

# Molecular sieving of ethylene from ethane using a rigid metal–organic framework

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**There are great challenges in developing efficient adsorbents to replace the currently used and energy-intensive cryogenic distillation processes for olefin/paraffin separation, owing to the similar physical properties of the two molecules. Here we report an ultramicroporous metal–organic framework [Ca(C<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>O)], synthesized from calcium nitrate and squaric acid, that possesses rigid one-dimensional channels. These apertures are of a similar size to ethylene molecules, but owing to the size, shape and rigidity of the pores, act as molecular sieves to prevent the transport of ethane. The efficiency of this molecular sieve for the separation of ethylene/ethane mixtures is validated by breakthrough experiments with high ethylene productivity under ambient conditions. This material can be easily synthesized at the kilogram scale using an environmentally friendly method and is water-stable, which is important for potential industrial implementation. The strategy of using highly rigid metal–organic frameworks with well defined and rigid pores could also be extended to other porous materials for chemical separation processes.**

Ethylene/ethane separation is a critical process in the petrochemical industry, giving a worldwide ethylene production exceeding 150 million metric tons in 2016. Owing to the very similar sizes and volatilities of these hydrocarbon molecules, the purification of ethylene is currently accomplished by repeated distillation–compression cycling of the mixture under harsh conditions in a huge splitter column of 120–180 trays. This well established industrial separation technology is one of the most energy-intensive processes in the chemical industry; it relies highly on thermal energy and consumes ten times more energy than membrane-based separation technologies or other non-thermal ones<sup>1,2</sup>. It is estimated that, compared to conventional splitters, these advanced non-thermal separation technologies can save the process energy of up to 0.3–1.5 GJ per metric ton of ethylene<sup>3</sup>. To replace the cryogenic distillation processes, exploration of new adsorptive separation technologies based on porous materials is strongly motivated by the tremendous energy savings. As customizable porous materials, metal–organic frameworks (MOFs) are highly versatile in pore engineering, affording precise tuning and functionalization of the pore structure<sup>4,5</sup>, and thus have been intensively investigated as excellent adsorbents for selective gas separation<sup>6–13</sup>. However, for ethylene/ethane separation, the major barrier to improving the selectivity for separating these gases is their very similar physical properties. Various functionalized MOF adsorbents, including those featuring open metal sites that help to enhance the olefin binding affinity, have been explored to overcome this challenge<sup>14,15</sup>. However, their co-adsorption of analogous alkanes is inevitable and unfavourable for efficient olefin purification via swing adsorption or membrane-based methods, let alone other problems associated with active metal sites involving the recovery of adsorbent and olefin products (high energy consumption and possible olefin polymerization)<sup>16,17</sup> and water/humidity stability issues.

Ideal separation approaches such as molecular sieving, which allow the complete separation of one component from others based on molecular size or shape cut-off, avoid the co-adsorption

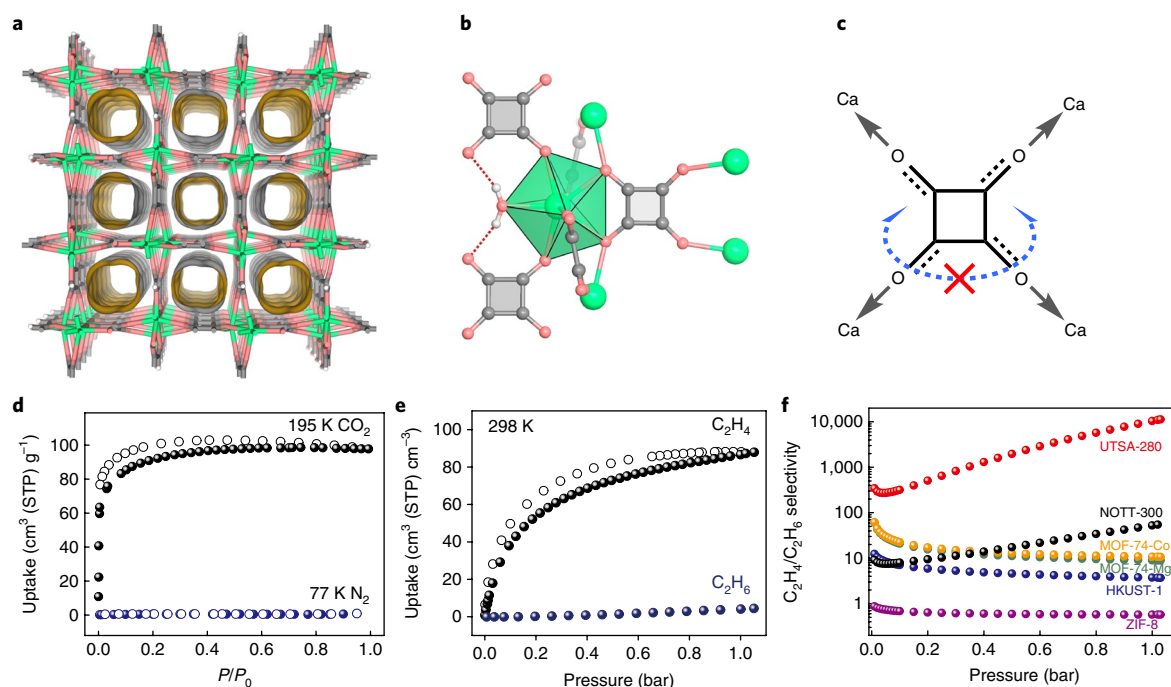
of impurities without sacrificing the valuable uptake capacity of porous media and enable infinite selectivity, which is also beneficial to membrane-based separation<sup>18,19</sup>. Accordingly, precise size/shape-matching is vital towards specific recognition of olefin/paraffin<sup>20,21</sup>. Considering the even smaller shape difference between ethylene/ethane (only 0.028 nm in kinetic diameter) and their nearly identical physical properties (Supplementary Fig. 1 and Supplementary Table 1), it is particularly challenging to design MOFs as molecular sieves for this gas separation. The existing dynamic nature of organic moieties (for example, freedom of rotation; Supplementary Fig. 2) makes this separation even more challenging, because such a structural feature can readily change the sizes of pore apertures during the sorption process. Extensive research endeavours have been pursued to tailor-make MOFs for specific molecular sieving of some important hydrocarbons<sup>9,10,22,23</sup>, but it is yet to be shown that MOFs can sieve ethylene while completely excluding ethane.

