity (3056), significantly surpassing current benchmark materials. These values notably exceeded those of state-of-the-art materials, including Zn-ox-mtz ($68.78 \text{ cm}^3 \text{ g}^{-1}$; 12.6; 1064.9),⁸ MUF-16 ($48 \text{ cm}^3 \text{ g}^{-1}$; 12.0; 510),⁸ and PMOF-1 ($53.3 \text{ cm}^3 \text{ g}^{-1}$; 7.1; 694).¹¹ Comparative analysis with other cation-exchanged MER frameworks revealed distinct differences in performance (Fig. 2d). K-MER-2.0 demonstrated a CO_2 adsorption capacity of $70.9 \text{ cm}^3 \text{ g}^{-1}$ with reversible adsorption and favorable low-pressure adsorption characteristics, while Na-MER-2.0 showed reduced capacity ($49.6 \text{ cm}^3 \text{ g}^{-1}$) accompanied by an adsorption isotherm inflection point shift to 7.5 kPa and significant adsorption-desorption hysteresis. These characteristics substantially compromised the separation performance of Na-MER-2.0, despite its comparable uptake ratio

(14.6) to K-MER-2.0. Cs-MER-2.0 exhibited even poorer performance with CO_2 uptake of $20.6 \text{ cm}^3 \text{ g}^{-1}$ and a low uptake ratio of 5.9 (Table S3).

Thermodynamic analysis through variable-temperature adsorption isotherms revealed a zero-coverage CO_2 adsorption enthalpy (Q_{st}) of 34.9 kJ mol^{-1} for K-MER-2.0 (Fig. 2e and f). This physisorption-dominated mechanism, evidenced by the moderate Q_{st} value, facilitates material regeneration compared to frameworks with higher enthalpies, such as NKMOF-9a (69.5 kJ mol^{-1})²⁶ and CD-MOF-2 (67.2 kJ mol^{-1})²⁷ (Table S4). Notably, the CO_2 adsorption enthalpy profile of K-MER-2.0 exhibited an atypical trend of an initial increase followed by a gradual decline (Fig. 2f), which we attribute to the limited pore accessibility and shielding effects on high-energy adsorption sites at low CO_2 loadings. The temperature-dependent adsorption behavior showed systematic shifts in isotherm inflection points from 0.04 kPa (273 K) to 1.0 kPa (313 K) (Fig. S12), consistent with established gas adsorption thermodynamics.²⁸ This predictable temperature response further supports the potential of K-MER-2.0 for practical separation applications under varying operational conditions.

The CO_2 adsorption kinetics of K-MER-2.0 were systematically investigated under varying pressure conditions (15, 50 and 96 kPa), as shown in Fig. S13. Under low-pressure conditions (15 kPa), the adsorption capacity demonstrated rapid initial uptake, reaching 43.7 mg g^{-1} ($22.2 \text{ cm}^3 \text{ g}^{-1}$) within 1.7 minutes, followed by gradual equilibration to a maximum capacity of



102.2 mg g⁻¹ (52.0 cm³ g⁻¹) over 15 minutes. In contrast, when subjected to elevated pressures (50 and 96 kPa), the system exhibited instantaneous equilibrium characteristics upon pressure stabilization, achieving CO₂ adsorption capacities of 119.6 mg g⁻¹ (60.9 cm³ g⁻¹) and 128.7 mg g⁻¹ (65.5 cm³ g⁻¹), respectively. This pressure-dependent kinetic behavior highlights the rapid adsorption response of the material at higher pressures, which significantly enhances separation efficiency by minimizing the unnecessary consumption of selective adsorption capacity during non-productive stages involving simultaneous gas permeation.²³ The distinct kinetic profiles observed under different pressure conditions provide critical insights for optimizing operational parameters in gas separation applications.

