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Exclusive Recognition of CO_2 from Hydrocarbons by Aluminum Formate with Hydrogen-Confined Pore Cavities

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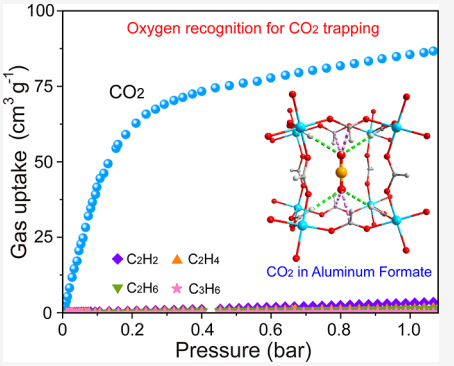
ABSTRACT: Exclusive capture of carbon dioxide (CO_2) from hydrocarbons via adsorptive separation is an important technology in the petrochemical industry, especially for acetylene (C_2H_2) production. However, the physicochemical similarities between CO_2 and C_2H_2 hamper the development of CO_2-preferential sorbents, and CO_2 is mainly discerned via C recognition with low efficiency. Here, we report that the ultramicroporous material $Al(HCOO)_3$, ALF, can exclusively capture CO_2 from hydrocarbon mixtures, including those containing C_2H_2 and CH_4. ALF shows a remarkable CO_2 capacity of 86.2 $cm^3\ g^{-1}$ and record-high CO_2/C_2H_2 and CO_2/CH_4 uptake ratios. The inverse CO_2/C_2H_2 separation and exclusive CO_2 capture performance from hydrocarbons are validated via adsorption isotherms and dynamic breakthrough experiments. Notably, the hydrogen-confined pore cavities with appropriate dimensional size provide an ideal pore chemistry to specifically match CO_2 via a hydrogen bonding mechanism, with all hydrocarbons rejected. This molecular recognition mechanism is unveiled by in situ Fourier-transform infrared spectroscopy, X-ray diffraction studies, and molecular simulations.



INTRODUCTION

Selective isolation of CO_2 from hydrocarbons is an essential industrial purification process, given the importance of hydrocarbons as raw materials for the chemical and material industries.[1−4] For example, CO_2 removal is crucial for both natural gas upgrading and the purification of hydrocarbon feedstocks prior to polymerization or chemical derivatization.[4−8] However, conventional techniques predominantly rely on absorption, extraction, and cryogenic distillation, which suffer from drawbacks such as inefficiency, high cost, and energy penalties.[2,3,9] These problems are particularly severe when separating CO_2 from acetylene (C_2H_2) as the molecules have almost identical molecular sizes and similar physicochemical properties (Figure S1).[4,10−16] Comparatively, adsorptive separation has shown great promise to supplement the traditional separation methods owing to its improved energy efficiency.[1,17−19] Extensive industrial experience has been accumulated in isolating light (less adsorbed) products. To utilize this experience and account for the presence of CO_2 as an unwanted impurity in typical feed gases (3−50% concentration), CO_2-selective sorbents are considered to be more advantageous.[4,5,11,14,16,20−25] A major bottleneck in developing sorbents for CO_2 capture from hydrocarbons is to construct the materials with the capability of preferentially trapping CO_2 over C_2H_2. A few reports have suggested that the direct production of pure C_2H_2 via a one-step sorption procedure using CO_2-selective sorbents may garner ca. 40% energy saving compared with the process using C_2H_2-selective sorbents.[20−23,25−27] Regardless, ubiquitous mechanisms of CO_2 capture, such as those leveraging on the recognition of carbon atoms with acidic chemical functions and/or π-bonds, bind C_2H_2 similarly to, if not more strongly than, CO_2, rendering them ineffectual for this separation (Scheme 1).[18] Consequently, exploiting improved operational simplicity and energy efficiency under CO_2-sequestering process configurations must leverage alternative recognition methods, which are urgently needed.