During our exploration of MOF candidates with pore aperture sizes of 3.4–4.4 Å constructed from the rigid organic linkers to minimize the linker rotation/vibration, we have targeted a readily available MOF molecular sieve [Ca(C<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>O)] (termed UTSA-280) that features rigid one-dimensional channels, exhibiting molecular size exclusion of ethane from ethylene under ambient conditions. This material exhibits optimal channel spaces that enable recognition of ethylene molecules of high packing intensity and exceptional selectivity with ethylene productivity of 1.86 mol kg<sup>−1</sup> under ambient conditions, as has been established by the experimental breakthrough curves. Its straightforward synthesis at a large scale under an environmentally friendly condition, and its water-stability, highlight the promise of this molecular sieving material for industrial C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> separation in the future.

## Pore structure and single-gas sorption isotherm

Using the common chemical raw materials calcium nitrate and squaric acid, [Ca(C<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>O)]·xH<sub>2</sub>O was synthesized under mild

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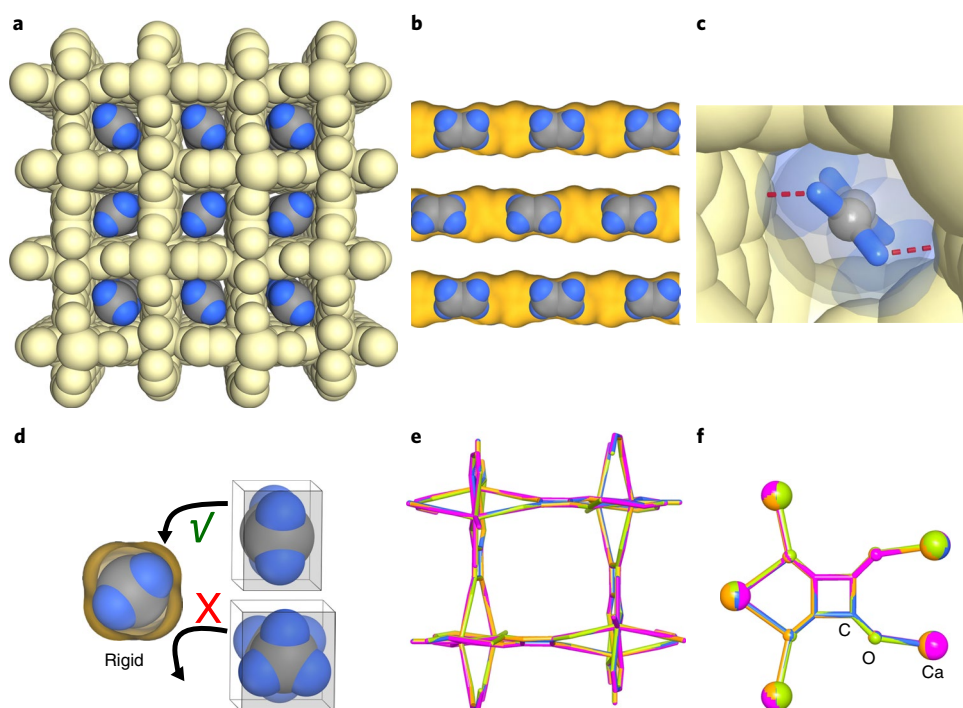


**Fig. 1 | Structure and gas sorption properties of UTSA-280.** **a**, The crystal structure of guest-free UTSA-280 determined from single-crystal X-ray diffraction, showing one-dimensional channels viewed along the [001] direction. Green, light coral and grey nodes represent Ca, O and C atoms, respectively. **b**, The local coordination environments of the squarate linker and calcium atoms. **c**, A schematic diagram showing the coordination constraints applied on the  $C_4O_4^{2-}$  linker. **d**, **e**, Single-component sorption isotherms of carbon dioxide (black) at 195 K, nitrogen (blue) at 77 K (**d**) and ethylene (black), ethane (indigo) at 298 K for UTSA-280 (**e**). **f**, Qualitative comparison of IAST adsorption selectivities of different MOFs for an equimolar ethylene/ethane mixture at 298 K.

