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A robust Th-azole framework for highly efficient purification of C$_2$H$_4$ from a C$_2$H$_4$/C$_2$H$_2$/C$_2$H$_6$ mixture

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Separation of C$_2$H$_4$ from C$_2$H$_4$/C$_2$H$_2$/C$_2$H$_6$ mixture with high working capacity is still a challenging task. Herein, we deliberately design a Th-metal-organic framework (MOF) for highly efficient separation of C$_2$H$_4$ from a binary C$_2$H$_6$/C$_2$H$_4$ and ternary C$_2$H$_4$/C$_2$H$_2$/C$_2$H$_6$ mixture. The synthesized MOF Azole-Th-1 shows a UiO-66-type structure with fcu topology built on a Th$_6$ secondary building unit and a tetrazole-based linker. Such noticeable structure, is connected by a N,O-donor ligand with high chemical stability. At 100 kPa and 298 K Azole-Th-1 performs excellent separation of C$_2$H$_4$ (purity > 99.9%) from not only a binary C$_2$H$_6$/C$_2$H$_4$ (1:9, v/v) mixture but also a ternary mixture of C$_2$H$_6$/C$_2$H$_2$/C$_2$H$_4$ (9:1:90, v/v/v), and the corresponding working capacity can reach up to 1.13 and 1.34 mmol g$^{-1}$, respectively. The separation mechanism, as unveiled by the density functional theory calculation, is due to a stronger van der Waals interaction between ethane and the MOF skeleton.
Ethylene is one of the most widely used feedstock molecules for the production of polymers and high-value organic chemicals\textsuperscript{3,2}. It is usually produced by the thermal cracking of hydrocarbons. The removal of ethane and acetylene by-products that inevitably arise during these processes is one of the most challenging chemical separations due to the similarity of the physicochemical properties of ethane (kinetic diameter 4.4 Å, boiling point 184.55 K), ethylene (kinetic diameter 4.2 Å, boiling point 169.42 K), and acetylene kinetic diameter 3.3 Å, boiling point 188.40 K)\textsuperscript{2,7}.

At present, cryogenic distillation is the main technology used to separate ethane and ethylene with the requirement of high pressure (5–28 bar) and low temperature (180–258 K)\textsuperscript{3,9}, which indicates that this process is expensive and comes with a high energy penalty. And partial hydrogenation of acetylene into ethylene over catalyst\textsuperscript{10} or solvent extraction of cracked olefins\textsuperscript{11} are also involved with the purification of ethylene from acetylene. Adsorptive separation by porous materials is an alternative technology, especially, some metal-organic framework (MOF)\textsuperscript{2–21} with high volume, designable pore characteristics, and countless structural possibilities, can be employed into the gas separation processes, the adsorption selectivity and capacity are higher than the results of conventional adsorbents\textsuperscript{22–24} such as zeolites and carbon-based, especially the adsorption and separation for C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4}\textsubscript{8,22,25–29}.

For the MOFs with open metal site, the ethylene can easily bind to it, leading to highly selective uptake of ethylene over ethane, due to the electrostatic interaction between the n-electron in ethylene and the positive charge in open metal sites\textsuperscript{36,40–44}, such as, HKUST-1\textsuperscript{14}; particularly in the low pressure region, is preferential adsorption of ethylene, which is supported by some theoretical calculations\textsuperscript{45,46}. In contract, for some special MOFs, when the coordination positions of metal reaches to saturate, they can enable favorable adsorption towards ethane over ethylene through their unique pore wall that affords stronger van der Waals (vdW) interaction between the H of C\textsubscript{2}H\textsubscript{6} and the MOF skeleton\textsuperscript{8,22,25–29,32,34,35,47}. For example, ZIF-7 presents the first example of a microporous solid displaying the selective adsorption of paraffins over olefins\textsuperscript{48}. However, MOFs showing such uncommon adsorption phenomenon (C\textsubscript{2}H\textsubscript{6} over C\textsubscript{2}H\textsubscript{4}) is still rare until now.

