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Short Communication

Twisted pore aperture of MOF induced three-dimensional restricted sieving separation for CO₂ and C₂H₂ mixtures

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Acetylene (C₂H₂) is one of the most important chemical raw materials and is widely used as a feedstock for the production of various fine chemicals and electronic materials [1]. In industry, C₂H₂ is mainly produced through partial methane combustion and thermal hydrocarbon cracking [2], which is always accompanied by a low concentration of carbon dioxide (CO₂) impurity, causing negative effects on follow-up utilization. Therefore, the separation of C₂H₂ and CO₂ is crucial for C₂H₂ purification. Compared to the traditional highly energy-intensive solvent extraction and low-temperature distillation separation methods, the adsorptive separation based on porous materials is a promising alternative technology [3,4]. However, the separation of CO₂/C₂H₂ is scientifically challenging due to their similar physical and chemical properties (Table S1 online) [5].

Molecular-sieving separation is considered as an ideal way for adsorption separation since it can afford the theoretically infinite selectivity and high separation efficiency. Metal-organic frameworks (MOFs) are excellent porous mediums to achieve molecular-sieving effects for specific gas mixtures, due to their structural diversity, and adjustable structure [6]. Actually, a series of molecular-sieving MOF adsorbents have been developed for light hydrocarbon purification based on the differences in cross-sectional areas of target molecules (Table S2 online), namely the two-dimensional (2D) restricted mechanism. The complexity of different gas separations can be classified by the molecular kinetic diameter differences [7], as shown in Fig. 1a. However, for the CO₂/C₂H₂ separation, due to the same kinetic diameter (3.3 Å) and very close cross-sectional areas (3.2 Å × 3.3 Å for CO₂ and 3.3 Å × 3.3 Å for C₂H₂) (Fig. 1b and Table S1 online), molecular-sieving separa-

tion of CO₂/C₂H₂ by the traditional 2D restricted mechanism is considered impractical [8–11]. In spite of this, the difference in their three-dimensional (3D) sizes (CO₂, 3.2 Å × 3.3 Å × 5.4 Å; C₂H₂, 3.3 Å × 3.3 Å × 5.7 Å) still provides a narrow window of opportunity to achieve ideal molecular-sieving separation of CO₂ and C₂H₂ via 3D restricted effect (Fig. 1b and c). Specifically speaking, linear C₂H₂ with longer molecular size will be significantly restricted in the twisted pore aperture MOF compared with shorter CO₂ molecule, and the 3D restricting effect can lead to a molecular-sieving effect for target molecules with nearly identical cross-sectional areas but different molecular lengths (Fig. 1d and e). However, 3D restricted sieving based on the length difference of linear molecules with nearly identical cross-sectional areas has not been reported. Therefore, we propose 3D restricted sieving strategy by constructing twisted pore aperture in MOF for molecular-sieving separation (Fig. 1e), which can provide a new routine for highly efficient separation of some challenging separation systems.

As a proof-of-concept experiment, two cheap and robust isostructural M-Trz (Trz = 1,2,4-triazole) MOFs with twisted pore aperture, namely Ni-Trz and Cu-Trz, were employed for CO₂/C₂H₂ separation. Ni-Trz with relatively wider aperture size undergoes co-adsorption of CO₂ and C₂H₂, while Cu-Trz with slightly narrower aperture size shows efficient CO₂ adsorption and selective molecular exclusion for C₂H₂.

The two isostructural MOFs, Ni-Trz and Cu-Trz, were synthesized by hydrothermal method [12,13]. Powder X-ray diffraction (PXRD) patterns confirmed the phase purity of Ni-Trz and Cu-Trz (Fig. S1 online). The trinuclear metal clusters are interlinked by the Trz ligands, generating rigid narrow channels (Fig. 1f). It should be noted that the narrow aperture of the M-Trz MOF contains six hydrogen atoms, which are divided into two layers due to the different orientation of the C–H bond, and hydrogen atoms in the two layers are arranged in the vertex of two twisted triangles, resulting in a twisted pore aperture (Fig. 1g). In addition, the precise control