conditions in water (Supplementary Figs. 3 and 4)<sup>24</sup>. In the as-synthesized UTSA-280 $\cdot$ H<sub>2</sub>O, the pentagonal bipyramidal Ca atom is coordinated by seven O atoms from five different  $C_4O_4^{2-}$  linkers and one water molecule, bridged by the organic linkers to form one-dimensional infinite chains, resulting in one-dimensional channels occupied by guest water molecules (Fig. 1a). The hydrogen bonding between the coordinated H<sub>2</sub>O molecules and the O atoms of the  $C_4O_4^{2-}$  linkers further stabilizes the framework (Supplementary Fig. 5). Notably, the  $C_4O_4^{2-}$  linkers are subject to mutual coordination constraints from two different calcium-oxo chains, as they coordinate to Ca atoms in different directions that are perpendicular to each other (Fig. 1b), which can effectively restrain the rotations of the organic linkers (Fig. 1c). After removing the guest water molecules, the framework of activated UTSA-280 is fully maintained, as determined by single-crystal X-ray diffraction experiments (Fig. 1 and Supplementary Table 2). The coordinated H<sub>2</sub>O molecule is retained in the structure. One-dimensional open cylindrical channels are obtained after guest removal, showing aperture sizes with slightly different shapes of  $3.2 \times 4.5 \text{ \AA}^2$  and  $3.8 \times 3.8 \text{ \AA}^2$  (Fig. 1a). These apertures display similar cross-sectional areas of about  $14.4 \text{ \AA}^2$ , which are larger than the minimum cross-sectional area of C<sub>2</sub>H<sub>4</sub> ( $13.7 \text{ \AA}^2$ ) but smaller than that of C<sub>2</sub>H<sub>6</sub> ( $15.5 \text{ \AA}^2$ )<sup>25</sup>, suggesting great size/shape sieving potential for C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> separation. The total solvent-accessible volume was estimated to be 27.8% of the unit-cell volume. While UTSA-280 is remarkably stable in water (Supplementary Fig. 3), we note that the existence of the coordinated water molecules is essential for guest-free UTSA-280 to display permanent porosity. The activation of UTSA-280 $\cdot$ H<sub>2</sub>O should be performed under relatively mild conditions (see Supplementary Information) to retain the coordinated water. The Brunauer–Emmett–Teller surface area of activated UTSA-280 was measured to be  $\sim 331 \text{ m}^2 \text{ g}^{-1}$  (Langmuir surface area:  $\sim 455 \text{ m}^2 \text{ g}^{-1}$ ) by CO<sub>2</sub> sorption experiment at 195 K (Fig. 1d and Supplementary Fig. 6). The experimental total

pore volume is  $\sim 0.18 \text{ cm}^3 \text{ g}^{-1}$ , matching well with the theoretical one calculated from the crystal structure ( $0.18 \text{ cm}^3 \text{ g}^{-1}$ ).

Pure-component equilibrium adsorption isotherms for C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were collected at ambient conditions. Figure 1e shows the data obtained at 298 K. The C<sub>2</sub>H<sub>4</sub> uptake in UTSA-280 reaches  $88.1 \text{ cm}^3 \text{ cm}^{-3}$  ( $2.5 \text{ mmol g}^{-1}$ ) at 298 K and 1 bar, higher than those of the benchmark zeolites that are widely studied for ethylene/ethane separation, such as zeolite 5A and cation-exchanged ETS-10 (Engelhard Titanosilicate-10) ( $1.0\text{--}2.3 \text{ mmol g}^{-1}$ )<sup>26,27</sup>. In contrast, under the same conditions, UTSA-280 adsorbs a negligible amount of ethane ( $0.098 \text{ mmol g}^{-1}$ ), which means that the ethane molecule is excluded by the pore apertures, consistent with our structural pore size analysis. At lower temperature (273 K), while a larger C<sub>2</sub>H<sub>4</sub> uptake can be observed, there is still no uptake increase for C<sub>2</sub>H<sub>6</sub> (Supplementary Fig. 7). This remains true even at 195 K. Notably, according to the amount of adsorbed C<sub>2</sub>H<sub>4</sub> and the pore volume, the density of C<sub>2</sub>H<sub>4</sub> in the pore channel at room temperature is up to  $389 \text{ g l}^{-1}$ , which is about 342 times the gaseous C<sub>2</sub>H<sub>4</sub> density of  $1.138 \text{ g l}^{-1}$  (298 K, 1 bar) and close to the liquid C<sub>2</sub>H<sub>4</sub> density of  $568 \text{ g l}^{-1}$  (169.4 K, 1 bar), implying highly efficient packing of ethylene molecules in UTSA-280. From the measured isotherms, record-high apparent C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> selectivity, exceeding 10,000 (Fig. 1f, Supplementary Fig. 8 and Supplementary Table 3), can be calculated for the qualitative comparison, which is orders of magnitude larger than those of FeMOF-74 (13.6)<sup>7</sup>, NOTT-300 (48.7)<sup>8</sup>,  $\pi$ -complexation sorbents<sup>28</sup>, such as PAF-1-SO<sub>3</sub>Ag (27)<sup>29</sup>, and so on (Supplementary Table 4)<sup>30</sup>. However, it should be noted that such calculated selectivity is often subject to uncertainties owing to the large error from the ultralow apparent C<sub>2</sub>H<sub>6</sub> uptake. Theoretically, the C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> selectivity of UTSA-280 should be infinite, which is promising for molecular exclusion of ethane from ethylene. Subsequently, multiple cycling sorption measurements were conducted carefully to test the material cyclability, showing no



**Fig. 2 | Single-crystal structure of UTSA-280•0.20C<sub>2</sub>H<sub>4</sub> and preferential C<sub>2</sub>H<sub>4</sub> binding.** **a, b**, Top and side views of the packing diagram of the C<sub>2</sub>H<sub>4</sub> adsorbed structure. The framework and pore surface are shown in pale gold and orange. The light blue and grey spheres represent H and C atoms of C<sub>2</sub>H<sub>4</sub> molecules. **c**, Preferential binding site for C<sub>2</sub>H<sub>4</sub> molecules and their close contacts with the framework. **d**, Schematic diagram of the size/shape sieving based on the minimum cross-sectional areas of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> molecules. **e, f**, Conformational comparisons of the pore structures (**e**) and C<sub>4</sub>O<sub>4</sub><sup>2-</sup> linkers (**f**) in the single-crystal structures of UTSA-280•H<sub>2</sub>O (lime), UTSA-280 (pink), UTSA-280•0.16C<sub>2</sub>H<sub>4</sub> (light orange) and UTSA-280•0.20C<sub>2</sub>H<sub>4</sub> (light blue).

C<sub>2</sub>H<sub>6</sub> adsorption and no loss of C<sub>2</sub>H<sub>4</sub> uptake capacity in UTSA-280 (Supplementary Figs. 9–13).