To investigate the impact of the Si/Al ratio on CO₂/C₂H₂ separation performance in K-MER, we synthesized K-MER samples with other Si/Al ratios of 2.7 and 3.8, denoted K-MER-2.7 and K-MER-3.8 (Fig. S14 and Table S1). The decreased K⁺ content resulting from higher Si/Al ratios increases the void volume of MER zeolites, boosting the static CO₂ adsorption capacity from 70.9 cm³ g⁻¹ (K-MER-2.0) to 75.9 cm³ g⁻¹ (K-MER-2.7) and 85.2 cm³ g⁻¹ (K-MER-3.8) (Fig. S15). Meanwhile, the reduction of K⁺ content in the pore of the MER zeolite weakens the interactions between K⁺ and the zeolite framework, causing the CO₂ adsorption inflection point to shift from 0.4 kPa (K-MER-2.0) to 0.1 kPa (K-MER-2.7), with a further decline to below 0.02 kPa for K-MER-3.8 (Fig. S16). However, the C₂H₂ adsorption capacity significantly increases from 5.3 cm³ g⁻¹ (K-MER-2.0) to 11.3 cm³ g⁻¹ (K-MER-2.7) and 52.3 cm³ g⁻¹ (K-MER-

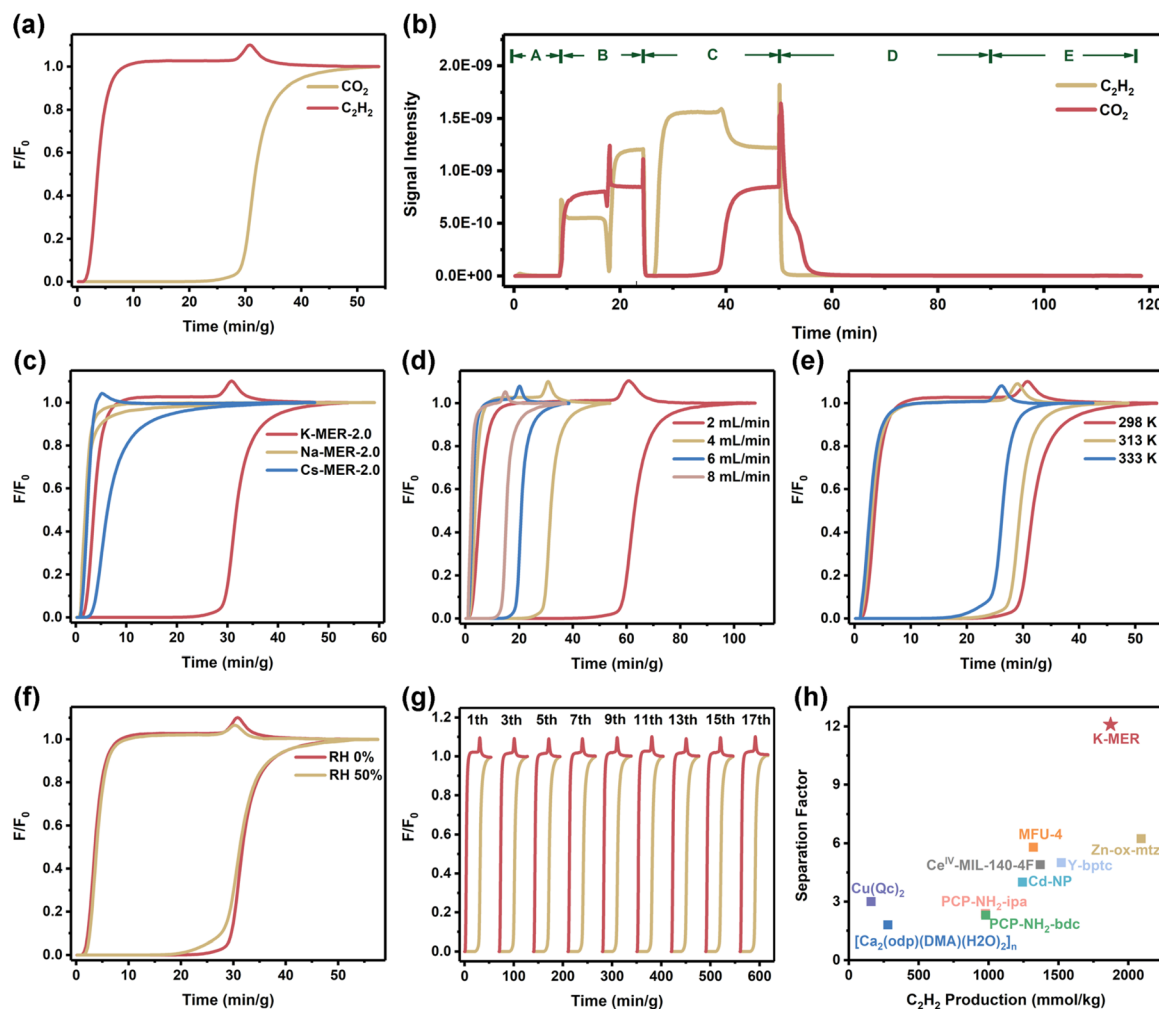


Fig. 3 Column breakthrough studies of a CO₂/C₂H₂ separation system using K-MER-2.0. (a) Experimental breakthrough curves of K-MER-2.0 for CO₂/C₂H₂ (50/50, v/v) mixtures at 298 K with a flow rate of 4 mL min⁻¹. (b) Mass spectrum signal curves of CO₂/C₂H₂ over the whole K-MER-2.0 measurement process. A: sample activation process; B: signal stabilization process of CO₂/C₂H₂ before breakthrough measurement; C: breakthrough measurement process (298 K); D: desorption process of the sample accompanied by 25 mL per min helium at 353 K; E: desorption process when the temperature started to rise to 473 K and remained there for 20 min. (c) A comparison of breakthrough curves of K-MER-2.0, Na-MER-2.0, and Cs-MER-2.0 for CO₂/C₂H₂ (50/50, v/v) mixtures at 298 K with a flow rate of 4 mL min⁻¹. (d) Breakthrough curves for CO₂/C₂H₂ (50/50, v/v) mixtures at 298 K with flow rates of 2, 4, 6, and 8 mL min⁻¹. (e) Breakthrough curves for CO₂/C₂H₂ (50/50, v/v) mixtures at 298 K, 313 K, and 333 K with a flow rate of 4 mL min⁻¹. (f) Effects of H₂O (RH = 50%) on CO₂/C₂H₂ (50/50, v/v) separation at 298 K with a flow rate of 4 mL min⁻¹. (g) A study of recyclability for the separation of CO₂/C₂H₂ (50/50, v/v) at 298 K with a flow rate of 4 mL min⁻¹. Sample regeneration was achieved by treatment in helium at 353 K. (h) A comparison of separation factor and pure C₂H₂ production of state-of-the-art materials.