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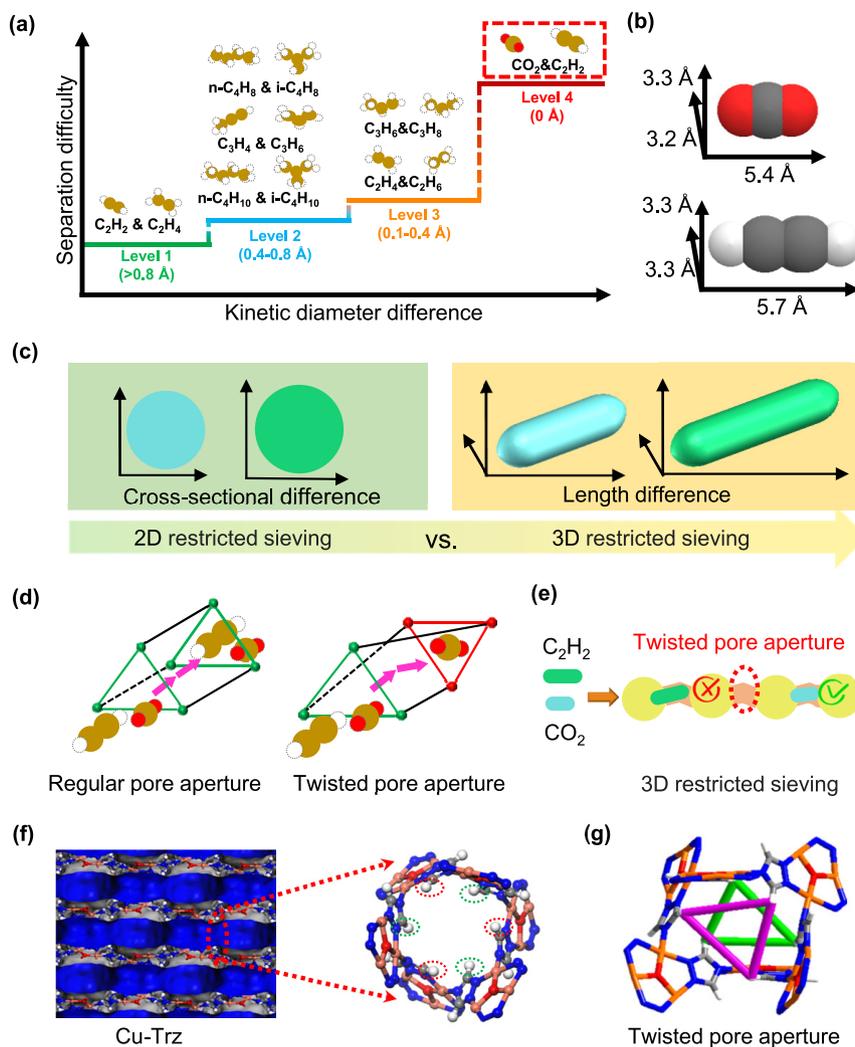


Fig. 1. Twisted pore aperture of MOF induced 3D restricted molecular-sieving mechanism for $\text{CO}_2/\text{C}_2\text{H}_2$ separation. (a) The complexity of different gas separations classified by the molecular kinetic diameter differences. (b) The molecular dimensions of CO_2 and C_2H_2 . (c) The comparison of traditional 2D restricted molecular-sieving mechanism and the proposed 3D restricted molecular-sieving mechanism (d, e) Schematic diagram of the 3D restricted molecular-sieving mechanism induced by the twisted pore aperture for $\text{CO}_2/\text{C}_2\text{H}_2$ separation. (f, g) The Connolly surface structure of Cu-Trz MOF and its twisted pore aperture.

of aperture size at 0.1 Å scale via a judicious choice of ligand alone is challenging since traditional ligand expansion and functional group modification can only change the pore size at nanometer or angstrom scale with a large gap. Herein, the additional regulation on the aperture size of the twisted pore in M-Trz MOFs was achieved by modulating the coordination bond length of M-Trz MOFs. The coordination bond length of the Cu-N bond in Cu-Trz is 1.96 Å while it is 1.98 Å for Ni-N bond in Ni-Trz. As expected, the size of the coplanar M_3O based fragments in the isostructural MOFs successfully inherits this subtle difference, which can result in a regulation of twisted pore aperture (Fig. S2 online). Since M-Trz has twisted pore aperture, the linear molecules with different lengths will be subject to different restricting effects during the mass transfer process, which we believe is promising for the 3D restricting molecular-sieving separation of $\text{CO}_2/\text{C}_2\text{H}_2$ mixtures.