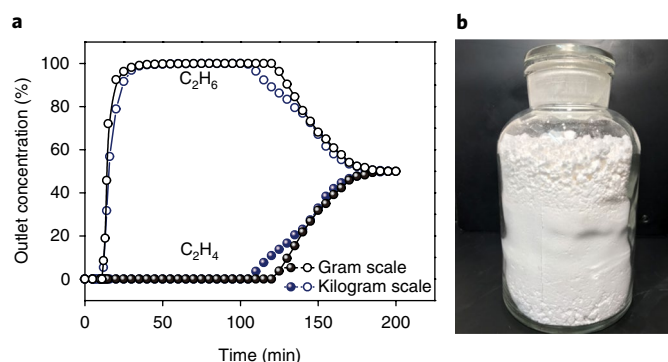
The coverage-dependent isosteric heat of adsorption ( $Q_{st}$ ) for ethylene was estimated on the basis of the Clausius–Clapeyron equation (Supplementary Fig. 14). The experimental  $Q_{st}$  value for C<sub>2</sub>H<sub>4</sub> (ranging from 20.5 to 35.0 kJ mol<sup>-1</sup>) in UTSA-280 was found to be markedly lower than those of many efficient C<sub>2</sub>H<sub>4</sub> sorbents (Supplementary Table 4), such as MOFs functionalized with open metal sites (40–85 kJ mol<sup>-1</sup>)<sup>7,31</sup> and  $\pi$ -complexation sorbents (60–120 kJ mol<sup>-1</sup>)<sup>29,32</sup>. Such a low apparent adsorption enthalpy implies the potential to regenerate this MOF under mild conditions, thus avoiding C<sub>2</sub>H<sub>4</sub> oligomerization/polymerization that may happen following the catalysis of open metal sites<sup>16,17</sup>.

### Sieving mechanism and breakthrough separation

Presumably, the main host–guest interactions between C<sub>2</sub>H<sub>4</sub> and UTSA-280 are C–H $\cdots\pi$  and C–H $\cdots$ O interactions, which usually have an important role in protein folding and molecular recognition. To determine the nature of the interactions of C<sub>2</sub>H<sub>4</sub> molecules within UTSA-280 structurally, single-crystal X-ray diffraction experiments were carried out. Data for UTSA-280•0.2C<sub>2</sub>H<sub>4</sub> were collected at room temperature on a C<sub>2</sub>H<sub>4</sub>-loaded sample (Fig. 2 and Supplementary Table 2). Non-hydrogen atoms of the adsorbate can be located by employing this technique. Following the C<sub>2</sub>H<sub>4</sub> loading, the framework of [Ca(C<sub>4</sub>O<sub>4</sub>)(H<sub>2</sub>O)]•0.2C<sub>2</sub>H<sub>4</sub> retains the same as the synthesized and activated ones, while remarkable intensity increases in residual electron density peaks ( $F_o - F_c$  contoured raising to 1.9 e Å<sup>-3</sup> in UTSA-280•0.2C<sub>2</sub>H<sub>4</sub>) were clearly observed within the cylindrical channel, demonstrating the presence of C<sub>2</sub>H<sub>4</sub> molecules (Supplementary Fig. 15). A single crystallographic type of adsorbed C<sub>2</sub>H<sub>4</sub> molecule can be successfully located in the middle of the channel from dispersed electron density peaks (Fig. 2a, b and Supplementary Figs. 16 and 17). The refined C<sub>2</sub>H<sub>4</sub> shows two-fold

disordering over two sites with partial occupancy, which oriented linearly with its C=C axis along the channel and tilted with its minimum cross-section along the diagonal of the pore aperture. The orientation of C<sub>2</sub>H<sub>4</sub> molecules inside the channels can minimize any possible steric hindrance and electrostatic repulsion from the framework. Weak C–H $\cdots$ O hydrogen bonding (3.32–3.44 Å),  $\pi\cdots\pi$  stacking (3.31 Å) and van der Waals (vdW) interactions (shortest C–H $\cdots\pi$  distance of 3.32 Å) are found between discrete C<sub>2</sub>H<sub>4</sub> molecules and the aromatic rings of the C<sub>4</sub>O<sub>4</sub><sup>2-</sup> ligand or coordinated water molecules (Fig. 2c), which are significantly larger than those observed in MOFs with strong binding sites (for example, 2.42 Å for C<sub>2</sub>H<sub>4</sub> with the open Fe site in Fe-MOF-74)<sup>7</sup>, being consistent with its lower adsorption enthalpy. Considering the vdW radii of atoms, the tilted C<sub>2</sub>H<sub>4</sub> molecule fits the narrow pore channel well (Fig. 2d). In contrast, owing to the cross-section being larger (15.5 Å<sup>2</sup>) than the pore aperture (14.4 Å<sup>2</sup>), significant steric hindrance is unavoidable when a C<sub>2</sub>H<sub>6</sub> molecule of staggered conformation is put inside the channels with whichever orientations, which is well confirmed by the calculated potential energy variation of C<sub>2</sub>H<sub>6</sub> along the pore channel (Supplementary Fig. 18). Importantly, structural comparison of UTSA-280 with different guest inclusions shows that the pore structure is basically not changed (Fig. 2e), in which no conformation change or abnormal atomic displacement parameter is observed for the C<sub>4</sub>O<sub>4</sub><sup>2-</sup> linker (Fig. 2f and Supplementary Figs. 5, 16 and 17), confirming a relatively high degree of pore and framework rigidity. This rigidity is also supported by additional diffraction data for UTSA-280 under various other external stimuli, including temperature variation (Supplementary Figs. 19–22). Therefore, the pore aperture size is unlikely to become large enough to accommodate C<sub>2</sub>H<sub>6</sub> molecules during the sorption process. Overall, the specific C<sub>2</sub>H<sub>4</sub> adsorption is because C<sub>2</sub>H<sub>4</sub> molecules can diffuse into the confined channel utilizing its optimal orientation, while C<sub>2</sub>H<sub>6</sub> molecules are subject to the inaccessibility of this rigid pore channel.