3.8) (Fig. S15). Consequently, the CO₂/C₂H₂ adsorption ratio decreases from 13.4 (K-MER-2.0) to 6.7 (K-MER-2.7) and 1.6 (K-MER-3.8) (Table S5). The increase in Si/Al ratios reduces pore blockage in K-MER zeolites, allowing C₂H₂ adsorption to occur—a phenomenon consistent with previous literature.²² Overall, K-MER-2.0 exhibited significantly superior separation performance compared to K-MER-2.7 and K-MER-3.8.

To evaluate the practical separation performance of K-MER-2.0 under realistic flow conditions, dynamic breakthrough experiments were conducted using a CO₂/C₂H₂ (50/50, v/v) gas mixture at a total flow rate of 4 mL min⁻¹, following established protocols in gas separation studies (Fig. 3a).²⁹ The breakthrough curves revealed distinct adsorption behaviors: C₂H₂ exhibited rapid breakthrough at 1.0 min g⁻¹ with subsequent saturation, while CO₂ demonstrated prolonged retention with a breakthrough time of 24.4 min g⁻¹. Quantitative analysis yielded dynamic adsorption capacities of 65.1 cm³ g⁻¹ for CO₂ and 5.4 cm³ g⁻¹ for C₂H₂, corresponding to an impressive separation factor (α) of 12.1 (Table S6). Notably, K-MER-2.0 achieved the direct production of high-purity C₂H₂ (99.6%) with a yield of 1872 mmol kg⁻¹ through single-step adsorption, eliminating the requirement for energy-intensive thermal desorption processes. Comparative performance analysis with state-of-the-art adsorbents highlights the superior separation characteristics of K-MER-2.0. Although Zn-ox-mtz (a leading MOF material) shows marginally higher C₂H₂ productivity (2091 mmol kg⁻¹),¹⁸ K-MER-2.0 demonstrates a two-fold enhancement in separation factor (12.1 vs. 6.24), significantly reducing acetylene loss during separation cycles (Fig. 3h and Table S7). Furthermore, K-MER-2.0 outperforms other benchmark materials, including Ce(IV)-MIL-140-4F (1370 mmol kg⁻¹, α = 4.9),³⁰ Y-bptc (1520 mmol kg⁻¹, α = 5),³¹ MFU-4 (1320 mmol kg⁻¹, α = 5.8),³² and Cd-NP (1242 mmol kg⁻¹, α = 4),³³ establishing it as the current performance leader among previously reported porous adsorbents, including MOFs and zeolites. (Table S7). Regeneration studies demonstrated exceptional desorption properties: complete CO₂ release occurred within 10 min under He purging at 353 K, with C₂H₂ signals dissipating immediately upon initiation of desorption (Fig. 3b). Subsequent temperature-programmed desorption to 473 K confirmed the absence of residual adsorbates *via* mass spectrometry, demonstrating full regenerability. This facile regeneration behavior

