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A highly connected metal–organic framework with stretched inorganic units for propylene/ethylene separation†

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Separating propylene from ethylene in the product mixture derived from the methanol-to-olefin conversion process in an energy-efficient way is challenging, and adsorptive separation utilizing porous materials such as metal–organic frameworks (MOFs) provides a potential solution. Herein, we constructed a highly connected MOF structure with “stretched” [Zn₈SiO₄] as metal nodes and mixed binding groups (carboxylate and pyrazolate) as linkers. The mixed binding groups adapted well to the increase in the inter-metal distance caused by the insertion of SiO₄⁴⁻ in the nodes, enabling the formation of a highly symmetrical 12-connected net with high porosity and suitable pore apertures. This framework exhibited an impressive C₃H₆ adsorption capacity of 180.5 cm³ g⁻¹ and a calculated C₃H₆/C₂H₄ selectivity of 8.6 at 298 K and 100 kPa, which was attributed to the abundant N/O sites on the pore surface that generated stronger interactions with C₃H₆. Furthermore, dynamic breakthrough experiments demonstrated that the framework was capable of effectively separating C₃H₆/C₂H₄ under various conditions, making it a promising benchmark adsorbent for industrial applications.

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Introduction

As two of the key olefins in the chemical industry, ethylene (C₂H₄) and propylene (C₃H₆) are crucial raw materials for the production of a wide variety of polymers and organic products. Traditionally, C₂H₄ and C₃H₆ are primarily produced *via* naphtha cracking, a process that relies on fossil resources.^{1,2} Recently, sustainable technology for converting methanol to olefins has emerged as an effective alternative for C₂H₄ and C₃H₆ production.^{3–5} This process yields products typically consisting of ~51 wt% C₂H₄ and 21 wt% C₃H₆,⁶ which need to be separated to efficiently use each component and meet the high-purity requirement for industrial use. Cryogenic distillation is the predominant method for olefin separation; however, cooling the gases to exceedingly low temperatures is markedly energy-intensive.⁷ To address this challenge, adsorptive

separations utilizing porous materials are being developed as a more energy-efficient technology.^{8–10}

MOFs offer significant advantages in terms of tunable pore sizes and functionalities,^{11–19} making them particularly suitable for adsorptive separation and purification.^{20–26} While MOFs have been widely used to separate various gas mixtures, the separation of C₃H₆ and C₂H₄ is still a great challenge. Their kinetic diameters are very similar (C₃H₆, 4.68 Å; C₂H₄, 4.16 Å),²² making their size-/shape-selective separation difficult. Therefore, designing differentiated interaction sites in the porous MOFs is a prerequisite for achieving a high separation selectivity.^{27,28} On the one hand, higher polarizability of C₃H₆ (62.6 × 10⁻²⁵ cm³) suggests stronger dispersion forces with the framework than C₂H₄ (42.5 × 10⁻²⁵ cm³).²² On the other hand, the interaction difference can be further amplified by introducing more weak-to-medium interactions, such as C–H···O/N hydrogen bonds and C–H···π interactions, between the framework and the guests.^{29,30}

Herein, we synthesized a MOF structure by the reticulation between a relatively rare [Zn₈SiO₄]-based secondary building unit (SBU) and 4-(1*H*-pyrazol-4-yl)benzoic acid (H₂PyBC). Compared with the traditional Zn–carboxylate MOFs, the SiO₄⁴⁻ in the SBU centre “stretched” the SBU size, and the mixed binding groups (carboxylate and pyrazolate) prompted its pointing direction to take on a cuboctahedron geometry, which further guided the overall framework into an **fcu** net with 12-connected (12-c) nodes. The framework exhibited a Brunauer–Emmett–Teller (BET) surface area of 1965 m² g⁻¹, with the pore

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size concentrated at 7.9 and 13.0 Å. Interestingly, the C₃H₆ adsorption capacity of the MOF reached 180.5 cm³ g⁻¹ at 298 K and 100 kPa, while the C₂H₄ uptake was merely 68.2 cm³ g⁻¹, indicating a stronger interaction between C₃H₆ and the framework. Grand canonical Monte Carlo (GCMC) simulations revealed a binding energy difference of 10.11 kJ mol⁻¹ for C₃H₆ and C₂H₄ when they interacted with the strongest binding sites on the backbone. Furthermore, dynamic breakthrough experiments concluded that for an equimolar C₃H₆/C₂H₄ mixture, the breakthrough time interval reaches 41.3 min at 298 K and maintains 35.3 min at 328 K, suggesting the potential of applying this MOF for C₃H₆/C₂H₄ separation.