**Fig. 3 | Column breakthrough results and scalable synthesis of UTSA-280.** **a**, Breakthrough curves for UTSA-280 from different scales for an equimolar binary mixture of  $C_2H_4/C_2H_6$  at 298 K and 1 bar. The breakthrough experiments were carried out in a packed column with 3.2 g sample at a flow rate of  $2 \text{ ml min}^{-1}$ . The points are experimental data, and the lines are drawn to guide the eye. **b**, 0.22 kg synthesis of  $UTSA-280 \cdot H_2O$  obtained from rapid mixing of a saturated aqueous solution of sodium squarate with an aqueous solution of calcium nitrate.

On the basis of the gas-loaded structure, we performed first-principles dispersion-corrected density functional theory (DFT) calculations to further confirm the  $C_2H_4$  adsorption nature in UTSA-280. We found that the calculated  $C_2H_4$  adsorption location and orientation are consistent with the experimental results from the diffraction data (Supplementary Fig. 23). Moreover, the adsorbed  $C_2H_4$  molecule interacts with the surrounding channel surface through  $\pi \cdots \pi$  stacking ( $3.31 \text{ \AA}$ ) and vdW interactions with the aromatic rings of the  $C_4O_4^{2-}$  linkers. Overall, the adsorption interaction is a weak dispersive interaction in nature. The dispersion-corrected DFT-calculated static binding energy is quite modest,  $\sim 37.8 \text{ kJ mol}^{-1}$ , and consistent with the relatively low isosteric heat ( $34.1 \text{ kJ mol}^{-1}$ ) observed experimentally in UTSA-280. Overall, such molecular exclusion of ethane from ethylene associated with low binding affinity indicates that UTSA-280 can serve as a promising molecular sieve for ethylene enrichment.

In the common process for ethylene production based on the cracking of heavier hydrocarbon fractions, followed by dehydrogenation reactions, the conversion yield of the later step is only around 50–60%<sup>33</sup>. Other processes such as catalytic dehydrogenation also give an equimolar mixture of  $C_2H_4$  and  $C_2H_6$ . Thus, the upgrading of ethylene from the  $C_2H_4/C_2H_6$  mixture is a very important process before further utilization. Although certain molecular exclusions can also be achieved on a few flexible porous materials<sup>34,35</sup>, the co-adsorption of other impurities during the opening of the pore structure makes their column breakthrough separation very tough, giving low-purity ethylene. To evaluate the performance of UTSA-280 in an adsorptive dynamic separation process, breakthrough experiments were performed, in which an equimolar  $C_2H_4/C_2H_6$  mixture was flowed over a packed column of the activated solid with a rate of  $2 \text{ ml min}^{-1}$  at 298 K (Fig. 3a and Supplementary Fig. 24). As expected, clean separation of the challenging  $C_2H_4/C_2H_6$  mixture was realized by using UTSA-280.  $C_2H_6$  was first to elute through the bed, and then the outlet gas quickly reached pure grade with no detectable  $C_2H_4$  (below the detection limit of the experimental setup), whereas the solid adsorbent retained  $C_2H_4$  for a remarkable time before the breakthrough of  $C_2H_4$ . Hence,  $C_2H_6$  can be removed from  $C_2H_4$  with no loss of valuable  $C_2H_4$ , which is in line with the sorption experiments. The amount of  $C_2H_4$  enriched from the equimolar  $C_2H_4/C_2H_6$  mixture was up to  $1.86 \text{ mol kg}^{-1}$  (Supplementary Fig. 25), which is slightly lower than the equilibrium capacity of UTSA-280 at 0.5 bar ( $2.05 \text{ mol kg}^{-1}$ ) owing to the relatively slow diffusion of  $C_2H_4$  into this MOF during the separation process (Supplementary Fig. 26). It can be further increased at higher pressures (Supplementary Fig. 27). Enriched  $C_2H_4$  can then be recovered with high purity during the regeneration step, which was carried out by

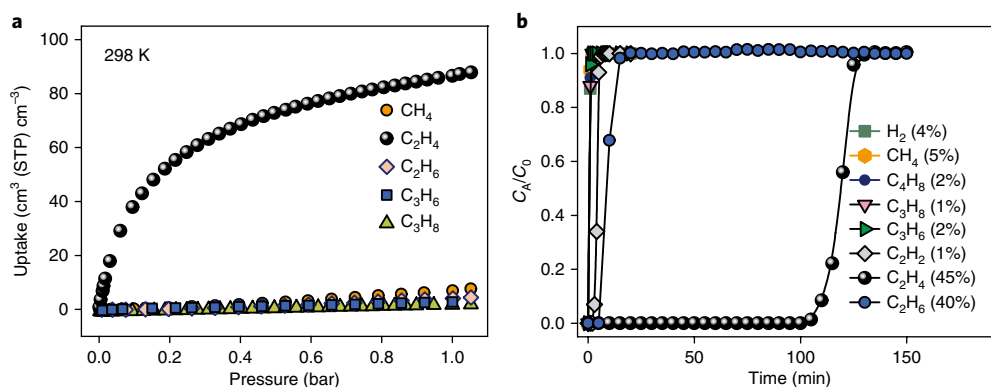
applying a vacuum (Supplementary Fig. 28). Moreover, regeneration of UTSA-280 under a He flow at 353 K revealed that the adsorbed gas can be completely recovered within 10 min (Supplementary Fig. 29), which is significantly faster than that of Ag-doped adsorbent (up to thousands of minutes)<sup>29</sup>. These results demonstrate that the challenging  $C_2H_6$  removal can be satisfactorily addressed under mild conditions (1–2 bar, 298 K), considering that the realistic pressure of cracked gas steam leaving from the thermal cracking furnace is  $\sim 1.55 \text{ bar}$  (ref. <sup>36</sup>). For benchmark zeolites with a small pore aperture for the kinetic separation, similar separation has been realized at 8.5 bar and 323 K (ref. <sup>30</sup>). Multiple cycling breakthrough experiments under the aforementioned operating conditions show the same retention time as the initial one, which revealed that UTSA-280 maintained its ethylene uptake capacity and molecular exclusion of ethane (Supplementary Fig. 30). For comparison with breakthrough experiments of UTSA-280, transient breakthrough simulation was also carried out (Supplementary Fig. 31), which was found to be certainly consistent with the experimental results.