aligns with the low CO₂ adsorption enthalpy of the material and reversible adsorption isotherms, suggesting minimal energy requirements for cyclic operation, which is a critical advantage for industrial implementation.

Compared to K-MER-2.0 (23.4 min g⁻¹), the CO₂/C₂H₂ breakthrough time differentials for Na-MER-2.0 and Cs-MER-2.0 significantly decreased to 0.35 and 1.79 min g⁻¹, respectively (Fig. 3c). Notably, K-MER-2.0 demonstrated superior separation performance with a pure C₂H₂ yield of 1872 mmol kg⁻¹ and separation factor of 12.1, substantially exceeding those of Na-MER-2.0 (0.015 mmol kg⁻¹, 1.4) and Cs-MER-2.0 (47 mmol kg⁻¹, 3.6). These remarkable disparities established K-MER-2.0 as the optimal candidate for subsequent investigations. Systematic evaluation revealed that K-MER-2.0 maintained consistent CO₂ dynamic adsorption capacities between 63.8 and 65.1 cm³ g⁻¹ across flow rates spanning 2–8 mL min⁻¹ (Fig. 3d). Thermal stability tests showed that the C₂H₂ productivity remained 1291 mmol kg⁻¹ (69.0% retention) even at 333 K (Fig. 3e). Addressing the well-documented moisture sensitivity of zeolites,²³ K-MER-2.0 exhibited exceptional humidity tolerance, retaining 80.0% of its CO₂ breakthrough time and 73.9% C₂H₂ production capacity under 50% relative humidity (Fig. 3f). Furthermore, the material demonstrated excellent regeneration stability through seventeen consecutive adsorption–desorption cycles (desorption at 353 K), with negligible variation in CO₂/C₂H₂ breakthrough profiles (Fig. 3g). The excellent cycling stability of K-MER-2.0 was also preserved under humid conditions (Fig. S17).

To systematically validate the universality of K-MER-2.0 in CO₂/hydrocarbon separation, we performed dynamic breakthrough experiments using isovolumetric binary mixtures of CO₂/C₂H₄, CO₂/C₂H₆, and CO₂/CH₄ under a constant total flow rate of 4 mL min⁻¹ (Fig. 4a–c and Table S8). The separation performance exhibited remarkable consistency across different hydrocarbon systems. For the CO₂/C₂H₄ separation system, K-MER-2.0 demonstrated a CO₂ dynamic adsorption capacity of 64.8 cm³ g⁻¹, achieving ethylene purification with 99.6% purity (1663 mmol kg⁻¹ yield) and a separation factor of 27.3. In the CO₂/C₂H₆ system, comparable CO₂ uptake capacity (65.1 cm³ g⁻¹) was observed while maintaining an ethane purity of 99.6% (1789 mmol kg⁻¹ yield), with a separation factor of 19.3. Similarly, in the CO₂/CH₄ separation experiments, the material