Ultramicroporous metal−organic frameworks (MOFs, pore size ≤7.0 Å), self-assembled by linking molecular units with well-defined shapes into periodic frameworks, are a sub-class of hybrid porous materials that distinguish themselves as promising candidates to address challenges of gas separations, especially light hydrocarbon separations.[1,17,28−33] Compared with nanoporous sorbents, the reduced pore dimensions and increased multiplicity of molecularly discriminating host−guest

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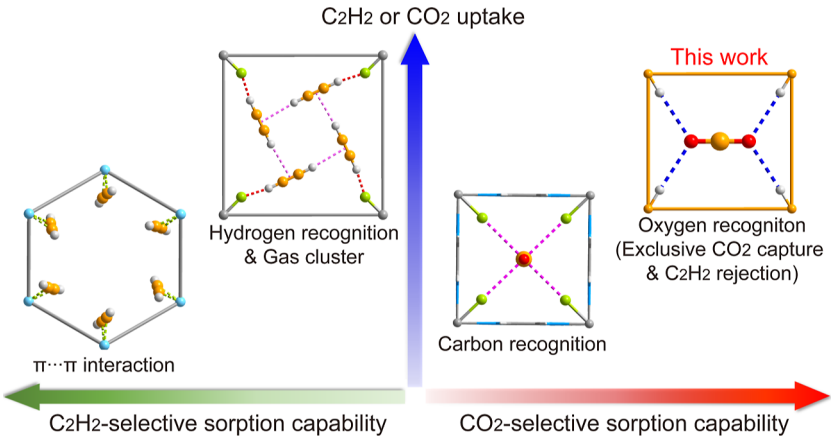
Scheme 1. Proposed Strategies for the Construction of C_2H_2- and CO_2-Selective Porous Materials



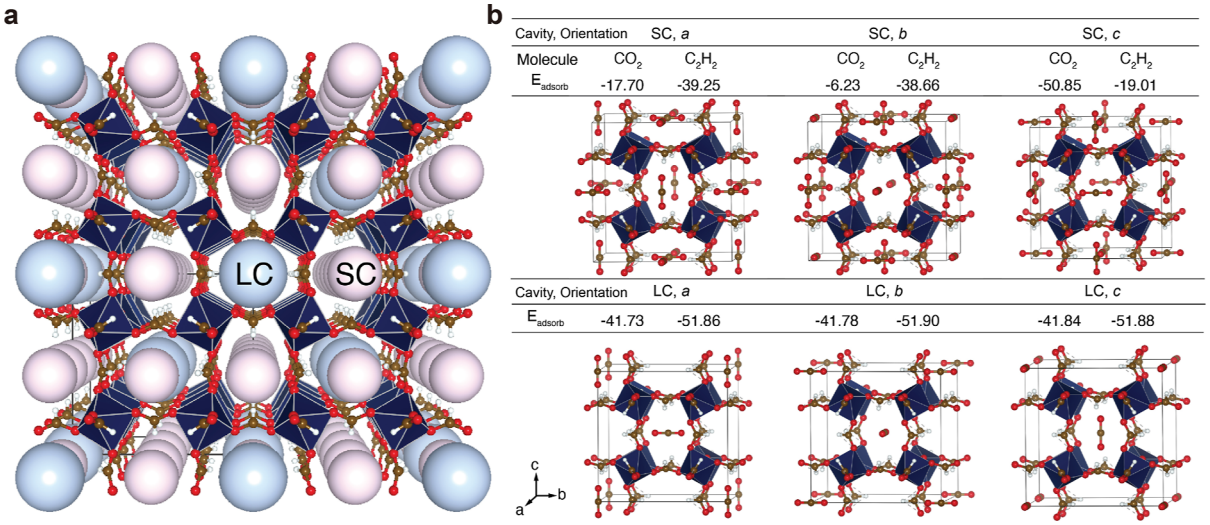


Figure 1. (a) Schematic illustration of the pore structure of ALF with two kinds of pore cavities, LC (pale blue balls) and SC (light purple balls), with pore windows confined by hydrogen atoms. (b) Computed heats of adsorption (E_{adsorb}, kJ/mol per molecule) of CO_2 and C_2H_2 in ALF with density functional theory: C_2H_2 and CO_2 adsorbed into LC and SC at three different orientations (CO_2 is used as a guide to show different orientations).