Experimental

Synthesis of FDM-201

A screening of the reaction conditions was carried out by using H₂PyBC and Zn(NO₃)₂·6H₂O as the main reactants with various modulators in 2.0 mL solvents. After the FDM-201 single crystals were obtained, the preparation was further scaled up proportionally.

Specifically, Zn(NO₃)₂·6H₂O (2340 mg, 7.87 mmol), H₂PyBC (168 mg, 0.89 mmol), and 1*H*-benzotriazole (HBTA, 220 mg, 1.85 mmol) are dissolved in 34.0 mL *N,N*-dimethylformamide (DMF) in a 100 mL pressure-resistant tube with a Teflon cap. 6.0 mL aqueous Na₂SiO₃ solution (0.015 M) is further added. After sonication, the tube with the clear solution is placed in an oven at 115 °C for 12 h, and colorless octahedral crystals are obtained. Yield: 73.0 mg, *i.e.*, 47% based on Na₂SiO₃.

Results and discussion

Colourless octahedral crystals of FDM-201 are synthesized *via* a solvothermal reaction using Zn(NO₃)₂·6H₂O, H₂PyBC, and Na₂SiO₃·9H₂O in a mixed solvent of DMF and water at 115 °C for 12 h. HBTA is introduced into the solution as a structural modulator to slow down the reaction and obtain high-quality single crystals of FDM-201. Single-crystal X-ray diffraction (SXRD) reveals that FDM-201 crystallizes in the cubic space

group *Fm* $\bar{3}$ *m*, with *a* = 23.76 Å. In the structure, each O in the SiO₄⁴⁻ bridges two Zn(II) to form a node with a cubic [Zn₈SiO₄] core (Fig. 1a). Each Zn(II) in the node is further coordinated with three N/O from the PyBC linkers (Fig. 1b and c), and twelve PyBC linkers are bound to the [Zn₈SiO₄] core. As a result, a three-dimensional (3D) network with the **fcu** topology (Fig. 1d) is reticulated by the 12-*c* cuboctahedral nodes and the PyBC linkers. It should be noted that the orientational disorder of PyBC is observed (Fig. S1†) due to the approximate interatomic distances between the coordinating atoms (O or N) within both the carboxylate and pyrazolate groups.

Although two MOFs with the same [Zn₈SiO₄] nodes have been previously reported,^{31,32} each node in the FDM-201 is connected to twelve neighbouring nodes, while formerly it tended to connect with only 6 or 8 nodes through the linker pairs (Fig. 2),³¹ and the binding groups were pure carboxylate rather than mixed carboxylate/pyrazolate. Compared with the conventional Zn₄O(COO)₆ (ref. 18) and Zn(NN)₂ (ref. 33 and 34) SBUs (Fig. 2a), the inter-metal distances in the [Zn₈SiO₄] nodes are lengthened because of the insertion of SiO₄⁴⁻ in the SBU centre, making the SBU “stretched”. Moreover, in order to cope with this SBU stretch, the metal-linker coordination needs to be distorted. Compared to the metal-pyrazolate linkage in FDM-201, the metal-carboxylate linkage in the previous example³¹ shows a higher degree of flexibility (Fig. 2b and c), causing the O–Zn···SiO···Zn–O moiety to deviate from a planar configuration when the Zn···Zn distance is lengthened. As a result, the “pairing” of neighbouring ligands in parallel directions in the pure carboxylate version is evident, making the SBU six-connected. With less distortion in the N–Zn···SiO···Zn–N, the configuration of the SBU with mixed carboxylate/pyrazolate adopts a cuboctahedral geometry in FDM-201. Overall, the binding group difference (carboxylate *vs.* pyrazolate) imposes different distortion extents in the metal coordination sphere and consequently influences the connecting directions of the stretched SBUs.