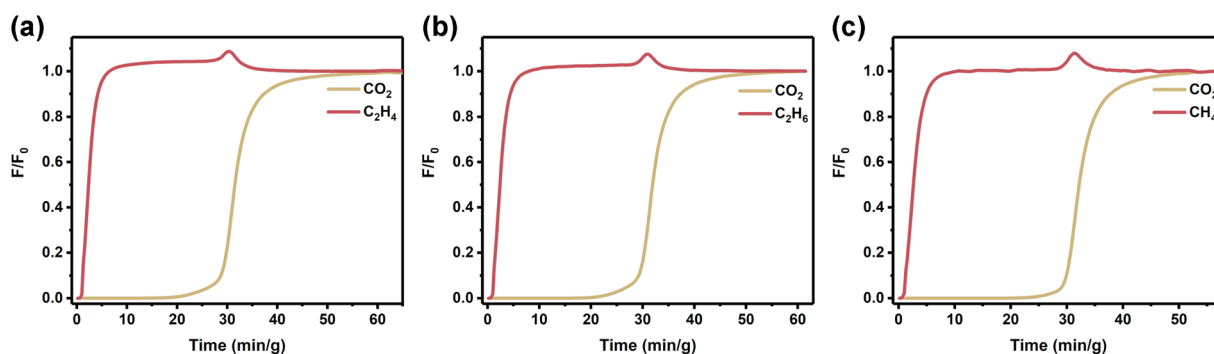


Fig. 4 Studies on the universality of K-MER-2.0 for separating CO₂ from other hydrocarbon mixtures. (a–c) Experimental breakthrough curves for isovolumetric CO₂/C₂H₄ (a), CO₂/C₂H₆ (b), and CO₂/CH₄ (c) mixtures at 298 K with a flow rate of 4 mL min⁻¹.



showed enhanced CO₂ capture capacity (66.1 cm³ g⁻¹) accompanied by methane purification to 99.6% purity (1992 mmol kg⁻¹ yield) and a separation factor of 13.9. These comprehensive results, supported by both static adsorption isotherms and dynamic breakthrough analyses, establish that K-MER-2.0 possesses exceptional versatility in gas separation applications. The material not only enables the reverse separation of CO₂/C₂H₂, but it also demonstrates superior separation performance for CO₂ removal from various hydrocarbon systems, including light alkenes (C₂H₄), alkanes (C₂H₆), and methane (CH₄).

The adsorption mechanisms of CO₂ in K-MER-2.0 have been systematically investigated through *in situ* CO₂ powder X-ray diffraction coupled with the static CO₂ adsorption isotherms. Notably, the flexible framework of K-MER-2.0 demonstrates a distinct structural transition from a contracted to an expanded state during CO₂ adsorption, as evidenced by characteristic inflection points in both static adsorption isotherms and *in situ* CO₂ PXRD patterns (Fig. S10 and S18). Meanwhile, it has been covered extensively in previous reports that this

structural transformation is accompanied by specific cation migration events: K⁺ ions relocate from initial positions at sites Ia (within the *d8r* cage) and sites II (in the *s8rs* between *pau* and *ste* cages) to energetically favorable positions at sites I (in the *s8rs* between *d8r* and *pau* cages) and sites III (in the *s8rs* between two adjacent *ste* cages) (Fig. S19).^{17,18,34–36} This concerted framework-cation interaction has been formally described as a cooperative cation-gated breathing mechanism.¹⁷ In striking contrast, C₂H₂ adsorption studies reveal fundamentally different behavior. The K-MER-2.0 framework maintains its contracted configuration throughout C₂H₂ exposure, as demonstrated by both the absence of inflection points in static adsorption isotherms and the negligible C₂H₂ uptake capacity of the material (5.3 cm³ g⁻¹) (Fig. 2a and Table S2). Periodic density functional theory (DFT) calculations were used to further explain the unique recognition ability of K-MER-2.0 towards CO₂. As shown in Fig. S20, the energy barrier for the transition from C₂H₂ adsorption on the contracted K-MER-2.0 framework to the expanded framework was 191.0 kJ mol⁻¹. In contrast, the energy barrier associated with the transition from