interactions can markedly enhance the gas separation performance. Among them, the inverse CO_2/C_2H_2 separation was rarely investigated due to limited knowledge of the relationships between pore chemistry and CO_2 preferential sorption behavior over C_2H_2. Recently, inverse CO_2/C_2H_2 adsorption was realized via the strategy to target the C atom in CO_2, but the capacity and selectivity were still moderate. For example, the hybrid ultramicroporous material, SIFSIX-3-Ni, is a prototypical example of inverse-selective material for CO_2/C_2H_2 separation.[4] The electronegative F atoms on the pore walls possess high CO_2 affinity via F···C interactions. In contrast, due to the capability of these sites to interact with H atoms of C_2H_2, the CO_2/C_2H_2 selectivity remained only moderate.[4] Although the related approaches leveraging electron transfer effects have afforded viable pore chemistry for inverse CO_2/C_2H_2 separation, they are yet to attain attractive CO_2 selectivity or uptake performance.[21] Furthermore, chemisorptive separation was also revealed to show the potential for selective trapping of CO_2 from C_2H_2, but the energy input for the adsorbent regeneration is still higher than that of physical adsorptive separation.[20] Considering the tendency for cross-species interaction (simultaneously interacting with C of CO_2 and H of C_2H_2) in CO_2-selective sorbents targeting the C atom during CO_2/C_2H_2 separation, we were motivated to search for alternative mechanisms accessible to ultramicroporous frameworks as a basis for CO_2 capacity and CO_2/C_2H_2 selectivity enhancements. We envisaged that incorporating specific electropositive recognition sites for the electronegative O atoms of CO_2 would exert opposite affinity for the acidic H atoms of C_2H_2 and other hydrocarbons, thus realizing favorable CO_2 capture performance.

Recently, we have shown that the robust ultramicroporous material, aluminum formate ($Al(HCOO)_3$ or ALF), exhibits a strong affinity for CO_2 capture from dried flue gases containing a mixture of CO_2 and N_2.[34] ALF, which adopts a ReO_3-type structure,[35] contains two types of cavities (Figure 1a). Three-quarters of the ALF cavities are smaller cavities (indicated as SC), in which the C−H groups from the bridging formate ligands are perfectly arranged to provide an ideal, hydrogen-bonded docking site for CO_2 (Figures 1a and S2). The hand-in-glove arrangement is so perfect that CO_2 acts as a template for forming the structure of the parent as-made compound, $ALF{\cdot}3/4CO_2{\cdot}1/4(HCOOH){\cdot}1/4H_2O$.[36] A quarter of the