The powder X-ray diffraction (PXRD) pattern of the as-synthesized FDM-201 matches with the corresponding simulated pattern, confirming its crystallinity and phase purity

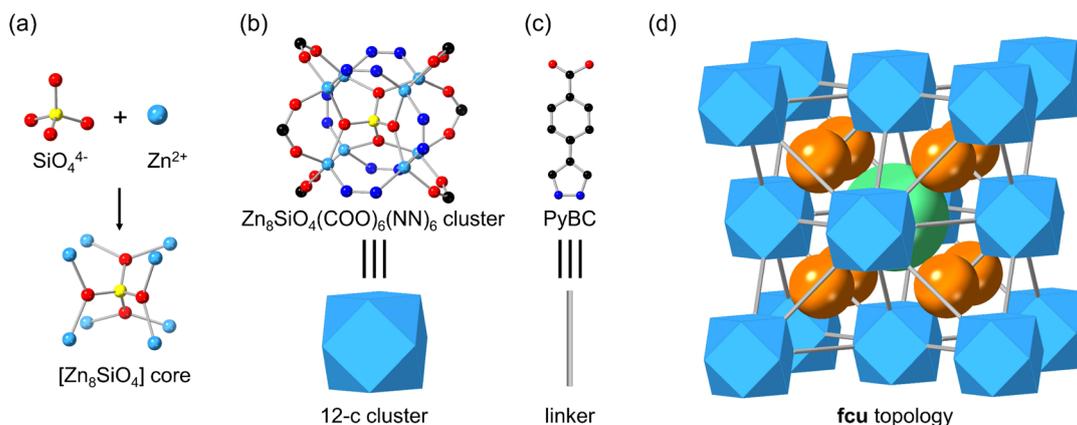


Fig. 1 Crystal structure of FDM-201. (a) A [Zn₈SiO₄] core is constructed by eight Zn(II) and a SiO₄⁴⁻. (b) The 12-connected units based on the [Zn₈SiO₄] cores are connected with (c) the PyBC linkers to afford (d) an MOF structure with the **fcu** topology. The octahedral cage and the tetrahedral cages are displayed as green and orange spheres. Atom colour code: Zn, light blue; Si, yellow; O, red; N, dark blue; C, black.



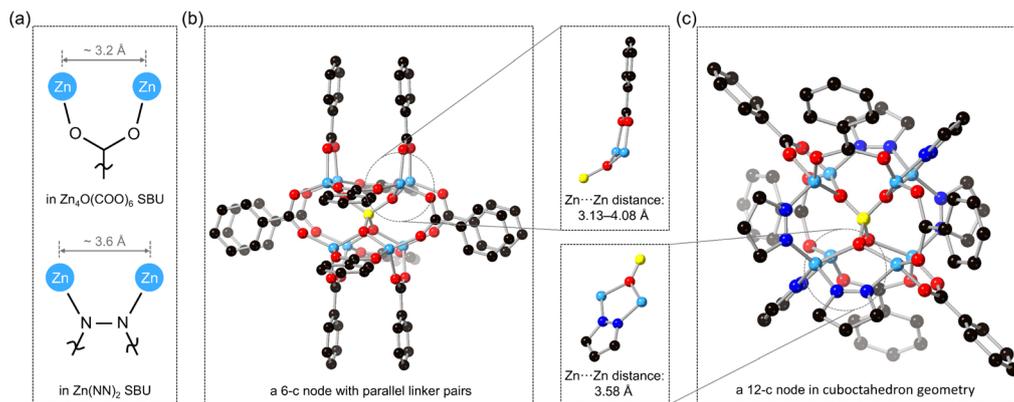


Fig. 2 Control of distinct coordination linkages giving rise to $[\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_6]_n$ ³¹ and FDM-201 with different topologies. (a) Typical Zn...Zn distance in the conventional $\text{Zn}_4\text{O}(\text{COO})_6$ and $\text{Zn}(\text{NN})_2$ units. (b) SBU in $[\text{Zn}_8(\text{SiO}_4)(\text{C}_8\text{H}_4\text{O}_4)_6]_n$ can be viewed as 6-c because the twelve linkers are organized into six pairs owing to the distortion in the O–Zn...SiO...Zn–O moiety. (c) SBU in FDM-201 showing cuboctahedron geometry, in which the O–Zn...SiO...Zn–O moiety is coplanar.