Motivated by the 3D restricting molecular-sieving effect, single-component adsorption isotherms of CO_2 and C_2H_2 in M-Trz were measured at ambient conditions. Fig. 2a shows that both CO_2 and C_2H_2 can be well adsorbed by Ni-Trz. Interestingly, for the case of Cu-Trz, a negligible uptake amount of C_2H_2 was observed under the same conditions, while CO_2 could still enter the channel freely (Fig. 2b). Similar results were also observed even at 273 and 190 K

(Figs. S3, S4 online), which excludes the possible thermodynamic separation based on the difference in gas affinity. This opposite adsorption result shows that the width of the twisted pore aperture is also important for the 3D restricted molecular-sieving separation, and too wide aperture size will lead to the co-adsorption phenomenon. Notably, Cu-Trz only has a C_2H_2 adsorption capacity of $1.1 \text{ cm}^3 \text{ g}^{-1}$ at 100 kPa and 298 K, which is a record lower than previously reported benchmark MOFs (Fig. S5 and Table S3 online). The negligible uptake amount of N_2 , CH_4 , C_2H_4 , and C_2H_6 as well as the high H_2O uptake further suggest that Cu-Trz can exclude larger molecules than C_2H_2 , while it can adsorb molecules smaller than CO_2 (Figs. S6-S9 online). Besides, the results of *in situ* XRD tests of Cu-Trz in the CO_2 adsorption show that the XRD patterns nearly kept consistent from vacuum to low pressure and up to 100 kPa (Fig. S10 online). This indicates that the Cu-Trz has excellent structural rigidity during CO_2 adsorption, which rules out the possible framework flexible-induced sieving behavior [14].

To further verify the distinct adsorption behaviors of C_2H_2 and CO_2 on the two isostructural MOFs, the kinetic adsorption properties of Ni-Trz and Cu-Trz were investigated using the time-dependent adsorption curves of C_2H_2 and CO_2 (Fig. S11 online). For Ni-Trz, both CO_2 and C_2H_2 were quickly adsorbed and the