Recently, Lu and co-workers\textsuperscript{49} report that they use TTT-100 to obtain the selective adsorption of ethane and acetylene over ethylene from a ternary mixture of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} (0.5:0.5:99, v/v/v) and achieve a C\textsubscript{2}H\textsubscript{4} purity greater than 99.9% (working capacity of 0.69 mmol g\textsuperscript{−1}) by a single-breakthrough operation. Zaworoko et al.\textsuperscript{38} use a synergistic sorbent separation method for the one-step production of polymer-grade C\textsubscript{2}H\textsubscript{4} from ternary mixture of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} (0.5:0.5:99, v/v/v) and the one-step production of polymer-grade C\textsubscript{2}H\textsubscript{4} from ternary mixture of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4} (0.5:0.5:99, v/v/v) (Fig. 3).

Results

Synthesis, structure, and characterization of Azole-Th-1. The reaction between ligand TBA and Th(NO\textsubscript{3})\textsubscript{4} and 4-(1H-tetrazol-5-yl) benzoic acid (TBA). This compound shows a UiO-66-type structure, except for the replacement of secondary building unit such as Zr\textsubscript{6} by Th\textsubscript{6} and linkers such as O-donor ligand by N,O-donor ligand. This unique tetravalent-based structure allows it to perform high C\textsubscript{2}H\textsubscript{4} separation at room temperature and selective adsorption of C\textsubscript{2}H\textsubscript{4} over C\textsubscript{2}H\textsubscript{2}, finally resulting in the promising application for C\textsubscript{2}H\textsubscript{4} separation from the binary C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} and ternary C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} mixture. Furthermore, both the grand canonical Monte Carlo (GCMC) simulations and density functional theory (DFT) calculations are carried out to disclose the separation mechanism.
about 250 °C, the crystal structure begins to collapse, which is in agreement with the results of temperature dependent PXRD tests (Fig. 2a). As shown in Fig. 2a, the PXRD of Azole-Th-1 samples from room temperature to 200 °C are matching with the experimental and simulated results. While the temperature reaches to 250 °C, the peaks of PXRD disappear, which indicates that the crystal structure is destroyed by such high temperature.

On the other hand, the chemical stability under water and different solvents environment, including seven organic solvents and a broad pH range from 1 to 12, were also traced by PXRD tests (Fig. 2b, c), where respective optical images of crystal were represented in Fig. 3. Note that the crystals of Azole-Th-1 render excellent stability in water and above solvents even after 30 days.

**Adsorption isotherm, selectivity, and breakthrough.** The moderate thermal stability and high chemical stability of Azole-Th-1 prompts us to study the gas adsorption performances. To characterize the permanent porosity of the obtained material, the N₂ adsorption isotherm at 77 K was measured. As shown in Fig. 4a, a fully reversible type I isotherm with a Brunauer Emmett Teller (BET) surface area of 983 m² g⁻¹ and a uniform pore size around 9.2 Å was exhibited. This pore size is comparable with that calculated LCD (the largest cavity diameter, 10.0 Å) by Zeo++ program (Supplementary Table 3).