### Effect of gas impurity on ethylene production

Besides the separation of  $C_2H_4$  from  $C_2H_6$ , there is tremendous current interest in the recovery of valuable ethylene from refinery gas streams (typically consisting of 51% methane, 21.4% ethylene, 21.1% ethane and 6.5% propane)<sup>28,37</sup>, which are usually used as fuel gas. An adsorptive separation process that uses this molecular sieve for the recovery of  $C_2H_4$  from similar mixtures could potentially result in substantial economic benefits. To evaluate the feasibility of using UTSA-280 for this task, we carried out breakthrough experiments for a quaternary  $CH_4/C_2H_4/C_2H_6/C_3H_8$  mixture (45/25/25/5). On the basis of the sieving effect (Fig. 4a), specific  $C_2H_4$  enrichment from the above quaternary gas mixture was realized with UTSA-280 (Supplementary Fig. 32). It should be noted that the realistic gas stream in ethylene plants is more complex; for example, a typical steam from ethane cracking contains 3.7–4.2%  $H_2$ , 3.7–5.4%  $CH_4$ , 0.3–1.2%  $C_2H_2$ , 45.7–49.7%  $C_2H_4$ , 32.7–41.3%  $C_2H_6$ , 0.8–1.5%  $C_3H_6$ , 0.2–0.3%  $C_3H_8$  and 0.3–0.8%  $C_4H_8$  (ref. <sup>36</sup>). Consequently, we have carried out breakthrough experiments for an octonary  $H_2/CH_4/C_2H_2/C_2H_4/C_2H_6/C_3H_6/C_3H_8/C_4H_8$  mixture (4/5/1/45/40/2/1/2), which also demonstrates that this MOF is competent to exclusively enrich  $C_2H_4$  from the complicated cracking stream (Fig. 4b).

### Scalable synthesis and stability

Among reported MOFs for  $C_2H_4/C_2H_6$  separation, MOFs with open metal sites are indeed efficient at capturing  $C_2H_4$  via strong coordination interactions, which can produce very high  $C_2H_4$  uptake at ambient conditions. However, MOFs with open metal sites are



**Fig. 4 | Separation performance of UTSA-280 for a gas mixture containing C<sub>2</sub>H<sub>4</sub>.** **a**, Single-component adsorption isotherms of CH<sub>4</sub> (orange circles), C<sub>2</sub>H<sub>4</sub> (black circles), C<sub>2</sub>H<sub>6</sub> (pink diamonds), C<sub>3</sub>H<sub>6</sub> (blue squares) and C<sub>3</sub>H<sub>8</sub> (lime triangles) in UTSA-280 at 298 K. **b**, Multi-component breakthrough curves for an octonary mixture of H<sub>2</sub>/CH<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>/C<sub>4</sub>H<sub>8</sub> (4/5/1/45/40/2/1/2) at 298 K and 1 bar. The breakthrough experiments were carried out in a packed column at a flow rate of 2 ml min<sup>-1</sup>. The points are experimental data, and the lines are drawn to guide the eye.

highly sensitive to moisture owing to their preferred coordination with water, resulting in a significantly reduced C<sub>2</sub>H<sub>4</sub> uptake capacity and/or binding affinity. In contrast, UTSA-280 is stable in water (Supplementary Fig. 33) as demonstrated by powder X-ray diffraction patterns of the sample after immersion in water for days. Moreover, gas sorption experiments of the reactivated UTSA-280 from the water-treated and moisture-exposed samples revealed that this material still maintains the same sorption performance for C<sub>2</sub>H<sub>4</sub> (Supplementary Fig. 34), indicating that UTSA-280 is water-stable<sup>38</sup>. As shown in Supplementary Figs. 35–37, further breakthrough experiments and selectivity calculations under moisture (10 to 1,137 parts per million H<sub>2</sub>O) also demonstrate that UTSA-280 can maintain its separation performance under more extreme conditions than would be found in a realistic process<sup>10</sup>. Such properties are apparently important for its potential industrial application. Furthermore, UTSA-280 is easily synthesized from very common chemical commodities via a ‘green’ and scalable method at room temperature (Fig. 3b and Supplementary Fig. 38), in which the only solvent is water. Overall, by virtue of the optimal and rigid pore channel of a known, water-stable, ultramicroporous MOF made by an environmentally friendly method, molecular exclusion of ethane from ethylene has been realized for promising energy-efficient separation technologies.

## Outlook

Optimal pore size and suitable functionality are essential features enabling porous materials to address key challenging gas separations. The above results illustrate that the ideal molecular exclusion of ethane from ethylene can be readily achieved by integrating the merits of size/shape match and high rigidity into the pore structure, which may greatly facilitate the very challenging membrane-based separation of such essential hydrocarbons. In principle, pore engineering in MOF chemistry is generally applicable to other types of porous material including porous organic polymers, covalent organic frameworks and hydrogen-bonded organic frameworks. A detailed examination of the pore features in various porous materials will be needed for the discovery of other molecular sieves in the future, and thus broaden the exploration of separation technologies with energy-efficient prospects, affording tremendous opportunity for valuable gas separations.

## Online content

Any methods, additional references, Nature Research reporting summaries, source data, statements of data availability and associated accession codes are available at <https://doi.org/10.1038/s41563-018-0206-2>.