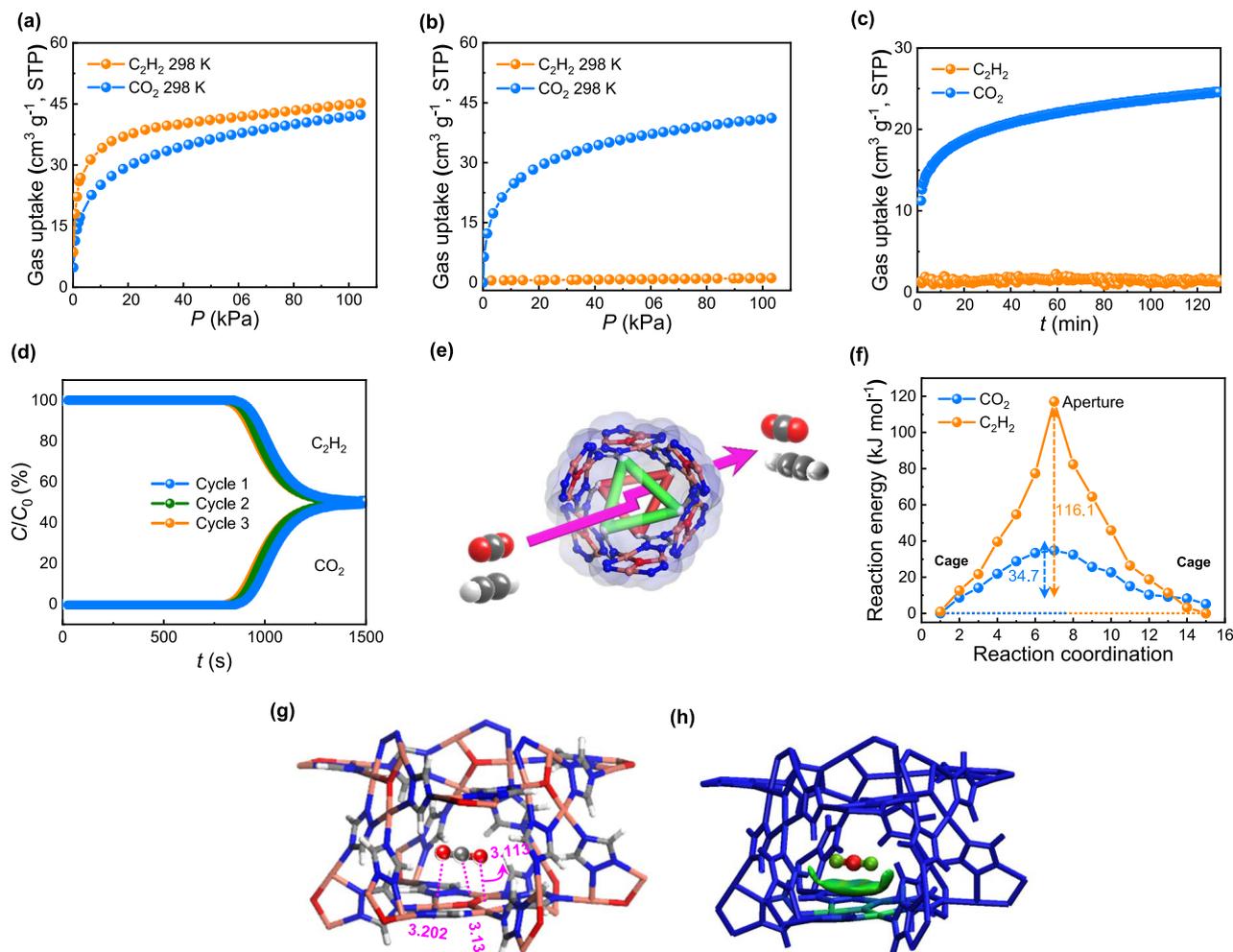


Fig. 2. Gas adsorption properties of M-Trz and First-principle density functional theory (DFT) calculated CO_2 and C_2H_2 diffusion and CO_2 adsorption in Cu-Trz. (a) Adsorption isotherms of CO_2 and C_2H_2 at 298 K for Ni-Trz. (b) Adsorption isotherms of CO_2 and C_2H_2 at 298 K for Cu-Trz. (c) Time-dependent gas uptake profiles of CO_2 and C_2H_2 for Cu-Trz at 298 K. (d) Three cycles of dynamic column breakthrough curves of $\text{CO}_2/\text{C}_2\text{H}_2$ separation on Cu-Trz. (e) Schematic diagram of CO_2 and C_2H_2 molecular diffusion through the twisted pore aperture of Cu-Trz. (f) The DFT calculated gas diffusion energy barrier associated with the CO_2 and C_2H_2 transport in twisted pore aperture. (g) Optimized geometry for the CO_2 interactions in Cu-Trz MOF. (h) The independent gradient mode (IGM) analysis for CO_2 adsorption in Cu-Trz, where the green isosurface denotes the weak vdW-type interactions (color codes for the contribution of individual atoms on intermolecular interactions: red atoms represent large contributions, green atoms express moderate contributions, and blue atoms show the negligible contributions).