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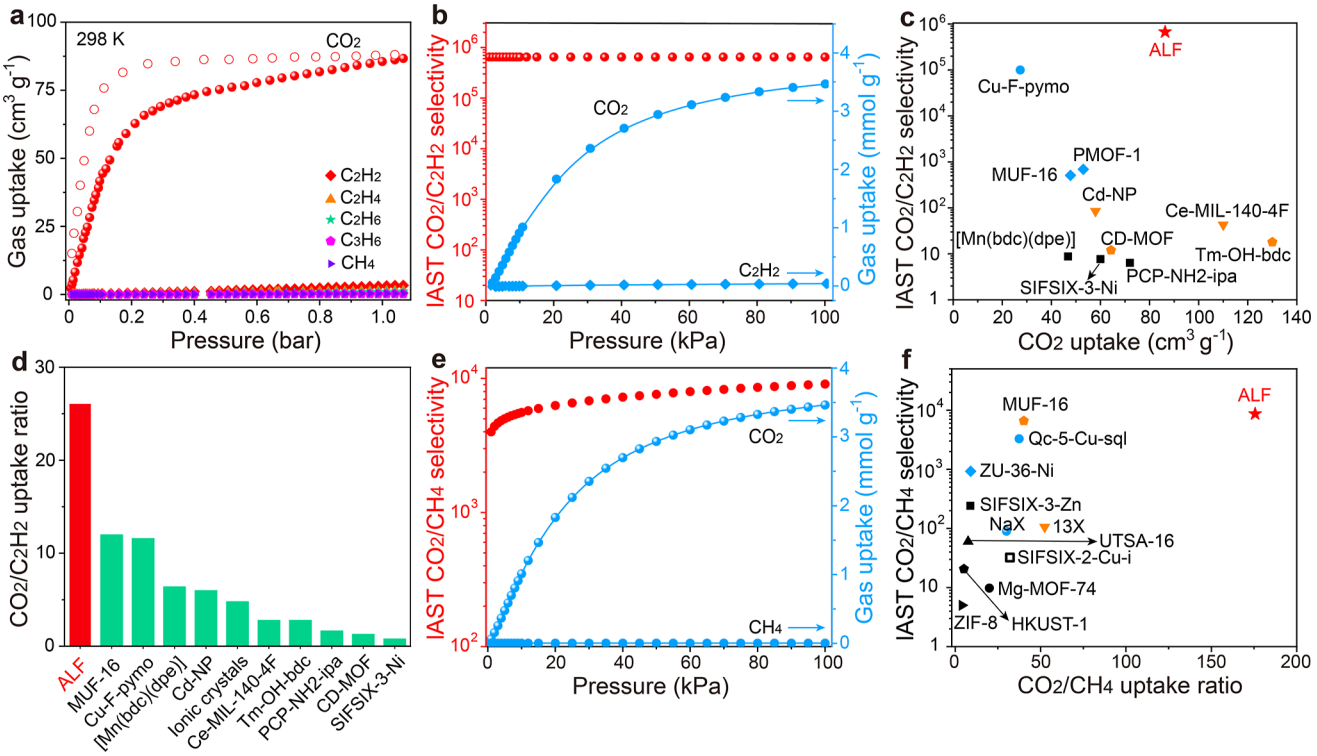

Figure 2. (a) CO_2 and hydrocarbon sorption isotherms on ALF at 298 K. (b) Predicted mixture adsorption isotherms and selectivity of ALF based on IAST for a 50/50 CO_2/C_2H_2 mixture at 298 K. (c) Comparison of IAST CO_2/C_2H_2 (50/50) selectivity and CO_2 uptake for state-of-the-art CO_2-selective materials. (d) Comparison of CO_2/C_2H_2 uptake ratios at 298 K and 1 bar between ALF and other CO_2-selective materials. (e) Predicted mixture adsorption isotherms and selectivity of ALF based on IAST for a 50/50 CO_2/CH_4 mixture at 298 K. (f) Comparison of IAST CO_2/CH_4 (50/50) selectivity and CO_2/CH_4 uptake ratios of selected porous materials at 298 K and 1 bar.

cavities in ALF are larger cavities (LC), and there are no formate C−H groups for such hydrogen bonding, but the pore window is restricted by two H atoms. Thus, both kinds of pore cavities in ALF are confined by H atoms.

In light of the above observations, we explored whether the unique hydrogen-confined pore cavities of ALF would make it a suitable candidate for the separation of CO_2-containing hydrocarbon mixtures, especially for CO_2/C_2H_2 and CO_2/CH_4 mixtures. We show that ALF achieves an exclusive CO_2 capture behavior with high capacity from hydrocarbons. Notably, ALF shows the ultrahigh CO_2/C_2H_2 separation selectivity of 6.5×10^5, which sets a new benchmark for inverse CO_2/C_2H_2 separation. We also present data for separating CO_2 from several C_1, C_2, and C_3 hydrocarbons. The dynamic breakthrough experiments confirmed the performance of ALF for highly efficient CO_2 capture from hydrocarbons and inverse separation of CO_2/C_2H_2 mixtures. The pore environments investigated by molecular simulations show that the electrostatic potential of the pore surface is complementary to CO_2, with CO_2 captured via H···O and C···O interactions. The ease of ALF synthesis using inexpensive and widely available precursors ($Al(OH)_3$ and formic acid) is another advantage that bodes well for future scale-up development.