This high porosity and desirable aperture encouraged us to further investigate C₂H₆/C₂H₄ separations in detail. Adsorption isotherms of single component C₂H₆ and C₂H₄ were collected at 298 K and 273 K, respectively, as presented in Fig. 4b and Supplementary Fig. 6. The adsorption isotherm of C₂H₆ is typically type I with a steep slope, which is a typical feature of strong adsorbates in microporous materials (Fig. 4b)²⁸–⁴³. And the adsorption amounts of C₂H₆ at both 273 and 298 K (121.7 and 100.2 cm³ g⁻¹) were also higher than the corresponding C₂H₄ (111.3 and 80.7 cm³ g⁻¹). Therefore, the Azole-Th-1 has a distinct preference for adsorbing ethane over ethylene. It is well-known that the magnitude of the adsorption enthalpies of porous materials reveals that the affinity of the pore surface toward adsorbents, determining the adsorptive selectivity.⁴⁹,⁶⁵. This can be directly reflected on the adsorption heat enthalpy (Q_ads) of C₂H₆ and C₂H₄, giving 28.6 kJ mol⁻¹ for C₂H₆ at the zero coverage, significantly higher than the values of 26.1 kJ mol⁻¹ for C₂H₄ (Fig. 4d), strongly suggesting a higher affinity between host and guest for C₂H₆ than C₂H₄, where the detail virial-type analysis were provided in Supplementary Fig. 7.
At room temperature and 100 kPa, Azole-Th-1 affords ultrahigh adsorption capacity of C₂H₆ up to 100.2 cm³ g⁻¹. This value exceeds most reported top-performing porous adsorbents for such use as shown in Table S2, including Fe₂(O₂)(dobdc)₃⁵, MAF-4⁹, ZIF-8³⁴, ZIF-7³², PCN-245²⁶, MIL-142A²⁸, Cu(Qc)²³⁷, Zn-atz-ipa³⁸, etc., which are summarized in Fig. 4f. Correspondingly, adsorption capacity of C₂H₄ at the same conditions is 81.1 cm³ g⁻¹, obviously, less than C₂H₆ about 20 cm³ g⁻¹. Hence, selective adsorption of C₂H₆ over C₂H₄ is suggested. To estimate the adsorption selectivity, we employed the ideal adsorption solution theory (IAST)⁶⁶ to analyze the experimental isotherm data, using composition of 50:50/10:90/1:15 C₂H₆/C₂H₄, as shown in Fig. 4e and Supplementary Fig. 8. The selectivity of C₂H₆ over C₂H₄ was up to 1.46 at room temperature and 100 kPa, Azole-Th-1 affords ultrahigh adsorption capacity of C₂H₆ up to 100.2 cm³ g⁻¹. This value exceeds most reported top-performing porous adsorbents for such use as shown in Table S2, including Fe₂(O₂)(dobdc)₃⁵, MAF-4⁹, ZIF-8³⁴, ZIF-7³², PCN-245²⁶, MIL-142A²⁸, Cu(Qc)²³⁷, Zn-atz-ipa³⁸, etc., which are summarized in Fig. 4f. Correspondingly, adsorption capacity of C₂H₄ at the same conditions is 81.1 cm³ g⁻¹, obviously, less than C₂H₆ about 20 cm³ g⁻¹. Hence, selective adsorption of C₂H₆ over C₂H₄ is suggested. To estimate the adsorption selectivity, we employed the ideal adsorption solution theory (IAST)⁶⁶ to analyze the experimental isotherm data, using composition of 50:50/10:90/1:15 C₂H₆/C₂H₄, as shown in Fig. 4e and Supplementary Fig. 8. The selectivity of C₂H₆ over C₂H₄ was up to 1.46 at room temperature and 100 kPa, Azole-Th-1 affords ultrahigh adsorption capacity of C₂H₆ up to 100.2 cm³ g⁻¹. This value exceeds most reported top-performing porous adsorbents for such use as shown in Table S2, including Fe₂(O₂)(dobdc)₃⁵, MAF-4⁹, ZIF-8³⁴, ZIF-7³², PCN-245²⁶, MIL-142A²⁸, Cu(Qc)²³⁷, Zn-atz-ipa³⁸, etc., which are summarized in Fig. 4f. Correspondingly, adsorption capacity of C₂H₄ at the same conditions is 81.1 cm³ g⁻¹, obviously, less than C₂H₆ about 20 cm³ g⁻¹. Hence, selective adsorption of C₂H₆ over C₂H₄ is suggested. To estimate the adsorption selectivity, we employed the ideal adsorption solution theory (IAST)⁶⁶ to analyze the experimental isotherm data, using composition of 50:50/10:90/1:15 C₂H₆/C₂H₄, as shown in Fig. 4e and Supplementary Fig. 8. The selectivity of C₂H₆ over C₂H₄ was up to 1.46 at room

**Fig. 3** The optical microscope images of Azole-Th-1 samples. a after soaking in water and seven different organic solvents 30 days, b after soaking in different pH solvents 30 days.