CO_2 possesses a faster adsorption rate than that of C_2H_2 for its small molecular length. For Cu-Trz, CO_2 was immediately adsorbed until equilibrium, while the adsorption of C_2H_2 remained negligible even after 130 min (Fig. 2c). Moreover, the diffusional time constants of Cu-Trz for C_2H_2 and CO_2 were calculated to be 2.374×10^{-7} and $6.423 \times 10^{-3} \text{ min}^{-1}$ based on the time-dependent adsorption curves (Fig. S12 and Table S4 online), respectively. This further indicates the molecular-sieving effect of Cu-Trz in dynamic adsorption and rules out the possibility of slow C_2H_2 adsorption. Meanwhile, the heats of adsorption of M-Trz were calculated by the adsorption isotherms of 298 and 323 K, and the adsorption heat of CO_2 at zero coverage in Cu-Trz is 53 kJ mol^{-1} (Figs. S13–S15 online), implying the strong CO_2 affinity of Cu-Trz. As for Ni-Trz (Figs. S16–S19 online), the adsorption heat of C_2H_2 at zero coverage is 60 kJ mol^{-1} , which is higher than that of CO_2 (40 kJ mol^{-1} , Fig. S20 online). To evaluate the actual CO_2 and C_2H_2 mixture separation performance of Cu-Trz MOFs, breakthrough experiments of $\text{CO}_2/\text{C}_2\text{H}_2$ (50:50, v:v) gas mixture were carried out at 298 K (Fig. S21 online). It can be found that the $\text{CO}_2/\text{C}_2\text{H}_2$ gas mixture can be efficiently separated by Cu-Trz. In addition, the prices of Trz ligand and metal salt of Cu-Trz are very

cheap among the reported CO_2 -selective MOF adsorbents (Fig. S22 and Tables S5, S6 online). Besides, the Cu-Trz MOF has excellent chemical stability and recycling ability (Fig. 2d and Figs. S23–S25 online), demonstrating that it is a new benchmark material for $\text{CO}_2/\text{C}_2\text{H}_2$ separation.

To further understand the molecular-sieving separation of $\text{CO}_2/\text{C}_2\text{H}_2$ mixture in Cu-Trz MOF at the molecular level, the gas diffusion energy barriers associated with the CO_2 and C_2H_2 transport via the narrow aperture were calculated by first-principle density functional theory (DFT). The corresponding configurations of CO_2 and C_2H_2 gas molecules diffusion along the minimum energy pathways (MEP) in Cu-Trz (Fig. 2e and Figs. S26, S27 online) clearly demonstrate how CO_2 and C_2H_2 molecules diffuse in the narrow channel via the twisted pore aperture. The calculated MEP profiles (Fig. 2f) show that the CO_2 molecule can migrate through the twisted pore aperture of Cu-Trz with an energy barrier of 34.8 kJ mol^{-1} . In sharp comparison, the diffusion energy barrier for C_2H_2 increases dramatically to $117.1 \text{ kJ mol}^{-1}$, implying it is kinetically forbidden for C_2H_2 molecule to transport via the narrow aperture of Cu-Trz [15]. This suggests an ideal molecular-sieving effect of Cu-Trz, which is in line with the excellent separation effi-

ciency of CO₂/C₂H₂ observed in the experiment. The DFT calculated configuration shows that CO₂ molecule in Cu-Trz MOF primarily located at open metal sites of Cu₃O cluster (Fig. 2g), in which the Cu–O distances between Cu site and CO₂ are 3.202 and 3.113 Å and the distance between C atom in CO₂ and μ₃-O of the Cu₃O cluster is 3.136 Å. This indicates that the linear CO₂ molecule can form multiple-point interactions with the plane Cu₃O cluster. The independent gradient mode (IGM) analysis between CO₂ molecule and Cu-Trz MOF framework further confirmed that the CO₂ molecule can interact with the skeleton by vdW type interaction (green isosurface in Fig. 2h). Besides, the host–guest interactions mainly are derived from the contributions of the plane Cu₃O cluster in the MOF framework. Interestingly, the central C atom of CO₂ makes a large contribution to the host–guest interactions (red atom) while the two O atoms of CO₂ render moderate contributions.

In summary, we proposed a 3D restricting molecular-sieving strategy by constructing twisted pore aperture in MOF for molecular-sieving separation of CO₂/C₂H₂, although it was considered impractical by traditional 2D restricting molecular-sieving mechanism due to their very similar cross-sectional areas. Owing to the 3D restricting effect induced by the twisted pore aperture structure, Cu-Trz MOF shows efficient CO₂ adsorption and size exclusion for C₂H₂ adsorption, achieving ideal molecular-sieving CO₂/C₂H₂ separation. The DFT calculation reveals the molecular-sieving mechanism that C₂H₂ with longer molecular size undergoes strong 3D restriction in the twisted pore aperture while the shorter CO₂ molecule can pass through the pore aperture easily. In addition, the Cu-Trz MOF has excellent chemical stability and recycling ability, as well as low cost, demonstrating that it is a new benchmark material for CO₂/C₂H₂ separation.