(Fig. 3a). The as-synthesized sample can be successfully activated by solvent exchange with acetone, followed by heating at 80 °C under vacuum. The sharp peaks in the PXRD pattern match well with those from the corresponding as-synthesized sample, indicating that it maintains high crystallinity after activation (Fig. 3a). Furthermore, FDM-201 possesses outstanding thermal stability, with no significant weight loss observed in the thermogravimetric analysis (TGA) until it reaches 450 °C in an air atmosphere (Fig. S6†). The crystals retain sharp PXRD peaks after being immersed in water for 6 h (Fig. S7†), although soaking for a longer time would induce a structural transformation. A diffraction peak ($2\theta = 6.9^\circ$) corresponding to a new condensed structure with a formula of $\text{Zn}_2\text{PyBC}(\text{OH})_2$ (Fig. S2, S8, and S9, see the discussion in the ESI†) emerges in the PXRD after being immersed in H_2O for 12 h, and the peak becomes more evident after 1 day (Fig. S8†). Immersing the crystals in boiling water would accelerate the structural transformation, as indicated by the completely new phase after 1 day (Fig. S8†). However, after soaking the FDM-201 crystals in a mixed $\text{H}_2\text{O}/\text{DMF}$ solvent (v/v, 4 : 1) for 7 days, we found that the structure is retained (Fig. S7†).

The crystal structure of FDM-201 reveals that it features two types of cages: an octahedral cage with an inscribed sphere diameter of 13.4 Å and a tetrahedral cage with 5.4 Å in diameter,

with the assumption that the linkers do not rotate. Based on Zeo++ calculation,³⁵ the simulated surface area of FDM-201 is 1898 $\text{m}^2 \text{g}^{-1}$, and its simulated pore volume is 0.70 $\text{cm}^3 \text{g}^{-1}$. Five parallel 87 K Ar adsorption isotherms are measured to experimentally verify the consistent and permanent porosity of FDM-201 (see Fig. 3b for one isotherm and Fig. S10† for all isotherms). The isotherms exhibit typical type I adsorptions, with a maximum Ar adsorption capacity of $583 \pm 6 \text{ cm}^3 \text{g}^{-1}$ at $P/P_0 = 0.99$. The BET surface area and pore volume of FDM-201 are calculated to be $1965 \pm 37 \text{ m}^2 \text{g}^{-1}$ and $0.74 \pm 0.01 \text{ cm}^3 \text{g}^{-1}$, respectively. The pore size distribution of FDM-201 is further analysed using the isotherm in Fig. 3b and a kernel based on the nonlocal density functional theory (NLDFT). The analysis reveals that the pore size distribution spans two intervals, from 6.1 to 10.5 Å and from 10.5 to 16.2 Å, with predominant concentrations at 7.9 and 13.0 Å, respectively (Fig. 3c). These values align approximately with theoretical predictions, indicating that the pores within the periodic and robust framework remain highly accessible after the activation.

The high BET surface area and pore volume of FDM-201, coupled with the abundant O/N interaction sites on the pore surfaces, intrigued us to explore its potential application in gas adsorption and separation. For gas separation, not only the pore size but also their apertures are critical. Analysis of the FDM-201

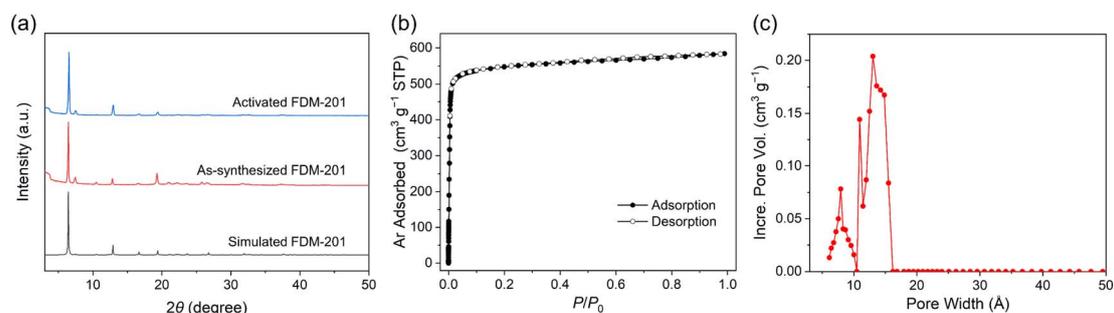


Fig. 3 Physical characterizations of FDM-201. (a) PXRD patterns of the simulated, as-synthesized, and activated FDM-201. (b) 87 K Ar adsorption isotherm of FDM-201. (c) Pore size distribution profile of FDM-201.