**Fig. 4** The adsorption and separation data of Azole-Th-1. a The N₂ adsorption at 77 K with the insert of the distribution of pore size. b The adsorption isotherms of C₂H₆ and C₂H₄ at 298 K, including experiments and simulations. c Experimental adsorption isotherms of Azole-Th-1 for C₂H₆, C₂H₄, and C₂H₂ at 298 K from 0.01 to 1 bar with the insert of enlargement from 0.01 to 0.1 bar. d The adsorption heat enthalpy of C₂H₆ and C₂H₄, calculated from the single-component C₂H₆ and C₂H₄ adsorption data at 298 and 273 K. e Predicted mixture adsorption isotherms and selectivity of Azole-Th-1 by IAST method for a 50/50 C₂H₆/C₂H₄ mixture at 298 K. f A comparison in selectivity and C₂H₆ adsorption capacity at 298 K and 1 bar between the reported top-performing porous adsorbents for C₂H₆/C₂H₄ separation and our MOF. The purple triangle is our MOF. Source data are provided as a Source Data file.
temperature and 100 kPa, which is slightly higher than that of other ratio mixture, both 1.44 for 10:90 and 1:15 C$_2$H$_6$/C$_2$H$_4$. To the best of our knowledge, Azole-Th-1 should be the first TH-MOF showing such abnormal adsorption behavior (C$_2$H$_6$ over C$_2$H$_4$).

Then, in order to check the actual separation ability of the gases mixture, the transient breakthrough simulations for C$_2$H$_6$/C$_2$H$_4$ (50/50, v/v) mixtures on Azole-Th-1 material was carried out at 298 K, as shown in Supplementary Fig. 9. This result demonstrates that the potential of producing pure product gas C$_2$H$_4$ during the time interval $\Delta t$, also suggests excellent C$_2$H$_6$/C$_2$H$_4$ separation performance. And then, to further confirm the real practical separation ability, the actual dynamic adsorption breakthrough experiments for C$_2$H$_6$/C$_2$H$_4$ (10/90, 50/50, 1/15, v/v) binary mixtures on Azole-Th-1 material were also carried out (Fig. 5a, b, and Supplementary Fig. 10). The C$_2$H$_4$ broke through the adsorption bed and yield a high purity gas (>99.9%) at first, whereas after a certain time C$_2$H$_6$ slowly eluted and reached to the equilibrium (Fig. 5a, b, and Supplementary Fig. 10). During this period of time, polymer-grade (>99.9%) C$_2$H$_4$ can be generated at the outlet. The breakthrough time of ethane was later than that of ethylene for these three ratio mixtures, meaning that the Azole-Th-1 preferred to adsorb ethane over ethylene. The long breakthrough time interval between C$_2$H$_4$ and C$_2$H$_6$ suggests that the Azole-Th-1 is quite effective for C$_2$H$_6$/C$_2$H$_4$ separation. The experimental breakthrough results was well in consistent with the simulated breakthrough (Fig. 5b, Supplementary Fig. 10b, d), strongly suggesting its superior application for C$_2$H$_4$ purification. Furthermore, cycling breakthrough experiments on Azole-Th-1 were carried out under the same conditions. The breakthrough time interval for C$_2$H$_6$/C$_2$H$_4$ mixtures in five cycles (Fig. 5c) is comparable, showing that this material has a good regenerability. According to the polymer grade C$_2$H$_4$ produced during time interval at different C$_2$H$_6$/C$_2$H$_4$ ratio, 3 min (50/50), 5 min (90/10), and 3.5 min (15/1), the productivities of C$_2$H$_4$ (>99.9%) were 0.68, 1.13, and 0.79 mmol g$^{-1}$, respectively. Hence, the polymer grade C$_2$H$_4$ with the max working capacity of 1.13 mmol g$^{-1}$ with >99.9% purity was harvested from 90/10 gas mixture, which working capacity is nearly 1.3 times for Fe$_2$(O$_2$)(dobdc) (0.79 mmol g$^{-1}$)$^{35}$ and 3.6 times for MAF-49 (0.28 mmol g$^{-1}$)$^{23}$, the two best materials for C$_2$H$_6$/C$_2$H$_4$ separation. Some more detailed comparison with other MOF materials is shown in Supplementary Table 2. After the breakthrough experiments, the PXRD pattern of our sample was also consistent with the PXRD before the breakthrough (Supplementary Fig. 11), which further indicated that this material has a good regenerability and high stability.