RESULTS AND DISCUSSION

Synthesis and Characterization of Aluminum Formate. The as-made ALF was synthesized according to a previously reported procedure by the reaction of $Al(OH)_3$ and Na_2CO_3 in formic acid solution at mild conditions and then activated at vacuum, giving rise to activated ALF.[36] The pore dimensions of two kinds of cavities, SC and LC (Figures 1a and S3), are very similar to the dimensions of CO_2 and C_2H_2 but smaller than those of other C_2 and C_3 hydrocarbons. The purity of the as-synthesized bulk samples was established by comparing the experimentally collected and simulated powder X-ray diffraction (PXRD) patterns (Figure S4). Additionally, ALF can retain its crystallinity after being exposed to air for one month.[34] The thermal stability of the activated material was further evaluated by thermogravimetric analysis (TGA), and the result shows that ALF is stable up to 503 K (230 °C) (Figure S5).

CO_2 and Hydrocarbon Sorption Performance. The small pore sizes of all cavities make ALF an interesting candidate for CO_2 adsorption and separation. Single-component CO_2 and C_2H_2 gas sorption isotherms on ALF were first collected at 298 K. It is intriguing to find that ALF adsorbs CO_2 with high capacity but shows negligible C_2H_2 uptakes (Figure 2a). To further investigate the behavior of ALF, we collected the sorption isotherms of other hydrocarbons, including CH_4, C_2H_4, C_2H_6, and C_3H_6. The results show that all these larger molecules are excluded by ALF. The combination of the exclusive CO_2 capture performance with high capacity and selectivity against these important hydrocarbons in ALF appears remarkable, with rare precedents.[5] Detailed analysis indicates that the capacity of CO_2 can reach 86.2 $cm^3\ g^{-1}$ (3.85 mmol g^{-1}) at 1 bar and 298 K, but C_2H_2 uptake is only 3.3 $cm^3\ g^{-1}$ under the same conditions. Even over a broad temperature range, ALF still exhibits high CO_2 uptakes (273−323 K, Figure S6) and negligible or low C_2H_2 uptakes (253−333 K, Figure S7). Notably, the CO_2 uptake is much higher than that of most state-of-the-art materials used for inverse CO_2/C_2H_2 separation (Table S1), such as MUF-16

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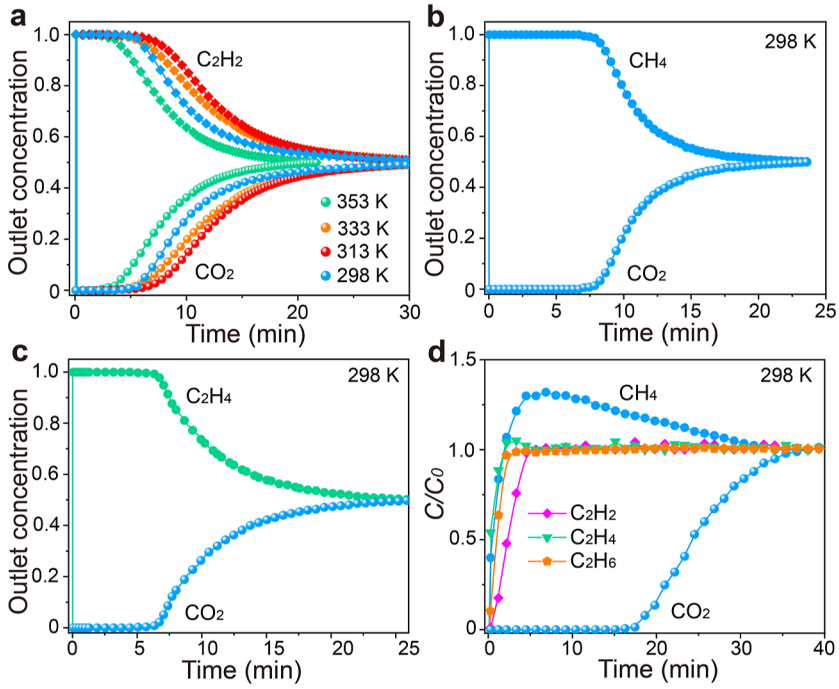