Conflict of interest

The authors declare that they have no known conflict of interest.

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Author contributions

Hejin Zhu, Hongliang Huang, and Chongli Zhong conceived the idea and designed the experiments. Hejin Zhu, Mingze Zheng, and Zefeng Jiang fabricated the materials and conducted the characterizations. Wenjuan Xue and Hongliang Huang conducted the DFT calculations and analyzed the separation mechanism. Hejin Zhu, Hongliang Huang, and Chongli Zhong analyzed the data and wrote the paper together.

Appendix A. Supplementary materials

Supplementary materials to this short communication can be found online at <https://doi.org/10.1016/j.scib.2023.09.008>.

References

- [1] Chen KJ, Scott HS, Madden DG, et al. Benchmark C₂H₂/CO₂ and CO₂/C₂H₂ separation by two closely related hybrid ultramicroporous materials. *Chem* 2016;1:753–63.
- [2] Lin R-B, Li L, Wu H, et al. Optimized separation of acetylene from carbon dioxide and ethylene in a microporous material. *J Am Chem Soc* 2017;139:8022–8.
- [3] Fu D, Xu Y, Zhao M, et al. Enhancement of gas-framework interaction in a metal-organic framework by cavity modification. *Sci Bull* 2016;61:1255–9.
- [4] Li J-R, Yu J, Lu W, et al. Porous materials with pre-designed single-molecule traps for CO₂ selective adsorption. *Nat Commun* 2014;4:1538.

- [5] Wang J, Zhang Y, Zhang P, et al. Optimizing pore space for flexible-robust metal-organic framework to boost trace acetylene removal. *J Am Chem Soc* 2020;142:9744–51.
- [6] Shi Z, Li X, Yao X, et al. MOF adsorbents capture CO₂ on an industrial scale. *Sci Bull* 2022;67:885–7.
- [7] Liang B, Zhang X, Xie Y, et al. An ultramicroporous metal-organic framework for high sieving separation of propylene from propane. *J Am Chem Soc* 2020;142:17795–801.
- [8] Luo TY, Liu C, Gan XY, et al. Multivariate stratified metal-organic frameworks: diversification using domain building blocks. *J Am Chem Soc* 2019;141:2161–8.
- [9] Li T, Kozłowski M-T, Doud E-A, et al. Stepwise ligand exchange for the preparation of a family of mesoporous MOFs. *J Am Chem Soc* 2013;135:11688–91.
- [10] Wang GD, Krishna R, Li YZ, et al. Boosting ethane/ethylene separation by MOFs through the amino-functionalization of pores. *Angew Chem Int Edit* 2022;6110.1002/anie.202213015.
- [11] Geng S, Lin E, Li X, et al. Scalable room-temperature synthesis of highly robust ethane-selective metal-organic frameworks for efficient ethylene purification. *J Am Chem Soc* 2021;143:8654–60.
- [12] Ouellette W, Yu MH, O'Connor CJ, et al. Hydrothermal chemistry of the copper-triazolate system: a microporous metal-organic framework constructed from magnetic (Cu₃(μ₃-OH)(triazolate)₃)²⁺ building blocks, and related materials. *Angew Chem Int Edit* 2006;45:3497–500.
- [13] Ouellette W, Prosvirin AV, Valeich J, et al. Hydrothermal synthesis, structural chemistry, and magnetic properties of materials of the MII/triazolate/anion family, Where MII = Mn, Fe, and Ni. *Inorg Chem* 2017;46:9067–908.
- [14] Cho HS, Lee Y, Wu J, et al. Understanding adsorption behavior of periodic mesoporous organosilica having a heterogeneous chemical environment: selective coverage and interpenetration of adsorbates inside the channel wall. *J Phys Chem C* 2019;123:24884–9.
- [15] Wang L, Xue W, Zhu H, et al. Stepwise engineering of a cage-like MOF pore aperture for the efficient separation of isomeric C₄ paraffins under humid conditions. *Angew Chem Int Edit* 2023;62:e202218596.



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