**Mechanism of gas adsorption by theoretical calculations.**

Theoretically, the determination of gas adsorption sites in the MOFs is of great significance for the design of some gas storage and separation materials based on MOFs$^{31,67}$. Herein, the ultra-high C$_2$H$_4$ storage capacity prompts us to explore the adsorption sites within this Azole-Th-1. Theoretical simulation is a powerful tool enabling us to unveil the adsorption mechanisms and provide the adsorption sites. Therefore, the C$_2$H$_4$/C$_2$H$_6$ binding affinity in Azole-Th-1 was firstly investigated by single-component sorption isotherms at 298 K and pressures up to 100 kPa. The GCMC simulations were performed for understanding the interactions and adsorption behaviors of C$_2$H$_6$ and C$_2$H$_4$ in Azole-Th-1 at the molecular level$^{25,26,33,34,39}$. As shown in isotherm of C$_2$H$_6$/C$_2$H$_4$
adsorption (Fig. 4b), the maximum C2H6 and C2H4 uptake for Azole-Th-1 are 106.6 and 80.2 cm\(^3\) g\(^{-1}\) at 100 kPa and 298 K, respectively, both adsorbed tendency and the adsorption quantity are consistent with the experimental results (100.2 and 80.7 cm\(^3\) g\(^{-1}\)), where the simulated details are listed in Supplementary Information.

The further investigations on the interaction between C2H6/C2H4 and MOF material can help us to understand the mechanism of gas adsorption, which could analysis the discrepancies the interactions between C2H6 and C2H4 with our material, respectively. According to the density distribution of C2H6 on Azole-Th-1 at 298 K and 100 kPa (Fig. 6), there are three main adsorbed areas in our material, including benzene region (I-region), the tetrazole heterocycle region (II-region), and carboxylate region (III-region), respectively. Then, the adsorptions under different pressure were analyzed (Supplementary Fig. 12). Due to the higher polarizability of C2H6 (44.7 \(\times\) 10\(^{-25}\) cm\(^3\)) compared with C2H4 (42.5 \(\times\) 10\(^{-25}\) cm\(^3\)), at the beginning of the adsorption, the C2H6 molecules are preferentially filled in region I at 2.6 kPa (Supplementary Fig. 12a), but the C2H4 molecules are almost not adsorbed until 10.3 kPa (Supplementary Fig. 12e). While the pressure is 5.1 kPa, the region II begins to be filled by C2H6 molecules (Supplementary Fig. 12b), the total capacity of adsorption reaches to 18.5 cm\(^3\) g\(^{-1}\), which corresponds to the adsorption capacity of C2H4 at 12.8 kPa (18.9 cm\(^3\) g\(^{-1}\)), at that moment the region II is empty until the pressure increases to 17.9 kPa (Supplementary Fig. 12f). With the increase of pressure (to 48.7 kPa), region I and region II are almost filled saturated by C2H6 molecules (Supplementary Fig. 12c), and region III begins to be filled by C2H4 already, the total capacity of adsorption reaches to 73.2 cm\(^3\) g\(^{-1}\). The vdW interactions between C2H6 with aromatic rings (regions I and II) and carboxylate (region III) are more remarkable than the interactions between C2H4 with them. While the pressure reaches to 100 kPa, these three regions are saturated generally by C2H6 (Supplementary Fig. 12d), whereas, the C2H4 molecules only continue to be filled into regions I and II (Supplementary Fig. 12g), the C2H4 uptake (106.2 cm\(^3\) g\(^{-1}\)) is significantly greater than the maximum C2H4 uptake (80.2 cm\(^3\) g\(^{-1}\)). Hence, according to the GCMC simulations, the Azole-Th-1 prefers to adsorbing the C2H6 from 0.001 to 100 kPa at 298 K, and the C2H4 adsorption capacity is far greater than C2H6, which could achieve the separation of C2H6 and C2H4.