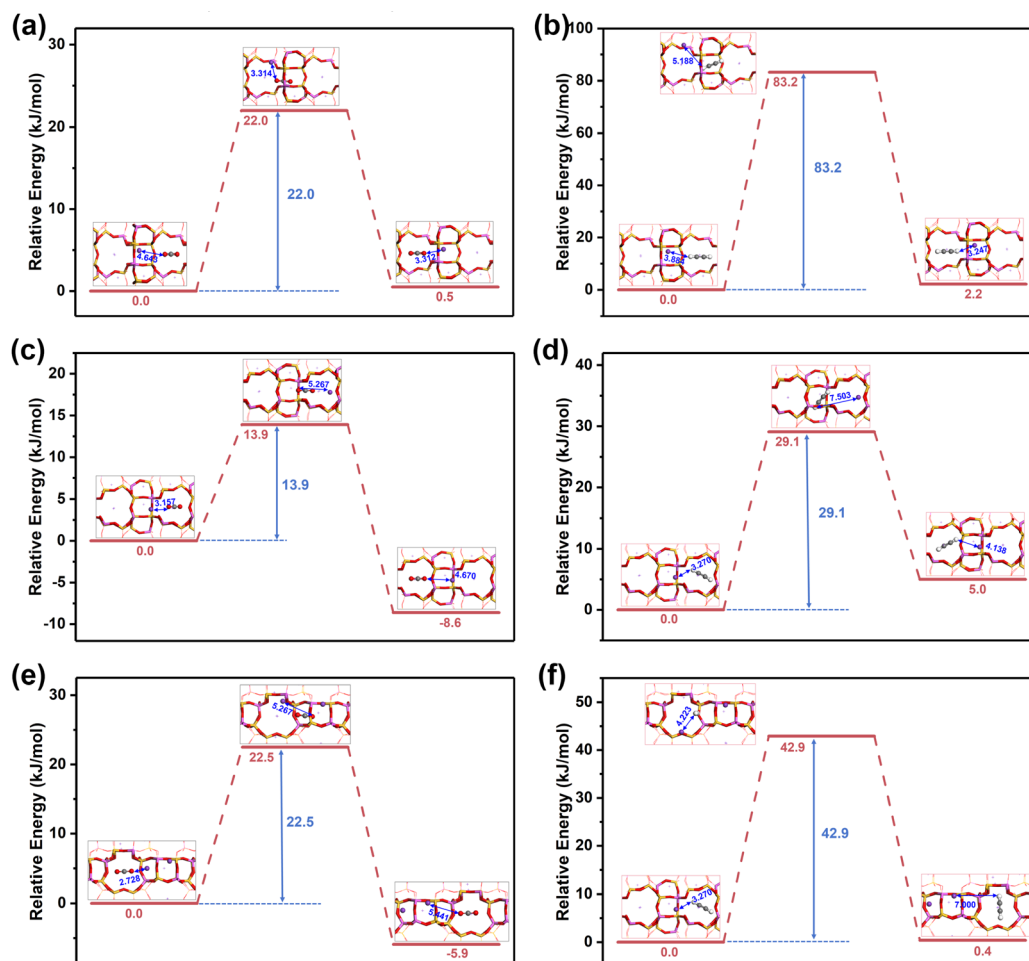


Fig. 5 DFT calculated trapdoor energy barriers for various diffusion pathways. (a and b) Energy barrier diagrams for the diffusion of CO₂ (a) and C₂H₂ (b) driving the migration of potassium ions (trapdoor effect) *via* pathway I. (c and d) Energy barrier diagrams for the diffusion of CO₂ (c) and C₂H₂ (d) driving the migration of potassium ions *via* pathway II. (e and f) Energy barrier diagrams for the diffusion of CO₂ (e) and C₂H₂ (f) driving the migration of potassium ions *via* pathway III. Herein, yellow, pink, red, purple, gray, and white represent silicon, aluminum, oxygen, potassium, carbon, and hydrogen atoms, respectively.