Figure 3. (a–c) Experimental fixed-bed breakthrough results for equimolar CO_2/C_2H_2 (a), CO_2/CH_4 (b), and CO_2/C_2H_4 (c) mixtures. (d) Breakthrough curves of the $CO_2/C_2H_2/C_2H_4/C_2H_6/CH_4$ (1/1/1/1/1) mixture on ALF at 298 K. Note: a flow rate of 2.0 mL min^{-1} was used for all breakthrough experiments.

(47.8 cm^3 g^{-1}),[5] Cd-NP (58 cm^3 g^{-1}),[27] SIFSIX-3-Ni (60.5 cm^3 g^{-1}),[4] and even the inverse sieving material Cu-F-pymo (26.7 cm^3 g^{-1}).[11]

To quantitatively evaluate the separation potential of ALF, the ideal adsorbed solution theory (IAST) was utilized to estimate the separation selectivity toward an equimolar CO_2/C_2H_2 mixture (Figure 2b). The inverse selectivity can reach 6.5 × 10^5, far exceeding those of most MOFs with inverse CO_2/C_2H_2 separation capabilities (Figure 2c and Table S1). For example, the inverse selectivities of Cd-NP[11] and MUF-16[5] are 10^5 and 510, respectively. According to the IAST calculations, ALF features a high CO_2 uptake of ∼3.5 mmol g^{-1} from an equimolar CO_2/C_2H_2 mixture while exhibiting a negligible C_2H_2 uptake (Figure 2b). The uptake ratio is another important parameter demonstrating the preference and separation potential of the adsorbent for certain molecules over others. For ALF, the calculated CO_2/C_2H_2 uptake ratio is 26.1, much higher than that reported for benchmark materials, such as Cu-F-pymo (11.6),[11] MUF-16 (12),[5] Ce-MIL-140-4F (2.8),[21] and Tm-OH-bdc (2.8)[22] (Figure 2d). Such a high CO_2 capacity and CO_2/C_2H_2 uptake ratio signify that ALF sets a new benchmark for inverse CO_2/C_2H_2 adsorption and separation (Figure 2c). Additionally, the uptake ratios and separation selectivity of ALF for other hydrocarbons are equally impressive (Figures 2e,f and S8, Table S2). The equimolar CO_2/CH_4 separation selectivity and CO_2/CH_4 uptake ratio can reach ∼9100 and ∼172, respectively, higher than those on MUF-16 (6686 and 40, respectively).[5] These results underline the outstanding separation performance of ALF in removing CO_2 from hydrocarbons.

CO_2 Separation Performance from Hydrocarbons. To intuitively evaluate the performance of CO_2 dynamic trapping and inverse sieving effects for CO_2/C_2H_2, fixed-bed breakthrough experiments were carried out (Figure 3). As expected, a complete separation of CO_2/C_2H_2 was observed with high-purity C_2H_2 immediately harvested from an ALF-packed column (Figure 3a). The calculated CO_2 trapped amount on ALF from the breakthrough experiment was ∼2.32 mmol g^{-1}, with the C_2H_2 productivity of ∼5.4 mmol g^{-1}—32 times higher than that on Cu-F-pymo (0.166 mmol g^{-1}).[11] The dynamic uptake of CO_2 in these runs was similar to our observations for static sorption experiments (Figure 2a). The CO_2 capture capacity was ∼2.75 mmol g^{-1} at 313 K, higher than those at other temperatures (2.64 and 2.0 mmol g^{-1} at 323 and 353 K, respectively). The CO_2 breakthrough time also follows the order that it is longer at 313 K compared with those at other temperatures. To further validate the temperature effect on the CO_2 capture performance, single-component CO_2 breakthrough curves were collected (Figure S9). Similarly, the results show that there is a suitable temperature favorable for CO_2 mass transfer. At 313 K, the dynamic CO_2 sorption amount is ∼3.1 mmol g^{-1}. Additionally, the higher flow rates and the existence of humidity would not compromise the CO_2 capture and C_2H_2 production performances of ALF (Figure S10). The CO_2 capture performance of ALF is meritorious and sets a new benchmark for inverse CO_2/C_2H_2 separations with the inverse sieving effect for C_2H_2. Furthermore, benefiting from the sieving effect for hydrocarbons, ALF is an exclusive and promising material to efficiently trap CO_2 from CO_2-containing hydrocarbon mixtures (Figure 3b–d). In particular, ALF, with its low cost and easy synthesis procedure, is a very promising porous material to remove CO_2 in natural gas sweetening, biogas processing, and hydrocarbon upgrading, especially C_2H_2 purification.