And then, according to the obtained adsorption regions, some DFT theoretical calculations about the mechanism of selective C2H6/C2H4 in Azole-Th-1 were investigated by the Dmol\(^3\) program package in the MS, the detail calculations were also presented in Supplementary Information. The determination of the adsorption point can quantify the interaction between the gas C2H6/C2H4 and Azole-Th-1 and analyze the mechanism of the gas adsorption. Because the calculations using the whole unit cell is too large, we used the fragmented cluster models cleaved from the unit cell for modeling the structures and energies to investigate the interaction points of C2H6/C2H4 adsorption. Due to the highly disordered structure of TBA, four fragment models were constructed. Accordingly, the fragment M1 to M4 were intercepted (Supplementary Fig. 13). Based on the distribution of density of C2H6/C2H4 through GCMC simulations, the geometries of fragmented models bound to C2H6/C2H4 were also obtained, as shown in Supplementary Fig. 14. By the calculations of binding energy for adsorbed geometries (Supplementary Table 5), obviously, the interactions between M1 to M4 with C2H6 (−43.09 kJ mol\(^{-1}\)) were stronger than the interactions between that of fragmented models with C2H4 (−33.52 kJ mol\(^{-1}\)), which results were in agreement with the heat of adsorption \(Q_d\). These can be attributed to the vdW interaction between the C–H in C2H6/C2H4 and conjugated \(\pi\)-systems in Azole-Th-1, especially, the conjugated region II (tetrazole).