the contracted K-MER-2.0 framework to the expanded framework for CO₂ adsorption was only $-37.6 \text{ kJ mol}^{-1}$, significantly lower than that for C₂H₂. These theoretical models were based on a previously reported K-MER structure with a closely matched Si/Al ratio.¹⁷ These computational findings were in good agreement with the experimental observations, demonstrating that K-MER-2.0 undergoes selective framework expansion during CO₂ adsorption while maintaining a constricted pore geometry that effectively excludes C₂H₂. Notably, the K-MER-2.0 framework remains in an expanded state throughout the CO₂/C₂H₂ dynamic breakthrough process due to the presence of CO₂. However, C₂H₂ remains difficult to adsorb by the swollen K-MER-2.0 framework (C₂H₂ dynamic uptake: $5.38 \text{ cm}^3 \text{ g}^{-1}$). To further investigate this phenomenon, we conducted additional DFT calculations based on the expanded structural model of the K-MER framework. It is well established that the K-MER structure contains three distinct gas diffusion pathways: (i) from the *d8r* cage to the *pau* cage (denoted Pathway I), (ii) between adjacent ste cages (denoted Pathway II), and (iii) from the ste cage to the *pau* cage (denoted Pathway III) (Fig. S21). All cage-type structures along the diffusion pathways are interconnected through an 8-membered ring (8 MR). Meanwhile, although the K-MER framework remains in an expanded state during CO₂/C₂H₂ dynamic breakthrough, the potassium (K⁺) ions located within the 8 MR continue to play a “trapdoors” role throughout the breakthrough process. As illustrated in Fig. 5a–f and Table S9, the energy barriers for CO₂ to displace K⁺ ions along all three diffusion pathways (Pathway I: 22.0 kJ mol^{-1} ; Pathway II: 13.9 kJ mol^{-1} ; Pathway III: 22.5 kJ mol^{-1}) are significantly lower than those for C₂H₂ (Pathway I: 83.2 kJ mol^{-1} ; Pathway II: 29.1 kJ mol^{-1} ; Pathway III: 42.9 kJ mol^{-1}). These DFT calculations reveal that, even when the K-MER framework is in an expanded state, C₂H₂ remains more difficult to adsorb by K-MER compared to CO₂, which is consistent with the ultra-low C₂H₂ uptake ($5.38 \text{ cm}^3 \text{ g}^{-1}$) and remarkable CO₂/C₂H₂ separation factor (12.1) observed in the CO₂/C₂H₂ (50/50, v/v, 4 mL min⁻¹) breakthrough experiments at 298 K. The cation gating–breathing synergetic mechanism of the material enables preferential accommodation of CO₂ molecules while effectively excluding C₂H₂, establishing a novel mechanism for gas separation that combines molecular sieving with framework adaptability.

Conclusions

In summary, we have successfully demonstrated the organic-template-free synthesis of a K-MER-2.0 zeolite that exhibits unprecedented CO₂/C₂H₂ reverse separation performance *via* a unique cation-gating and breathing synergistic mechanism. The material exhibits a CO₂ adsorption capacity of $70.9 \text{ cm}^3 \text{ g}^{-1}$ at 298 K and 101 kPa, along with exceptional separation metrics, including a CO₂/C₂H₂ uptake ratio of 13.4 and record-breaking IAST selectivity of 3056. More importantly, the K-MER-2.0 zeolite delivers a high dynamic adsorption capacity of $65.1 \text{ cm}^3 \text{ g}^{-1}$ and separation factor of 12.1, which enable single-step C₂H₂ production of $1872 \text{ mmol kg}^{-1}$ with 99.6% purity, surpassing conventional energy-intensive purification methods.

Mechanistic studies reveal CO₂-triggered cooperative cation-gated breathing behavior, where selective pore activation occurs exclusively for CO₂ adsorption, while also maintaining pore closure against C₂H₂ molecules. The excellent selective adsorption capacity could be further extended to other CO₂/hydrocarbon systems. The practical viability of the K-MER-2.0 zeolite is further enhanced by efficient adsorption kinetics, exceptional moisture stability, and outstanding regenerability. Critically, the organic-template-free synthesis protocol enables cost-efficient production, positioning K-MER-2.0 as a viable industrial candidate for scalable applications. This work establishes a new paradigm for gas separation through stimulus-responsive pore modulation, simultaneously advancing both industrial gas purification technologies and a fundamental understanding of dynamic molecular sieving with zeolitic materials.

Author contributions

R. L. and C. L. conceived the research design and drafted the initial manuscript; L. L. and J. H. performed sample characterization; D. M., W. B., and X. Z. carried out theoretical calculations; and X. S. and Z. L. supervised the project and revised the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary Information: experimental details and characterization of the adsorbent. See DOI: <https://doi.org/10.1039/d5sc03281d>.

Acknowledgements

This work was supported by the National Key Research and Development Program (no. 2023YFB3810700), the National Natural Science Foundation of China (22375070 and 22288101), and the “111 Center” (B17020). We also thank the Shanghai Synchrotron Radiation Facility of BL17UM (<https://cstr.cn/31124.02.SSRF.BL17UM>) for assistance with experimental measurements.

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