CO_2 Trapping Mechanism. It is reasonable that ALF with small pore sizes exhibits excellent size-selective sieving behavior toward mixtures of CO_2 with other large gas molecules, such as CH_4, C_2H_4, C_2H_6, and C_3H_6. However, the inverse sieving effect for CO_2 and C_2H_2 (where the kinetic

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diameters of both molecules are 3.3 Å) is unexpected. To understand the origins of this puzzling behavior, we investigated the in situ FTIR spectrum of CO_2-loaded ALF (Figure S11). The C═O bond peak of ∼1600 cm^{-1} (antisymmetric stretching vibration) is blue-shifted to ∼1615 cm^{-1}, and the bending vibration peaks of C−H bond at ∼467 and ∼490 cm^{-1} are blue-shifted to ∼474 and ∼500 cm^{-1}, respectively. These changes indicate that the trapped CO_2 molecules in ALF interact with the H or C atoms of formate groups in the pore channels. The new emerging peak at ∼1405 cm^{-1} is linked to the symmetric formate mode due to subtle structural modifications from CO_2 adsorption. Furthermore, the electrostatic potential of CO_2 can complement the pore surface potential surrounded by H and C atoms (Figures S12−S14). Notably, ALF can exclusively trap CO_2 from hydrocarbons owing to the combination of the specific electropositive pore windows and cavities restricted by H and C atoms with suitable pore chemistry and the narrow ultramicro pore. The mutual repulsion effect between H atoms of formate and H atoms of C_2H_2 leads to a repulsive interaction that hinders adsorption and also lowers the heat of adsorption (see below). This simplified electrostatic picture can qualitatively explain why only CO_2 can be trapped, with C_2H_2 being excluded. In situ C_2H_2 synchrotron diffraction experiments on ALF further confirmed that no C_2H_2 entered ALF over the course of 30 min time scales at 253 and 313 K (Figure S15 and Table S4, S5). This aligns with the presented isotherm data and verifies that ALF is selective against C_2H_2.

We performed dispersion-corrected density functional theory (DFT-D3) calculations to compare the heats of adsorption (E_{adsorb}) of CO_2 and C_2H_2 in ALF (Figure 1b). Although C_2H_2 does not readily adsorb into ALF, the results show that E_{adsorb} of C_2H_2 into SC and LC of ALF are favorable and broadly similar (around 39 and 52 kJ/mol for C_2H_2 in its preferred orientations in SC and LC, respectively) to those of CO_2 (around 51 and 42 kJ/mol for CO_2 in its preferred orientations in SC and LC, respectively). However, since all the C−H bonds of the formate ligands point toward SC instead of LC, C_2H_2 shows a preference for LC, whereas CO_2 prefers SC. By inspecting the results of adsorption calculations, we observed that CO_2 and C_2H_2 manifest preferred orientations in SC. CO_2 aligns toward the C−H bonds, whereas C_2H_2 favors the perpendicular directions (Figure 1b). In this way, the CO_2 molecules establish stabilizing hydrogen bonds with the C−H groups, which is not possible in the case of C_2H_2. In LC, CO_2 and C_2H_2 do not have preferred orientations in terms of adsorption energy, suggesting that they can show positional disorder. Based on these results, we believe that the separation of CO_2/C_2H_2 is not driven by thermodynamic effects since the heats of adsorption are both favorable. It appears to be a kinetic effect, which is consistent with the observation of modest C_2H_2 uptake into ALF at 313 K (Figure S7).