crystal structure further reveals that the octahedral and tetrahedral cages have relatively small apertures (triangles with an incircle of 3.9 Å) and make the pores inaccessible to C₃H₆ (kinetic diameter, 4.68 Å) and C₂H₄ (kinetic diameter, 4.16 Å). However, it should be noted that the benzene ring in the PyBC linker can easily rotate at ambient temperature,³⁶ leading to a “widening” of the pore aperture and an increase in the pore size. After considering the linker rotation, the sizes of the octahedral cage, tetrahedral cage, and pore aperture become 13.4, 8.3, and 6.2 Å. As a result, C₃H₆ and C₂H₄ can indeed be adsorbed by the FDM-201 framework.

To investigate the C₃H₆ and C₂H₄ adsorption capability of FDM-201 in experiments, single-component adsorption isotherms at 273, 298, and 328 K are collected (Fig. 4a and b). FDM-201 exhibits an adsorption uptake of 180.5 cm³ g⁻¹ for C₃H₆ at 298 K and 1 bar, much higher than that of the C₂H₄ case (68.2 cm³ g⁻¹). In addition, the adsorption capacity of C₃H₆/C₂H₄ is 200.5/108.4 cm³ g⁻¹ at 273 K and 137.4/31.6 cm³ g⁻¹ at 328 K. Remarkably, its C₃H₆ adsorption capacity at 298 K (180.5 cm³ g⁻¹) is among the many high-performance MOFs, such as spe-MOF (236.9 cm³ g⁻¹),³⁷ FJI-H8-Me (211.0 cm³ g⁻¹),²⁸ NEM-4 (197.4 cm³ g⁻¹),³⁸ MAC-4 (127.0 cm³ g⁻¹),³⁹ and CoV-bco-tpt (110.0 cm³ g⁻¹)⁴⁰ (see Table S7 in the ESI† for a summary of the C₃H₆ adsorption capacity of benchmark MOFs). The higher uptake of C₃H₆ than that of C₂H₄ under the tested temperature range suggests that FDM-201 is a potential candidate for C₃H₆/C₂H₄ separation.

Isosteric heat of adsorption (Q_{st}) is calculated based on the single-component gas adsorption isotherms at 273 and 298 K, employing the Clausius–Clapeyron equation (Table S4 and Fig. S11 and S12, see the ESI†). At zero coverage, the Q_{st} values of

FDM-201 for C₃H₆ and C₂H₄ are 27.1 and 19.1 kJ mol⁻¹, respectively (Fig. 4c). The notably higher Q_{st} for C₃H₆ confirms stronger interaction between C₃H₆ and the framework, and it is preferably adsorbed (see Table S5† for a summary of Q_{st} values of benchmark MOFs). It is worth noting that the Q_{st} value for C₃H₆ at high coverage is apparently higher than the value at zero coverage, indicating that at a high-pressure range, the C₃H₆–C₃H₆ interaction is stronger than the C₃H₆–framework interaction.

To preliminarily evaluate the C₃H₆/C₂H₄ separation performance of FDM-201, the ideal adsorption solution theory (IAST) is employed to calculate the selectivity (Table S6 and Fig. S13†). For an equimolar C₃H₆/C₂H₄ mixture at 100 kPa, the calculated selectivities at 273, 298, and 328 K are 11.9, 8.6, and 7.7, respectively (Fig. 4d). The selectivity at 298 K is comparable with that of the current outstanding materials, such as HOF-NBDA (11.1),⁴¹ MAC-4 (9.5),³⁹ and JLU-MOF132 (9.2),⁴² (Table S7†). Combined with the high adsorption capacity (C₃H₆, 180.5 cm³ g⁻¹), FDM-201 appears to be a fairly good option among the known materials for C₃H₆/C₂H₄ separation (Fig. 4e and Table S7†). Impressively, the selectivity only drops slightly to 7.7 at 328 K, suggesting a high selectivity even at a relatively elevated temperature proximate to the actual operating condition.⁴³ The IAST selectivity of FDM-201 for the C₃H₆/C₂H₄ mixtures at 20/50 and 10/90 (v/v) ratios are further calculated,^{37,44} and the framework maintains a high selectivity of 14.1/9.4/7.3 for C₃H₆/C₂H₄ (v/v, 20/50) at 273/298/328 K, and 14.8/9.4/7.2 for C₃H₆/C₂H₄ (v/v, 10/90) at these three temperatures (Fig. S14 and Table S8†).