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## Author contributions

R.-B.L., W.Z. and B.C. conceived the research idea and designed the experiments. R.-B.L., L.L. and H.-L.Z. performed the experiments and analysed data. H.-L.Z. participated in the structural determination of MOFs. R.K. performed the simulations of mixture separations. L.L., C.H., S.L. and J.L. participated in the breakthrough measurement. H.W. and W.Z. did the DFT calculation. R.-B.L., W.Z. and B.C. discussed and co-wrote the paper. All authors discussed the results and commented on the manuscript. R.-B.L., L.L. and H.-L.Z. contributed equally to this work.

## Competing interests

The authors declare no competing interests.

## Additional information

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## Methods

**Materials.** Calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 99%, Fisher Chemical), sodium hydroxide ( $\text{NaOH}$ , 98%, Alfa Aesar), glacial acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ , 99.7%, Fisher Chemical) and squaric acid (or 3,4-dihydroxycyclobut-3-ene-1,2-dione,  $\text{C}_4\text{H}_2\text{O}_4$ , 99.0%, Oakwood Chemicals) were purchased and used without further purification.

$\text{N}_2$  (99.999%),  $\text{CO}_2$  (99.999%),  $\text{C}_2\text{H}_4$  (99.5%),  $\text{C}_2\text{H}_6$  (99.5%) and  $\text{He}$  (99.999%) were purchased from Airgas. Mixed gases including  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 = 50/50$  (vol/vol),  $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8 = 45/25/25/5$  (vol/vol/vol/vol) and  $\text{H}_2/\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8/\text{C}_4\text{H}_{10} = 4/5/1/45/40/2/1/2$  (vol/vol/vol/vol/vol/vol/vol/vol) were purchased from Beijing Special Gas Co. Ltd.

**Synthesis of  $[\text{Ca}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})] \cdot x\text{H}_2\text{O}$ .** The synthesis of the single-crystal sample was performed following a reported method with minor modifications<sup>24</sup>. A solution of squaric acid (182 mg, 1.6 mmol) and  $\text{NaOH}$  (3.2 mmol, 128 mg) in 16 ml water was carefully layered on a solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (8.0 mmol, 1.888 g),  $\text{CH}_3\text{COOH}$  (2.75 ml, 2.882 g) and  $\text{NaOH}$  (32 mmol, 1.280 g) in 40 ml water. Colourless single crystals of  $[\text{Ca}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})] \cdot x\text{H}_2\text{O}$  were obtained in a few days. The resultant crystals were filtered, washed thoroughly with water and dried under air, with yields of 61% based on squaric acid. A microcrystalline powder sample was obtained by mixing a saturated aqueous solution (10 ml) of sodium squarate ( $\text{Na}_2\text{C}_4\text{O}_4$ , 1 mmol, 0.158 g) with an aqueous solution (10 ml) of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (5 mmol, 1.180 g). Microcrystalline powders came out immediately and the reaction completely finished within a few minutes; then, after 10 min at room temperature, the sample was filtered, washed thoroughly with water and dried under air, with a yield of 0.146 g (74% based on sodium squarate).

**Large-scale synthesis of  $[\text{Ca}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})] \cdot x\text{H}_2\text{O}$ .** Synthesis at 1,000-times scale was carried out as follows. A microcrystalline powder sample was obtained by mixing a saturated aqueous solution (3.29 l) of sodium squarate ( $\text{Na}_2\text{C}_4\text{O}_4$ , 1,190 mmol, 0.188 kg) with an aqueous solution (0.6 l) of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (5,950 mmol, 1.404 kg). Microcrystalline powders came out immediately and the reaction completely finished within a few minutes; then, after 10 min at room temperature, the sample was filtered, washed thoroughly with water and dried under air, with a yield of 0.219 kg (93% based on sodium squarate). Depending on the container size, the synthesis scale can be even higher.

**Preparation of  $[\text{Ca}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})]$  (UTSA-280).** A single crystal of as-synthesized  $[\text{Ca}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})] \cdot x\text{H}_2\text{O}$  was sealed in a glass capillary, activated in situ under high vacuum for 24 h at 100 °C, followed at 110 °C for another 48 h. The obtained  $[\text{Ca}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})]$  crystal was sealed for the X-ray diffraction experiment.

It should be noted that activation at higher temperatures or for longer times would lead to loss of the coordinated water and collapse of the crystalline framework structure, and thus the loss of molecular sieving capability.

**Single-component gas sorption measurement.** The gas sorption measurements were prepared according to ref.<sup>39</sup>, and reproduced here for completeness. The gas sorption isotherms were collected on an automatic volumetric adsorption apparatus (Micromeritics ASAP 2020 surface area analyser). Before the sorption measurements, the as-synthesized sample was washed with methanol three times and placed in a quartz tube and dried under high vacuum for 36–72 h at 110 °C (depending on the particle sizes) to remove the guest water molecules, giving the activated UTSA-280 for gas sorption analyses.

**Breakthrough separation experiments.** The breakthrough experiments were carried out in a dynamic gas breakthrough set-up<sup>39</sup>. A stainless-steel column with inner dimensions of 9 mm and a length of 150 mm was used for sample packing. A pelleted microcrystalline sample (3.2 g) with a particle size of 220–320  $\mu\text{m}$  was then packed into the column. The column was placed in a temperature-controlled environment (maintained at 298 K). The mixed gas flow and pressure were controlled by using a pressure controller valve and a mass flow controller. Outlet effluent from the column was continuously monitored using gas chromatography (GC-2014, Shimadzu) with a thermal conductivity detector. The column packed with activated sample was first purged with helium gas flow for 2 h at 373 K. The mixed gas flow rate during the breakthrough process is 2 standard cubic centimetres per minute using different gas mixtures at 1 bar. After the breakthrough experiment, the sample was regenerated with helium gas flow (50 standard cubic centimetres per minute) for about 15 min at 353 K.