To address this kinetic effect, we evaluated the translation barriers of both CO_2 and C_2H_2 to verify whether the adsorption of these molecules in ALF may be kinetically hindered. Nudged elastic band calculations were performed, and the energy barriers of translating C_2H_2 and CO_2 within ALF in the dilute limit (one molecule per unit cell of ALF) were computed (Tables S6, S7 and Figure S16). There are two main types of translation mechanisms that can happen in the ALF structure: (1) translation of a guest molecule (CO_2 or C_2H_2) between two small cavities and (2) guest molecule translation between a small and a large cavity. For scenario (1) (and from symmetry considerations on the ALF structure), both C_2H_2 and CO_2 should rotate by 90° when exchanging between two neighboring small cavities. For example, a CO_2 departing from its most stable adsorbing configuration (along the *c* direction in SC) will initially align along the crystallographic direction when exchanged with a nearby small cavity. This step will be followed by a rotation of CO_2 to reach its most stable orientation along the *c* direction. As for scenario (2), the translation can only happen between molecules aligned in the *b* direction, where the molecule points toward a large cavity and any direction in the nearby large cavity. We also found that both CO_2 and C_2H_2 can only translate along C═O or C−H bond directions, respectively, through the aperture between two cavities without rotations. The energy barriers of translating CO_2 between two adjacent small cavities are ∼654 or ∼292 meV, depending on the direction of translation (Figure S16), whereas for C_2H_2, the barriers are nearly direction-independent (∼437 and ∼535 meV). As for the translation between a small and a large cavity, CO_2 shows barriers of ∼152 or ∼624 meV. In contrast, the same translation mechanism for C_2H_2 is accompanied by unsurmountable translation barriers of ∼821 or ∼1018 meV. These results show that C_2H_2 access to the large cavity is highly impeded and that the passage of CO_2 between both types of apertures (between cavities) is easier than that of C_2H_2. Although the large cavity in ALF provides a higher heat of adsorption for C_2H_2, it remains inaccessible due to the extremely high activation barriers.

CONCLUSIONS

Efficient CO_2 capture from hydrocarbons is required to achieve both carbon neutrality and sustainable development and is also important for producing high-purity hydrocarbons. We report that ALF shows excellent exclusive CO_2 separation performance from CO_2-containing hydrocarbon mixtures. Notably, the hydrogen-confined pore cavity with an electropositive surface and appropriate dimension provides a perfect pore chemistry to devotedly match the potential of CO_2 via weak H···O and C···O interactions. The exclusive CO_2 trapping behavior was validated via single-component gas adsorption and dynamic breakthrough experiments using CO_2-containing hydrocarbon mixtures. ALF exhibits a benchmark inverse sieving separation performance for CO_2/C_2H_2 mixtures. High-purity C_2H_2 (99.99%) with a productivity of 5.4 mmol g^{-1} was obtained via only a one-step sorption procedure. Equally, the performance of ALF for separating CO_2 from methane is also impressive, suggesting that it could find utility in biogas processing.[37] The exclusive CO_2 capture behavior in an ultramicroporous material with hydrogen-confined pore cavities provides deep insights into the bottom-up design strategies of advanced porous materials used for molecular recognition.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c01705.

Details of experimental section, material synthesis, gas adsorption and separation procedures, FTIR spectra, PXRD patterns, TGA, and DFT calculations (PDF)

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Author Contributions

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Notes

The authors declare the following competing financial interest(s): A patent has been filed by the National University of Singapore based on the present results (SG Patent Application No. 10202260362V).

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