Separation potential (Δq) is a comprehensive metric that combines both adsorption capacity and selectivity to evaluate the separation ability of materials.⁴⁵ For C₃H₆-selective

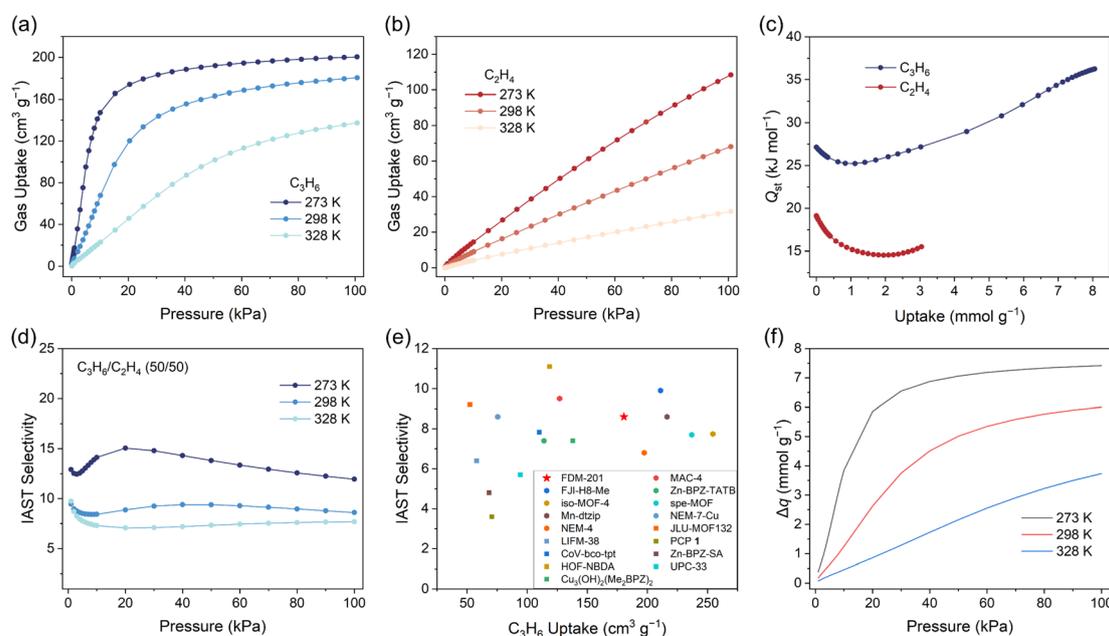


Fig. 4 Adsorption studies of FDM-201. (a) C₃H₆ and (b) C₂H₄ adsorption isotherms at 273, 298, and 328 K, respectively. (c) Q_{st} curves for C₃H₆ and C₂H₄. (d) IAST selectivity for equimolar C₃H₆/C₂H₄ at 273, 298, and 328 K. (e) Comparison of the C₃H₆ uptake and IAST selectivity between FDM-201 and the representative C₃H₆-selective MOF adsorbents. (f) Separation potential of FDM-201 for the equimolar C₃H₆/C₂H₄ mixture at 273, 298, and 328 K.



adsorbents, Δq presents a reliable prediction of the maximum amount of pure C_2H_4 recovered during a fixed-bed separation process. According to the IAST results on equimolar mixtures, Δq is calculated to be 7.42, 6.00, and 3.73 $mmol\ g^{-1}$ at 273, 298, and 328 K, respectively (Fig. 4f). The Δq value for FDM-201 at 298 K is much higher than some benchmark C_3H_6/C_2H_4 separating-MOFs, such as MAC-4 (4.4 $mmol\ g^{-1}$),³⁹ Zn-BPZ-TATB (3.74 $mmol\ g^{-1}$),³⁰ Zn-BPZ-SA (1.92 $mmol\ g^{-1}$),⁴⁶ and $Zn_2(oba)_2(dmimpym)$ (3.04 $mmol\ g^{-1}$).⁴⁷