**X-ray diffraction analysis of powder samples.** Powder X-ray diffraction patterns were collected using a Rigaku Ultima IV diffractometer ( $\text{Cu K}\alpha$   $\lambda = 1.540598 \text{ \AA}$ ) with an operating power of 40 kV, 44 mA and a scan rate of  $8.0^\circ \text{ min}^{-1}$ . The data were collected in the range of  $2\theta = 5\text{--}40^\circ$ . In situ powder X-ray diffraction patterns were collected using a Bruker D8 ADVANCE X-ray diffractometer equipped with an XRK high-temperature chamber and the high vacuum line under an operating power of 40 kV, 40 mA for  $\text{Cu K}\alpha$  radiation.

**Single-crystal X-ray diffraction experiments.** The single crystals of UTSA-280•0.16 $\text{C}_2\text{H}_4$  and UTSA-280•0.20 $\text{C}_2\text{H}_4$  were obtained by loading ethylene gas at about 300 and 600 mmHg and ambient temperature. Diffraction data were collected on a Bruker D8 Venture or Rigaku CCD (charge-coupled device) diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) at 298 K. Multi-scan absorption corrections were performed with a Bruker APEX III. The structures were solved by the direct method and refined with the full-matrix least-squares technique using the SHELXTL program. For the framework, anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms were generated geometrically. For gas molecules, ethylene was located from the strong electron density peaks and refined with isotropic displacement parameters. The C–C distances were restrained to 1.30(1) for ethylene. Hydrogen atoms on ethylene molecules were added with geometrical constraints. Crystal data for the compounds are summarized in Supplementary Table 2. CCDC 1582383–1582384 and 1855047–1855048 contain the supplementary crystallographic data for UTSA-280, UTSA-280•0.20 $\text{C}_2\text{H}_4$ , UTSA-280•0.16 $\text{C}_2\text{H}_4$  and UTSA-280• $\text{H}_2\text{O}$ , respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**DFT calculations.** The DFT calculations were performed according to ref.<sup>39</sup>, and reproduced here for completeness. First-principles DFT calculations were performed using the Quantum-Espresso package<sup>40</sup>. A semiempirical addition of dispersive forces to conventional DFT was included in the calculation to account for vdW interactions<sup>41</sup>. We used Vanderbilt-type ultrasoft pseudopotentials and generalized gradient approximation with a Perdew–Burke–Ernzerhof exchange correlation. A cutoff energy of 544 eV and a  $2 \times 2 \times 4$  k-point mesh (generated using the Monkhorst–Pack scheme) were found to be enough for the total energy to converge within 0.01 meV per atom. We first optimized the structure of UTSA-280. A  $\text{C}_2\text{H}_4$  gas molecule was then introduced to the optimized host structure at the experimentally identified adsorption site, followed by a full structural relaxation. To obtain the gas binding energy, an isolated gas molecule placed in a supercell (with the same cell dimensions as the MOF crystal) was also relaxed as a reference. The static binding energy (at  $T = 0 \text{ K}$ ) was then calculated using  $\Delta E = E(\text{MOF} + \text{gas molecule}) - E(\text{MOF}) - E(\text{gas molecule})$ . A negative  $\Delta E$  value would mean that the gas adsorption is energetically favourable. Note that in the main text, only the absolute value of  $\Delta E$  is cited to describe the binding strength.

**Fitting of pure-component isotherms.** The pure-component isotherm data for  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  in UTSA-280 were fitted with the single-site Langmuir–Freundlich model.

$$N = N_{\max} \frac{b p^{1/n}}{1 + b p^{1/n}} \quad (1)$$

where  $p$  (unit: kPa) is the pressure of the bulk gas at equilibrium with the adsorbed phase,  $N$  (unit:  $\text{mmol g}^{-1}$ ) is the adsorbed amount per mass of adsorbent,  $N_{\max}$  (unit:  $\text{mmol g}^{-1}$ ) is the saturation capacities,  $b$  (unit:  $1/\text{kPa}$ ) is the affinity coefficient and  $n$  represents the deviation from an ideal homogeneous surface. The fitted parameter values are presented in Supplementary Table 3.

**Isosteric heat of adsorption.** The binding energy of  $\text{C}_2\text{H}_4$  is reflected in the isosteric heat of adsorption,  $Q_{st}$ . The Clausius–Clapeyron equation was employed to calculate the enthalpies of  $\text{C}_2\text{H}_4$  adsorption:

$$\frac{\partial(\ln P)}{\partial(1/T)} = -\frac{Q_{st}}{R} \quad (2)$$

where  $P$  is the pressure,  $T$  is the temperature and  $R$  is the universal gas constant. Adsorption heats ( $Q_{st}$ ) of UTSA-280 for ethylene reported here are estimated using pure-component isotherms collected at 273, 298 and 313 K.

**IAST calculations of adsorption selectivities.** The adsorption selectivity for  $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$  separation is defined by

$$S_{\text{ads}} = \frac{q_1/q_2}{p_1/p_2} \quad (3)$$

$q_1$  and  $q_2$  are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures  $p_1$  and  $p_2$ .

**Transient breakthrough of  $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$  mixtures in fixed-bed adsorbents.**

For comparison with breakthrough experiments with UTSA-280, transient breakthrough simulations were undertaken using the same methodology as discussed in earlier publications<sup>42</sup>. The dimensions of the breakthrough tube, sample mass and flow rates were chosen to precisely match the experimental conditions. The

simulated breakthrough is shown in Supplementary Fig. 20. The breakthrough times of  $C_2H_6$  and  $C_2H_4$  are captured reasonably accurately. The simulated breakthroughs are sharper than those observed experimentally. The reason for this is that in the simulations, intracrystalline diffusional influences are ignored. The distended characteristics of the experimental breakthroughs with UTSA-280 are because of finite diffusional resistances.

We investigated the separation performance of UTSA-280 for separation of a 50/50  $C_2H_2/C_2H_4$  feed mixture. The total bulk gas phase is at 298 K and 100 kPa.

### Data availability

The data that support the plots within this paper and other finding of this study are available from the corresponding authors upon reasonable request.

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