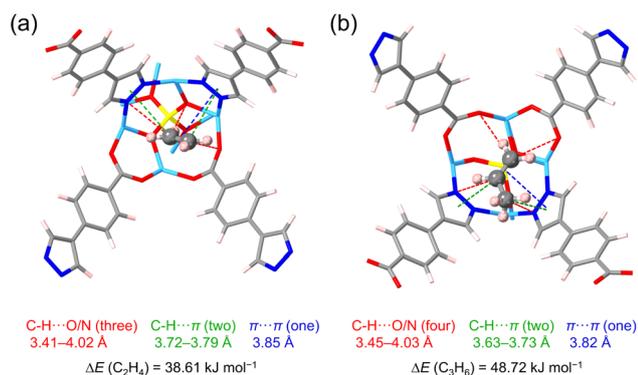


Fig. 5 Interactions between the preferential binding site and (a) C_2H_4 and (b) C_3H_6 . Atom colour code: Zn, light blue; Si, yellow; O, red; N, dark blue; C, grey; H, pink.

To gain a deep understanding of the interactions between the framework and the adsorbates, GCMC simulations are employed to investigate the preferential binding sites within the octahedral cage of FDM-201 for C_2H_4 and C_3H_6 . For both gases, the strongest adsorption sites, with multiple supramolecular interactions between the backbone and the guests, are located near the $[Zn_8SiO_4]$ core (Fig. 5). Specifically, three $C-H\cdots O/N$ hydrogen bonds ($C\cdots O/N$ bond length: 3.41–4.02 Å), two $C-H\cdots\pi$ interactions (3.72–3.79 Å) and one $\pi\cdots\pi$ interaction (3.85 Å) exist between one C_2H_4 and this site in FDM-201. The calculated binding energy is 38.61 $kJ\ mol^{-1}$. On the other hand, stronger interaction with four $C-H\cdots O/N$ hydrogen bonds (3.45–4.03 Å), two $C-H\cdots\pi$ interactions (3.63–3.73 Å), and one $\pi\cdots\pi$ interaction (3.82 Å) enabled the binding energy of C_3H_6 to this site to be 48.72 $kJ\ mol^{-1}$. Based on the simulation, the difference in the static binding energies between C_3H_6 and C_2H_4 is 10.11 $kJ\ mol^{-1}$, which is roughly in agreement with the difference in the Q_{st} calculated from the adsorption isotherms (8.0 $kJ\ mol^{-1}$) and corroborates with the preferred C_3H_6 adsorption in FDM-201.

To verify the actual C_3H_6/C_2H_4 separation performance, dynamic breakthrough experiments for binary C_3H_6/C_2H_4 (v/v, 50/50) mixtures are conducted at 298 and 328 K. Before the experiments, the acetone-exchanged sample is activated under vacuum at 80 °C for 12 h. Subsequently, it is packed into a stainless-steel column ($l = 15\ cm$, $d = 0.42\ cm$). The packed column is firstly purged with He at a flow rate of 20 $mL\ min^{-1}$

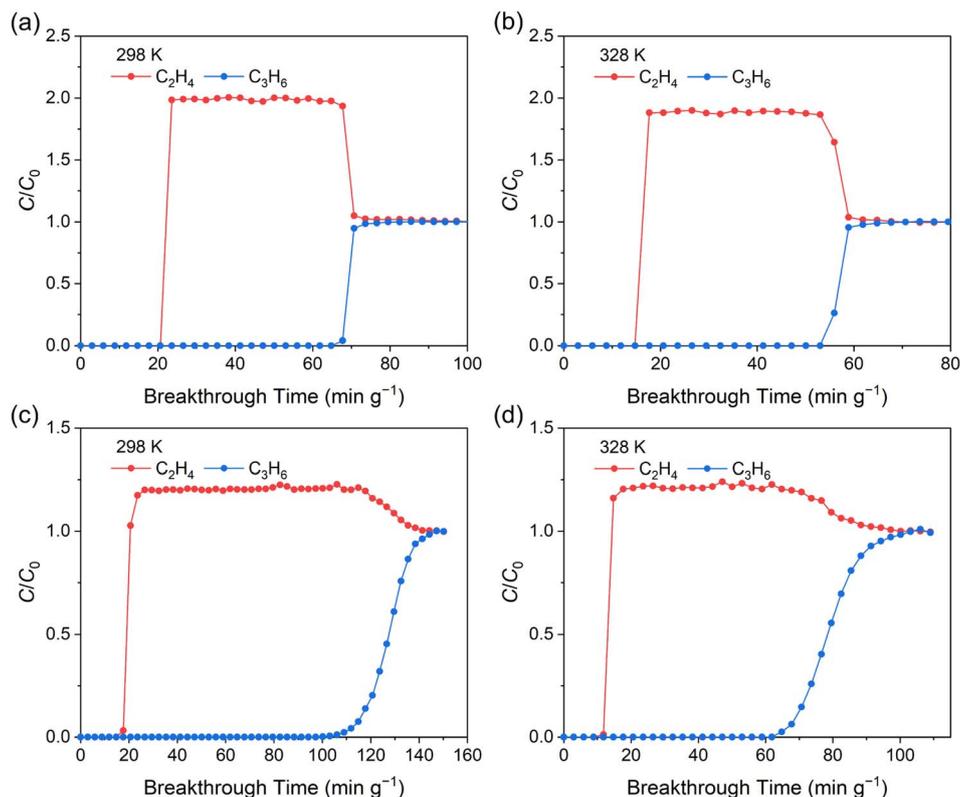


Fig. 6 Breakthrough curves for C_3H_6/C_2H_4 -based mixtures under a flow of 5 $mL\ min^{-1}$ for FDM-201 in a packed column. The testing conditions are (a) C_3H_6/C_2H_4 (v/v, 50/50) at 298 K, (b) C_3H_6/C_2H_4 (v/v, 50/50) at 328 K, (c) $C_3H_6/C_2H_4/He$ (v/v/v, 20/50/30) at 298 K, and (d) $C_3H_6/C_2H_4/He$ (v/v/v, 20/50/30) at 328 K.



for 30 min. At 298 K, under a mixed gas flow (flow rate, 5 mL min⁻¹), C₂H₄ first elutes from the column at 23.5 min, whereas C₃H₆ is under detection limit until 64.8 min (Fig. 6a). The breakthrough time interval, during which high-grade C₂H₄ can be collected, is calculated to be 41.3 min. At 328 K, FDM-201 can still efficiently separate C₃H₆ and C₂H₄, with an interval of 35.3 min (Fig. 6b). Furthermore, when the feed gas composition is adjusted to 20 : 50 : 30 (v/v/v, C₃H₆ to C₂H₄ to He, with the C₃H₆/C₂H₄ ratio close to the application scenario), FDM-201 continues to exhibit effective separation performance with the interval time being 82.4 and 53.0 min at 298 and 328 K, respectively (Fig. 6c and d). The breakthrough experiments have proved that FDM-201 is a promising candidate for highly efficient propylene/ethylene separation across different composition ratios and different temperatures.

Conclusion

In summary, we report the synthesis of a highly connected MOF structure with [Zn₈SiO₄]-based metal nodes. The embedding of the SiO₄⁴⁻ anion into the Zn₈ cube stretches the distance between the Zn(II) atoms, rendering the mixed pyrazolate/carboxylate binding groups an appropriate choice to maintain the inorganic unit in a highly symmetrical cuboctahedral geometry. The obtained FDM-201 with **fcu** topology exhibits a high BET surface area of 1965 m² g⁻¹, with pore sizes enabling high-capacity accessibility for both propylene and ethylene gas molecules. Moreover, the abundant N/O sites in FDM-201 provide a stronger affinity with propylene, making it a potential candidate for propylene/ethylene separation. This is evidenced by the single-component adsorption isotherms, IAST selectivity calculation, and adsorptive interaction simulations. Dynamic breakthrough experiments demonstrate that FDM-201 is capable of effectively separating equimolar C₃H₆/C₂H₄, with the breakthrough time interval reaching 41.3 min at 298 K. Overall, this study proposes that the selection of binding groups can modify the connectivity of a stretched SBU, thereby enabling the creation of subsequent MOFs with appropriate sizes and functionalities for gas separation applications.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for FDM-201 and Zn₂PyBC(OH)₂ have been deposited at the Cambridge Crystallographic Data Centre with the CCDC numbers 2418870 and 2418871 and can be obtained from <https://www.ccdc.cam.ac.uk/>.

Author contributions

Y. Rao: investigation, formal analysis, visualization, validation, writing – original draft. X. Li: formal analysis. H. Xi: formal analysis. Z. Jiang: formal analysis. W. Li: formal analysis. H. Zhou: formal analysis. Y. Zhang: formal analysis. C. Wu: formal analysis. Y.-B. Zhang: supervision. Q. Li: conceptualization, investigation, funding acquisition, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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