In our opinion, there are three factors for the stabilities of adsorbed structures, the number of H atoms, the distances of vdW interaction, and the polarizability, where the summary about previous two factors were listed in Supplementary Tab. 6. As shown in Supplementary Fig. 14, C2H6 and C2H4 molecules are bound to several aromatic rings of ligands at three directions within a pore through vdW interactions. A single C2H6 or C2H4 molecule can form six or four pairs of C–H–π interactions with conjugated regions at least, where the vdW interaction between C–H and benzene ring of ligand (region I) are in the majority. The greater the number of H atoms, the stronger the C–H–π interaction between gas with different models, and finally the greater the adsorption capacity of C2H4 compared with C2H6. Because of the use of previously unreported ligand, the conjugated region tetrazole can enhance the binding with gas. As shown in Supplementary Fig. 14, C2H6@M1 (all O-donors of ligands coordinated on the Th(IV) inner cluster), there are two
pairs of vdW interactions between C–H with carboxylic acid (region III). However, as to C\textsubscript{2}H\textsubscript{6}@M\textsubscript{2} (Fig. 6, all N-donor of analysis the stabilization of the adsorption structures. Besides the highly efficient separation of C\textsubscript{2}H\textsubscript{6} from a ternary mixture of C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}. As shown in Fig. 5d, highly efficient separation of C\textsubscript{2}H\textsubscript{4} from a 90:19 (v/v/v) gas mixture of C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} was achieved by passing the mixture over a packed column of activated Azole-Th-1 material. It can be observed that C\textsubscript{2}H\textsubscript{4} achieves a breakthrough first, with no evidence of C\textsubscript{2}H\textsubscript{2} or C\textsubscript{2}H\textsubscript{6} flow before its breakthrough, which indicates that this material can produce a high purity C\textsubscript{2}H\textsubscript{4} (>99.9%) after only a single-breakthrough operation. The working capacity is up to 1.34 mmol g\textsuperscript{-1}, far exceeding the top-performing materials reported by Lu et al. (0.69 mmol g\textsuperscript{-1})\textsuperscript{49} and Zaworoko et al. (0.32 mmol g\textsuperscript{-1})\textsuperscript{38}, strongly suggesting its promising applications in this target. Note that, according to the adsorption isotherm of C\textsubscript{2}H\textsubscript{4} (Fig. 4c), the maximum of capacities of C\textsubscript{2}H\textsubscript{4} (81.1 cm\textsuperscript{3} g\textsuperscript{-1}) and C\textsubscript{2}H\textsubscript{2} (80.7 cm\textsuperscript{3} g\textsuperscript{-1}) are almost equal to each other. In addition, the adsorption heat enthalpy of C\textsubscript{2}H\textsubscript{2} is 25.4 kJ mol\textsuperscript{-1} at the zero coverage, which is lower slightly than Q\textsubscript{e} of C\textsubscript{2}H\textsubscript{4} (26.1 kJ mol\textsuperscript{-1}). And why the high purity of C\textsubscript{2}H\textsubscript{4} (>99.9%) can be acquired. Therefore, in order to explore this problem, the C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} at low pressure region (<0.1 bar) was checked (inserted into Fig. 4c). Before the pressure of 0.05 bar, the adsorption of C\textsubscript{2}H\textsubscript{6} is obviously bigger than both C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}, giving a hierarchy of C\textsubscript{2}H\textsubscript{6}>C\textsubscript{2}H\textsubscript{2}>C\textsubscript{2}H\textsubscript{4}. This is well consistent with the separation conditions of 90:19 (v/v/v) gas mixture of C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}.

**Discussion**

In a word, we reported a Th-azole framework (Azole-Th-1) by introducing an previously unreported ligand TBA showing a preferential adsorption of ethane over ethylene. Notably, Azole-Th-1 samples exhibited good stability for soaking in water, various organic solvents, and different pH (1–12) solvents about 30 days, respectively. Moreover, preferential adsorption of ethane over ethylene was confirmed by measuring the adsorption isotherms and breakthrough curves. Azole-Th-1 had relative high ethane and ethylene adsorption capacities, 4.5 and 3.6 mmol g\textsuperscript{-1} at 298 K and 100 kPa, respectively. The adsorption selectivity of binary mixture C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{4}(1:1, v/v) was ~1.46 at pressure below 100 kPa and 298 K. Five cycles of ethane adsorption–desorption cycle experiments revealed that Azole-Th-1 had a good regenerability. The polymer grade C\textsubscript{2}H\textsubscript{4} with the max working capacities of 1.13 mmol g\textsuperscript{-1} with 99.9% purity was harvested from 10/90 gas mixture. Furthermore, Azole-Th-1 also can purify the C\textsubscript{2}H\textsubscript{4} (purity >99.9%) from ternary mixture C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} (90:1:9, v/v/v) with working capacities of 1.34 mmol g\textsuperscript{-1}. Some DFT calculations suggested that the greater vdW interaction between ethane and Azole-Th-1 than ethylene and material, −43.09 and −33.52 kJ mol\textsuperscript{-1}, respectively, which were in agreement with the isosteric heat of ethane (28.6 kJ mol\textsuperscript{-1}) and ethylene (26.1 kJ mol\textsuperscript{-1}). In brief, these excellent properties, the perfect pH stability and high C\textsubscript{2}H\textsubscript{4} purity (>99.9%) from a ternary 90:1:9 mixture of C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}, etc., make Azole-Th-1 a promising candidate for efficient separation of ethane/ethylene. It will be much more challenging and difficult to separate more complex gas mixtures. Those small gas molecules such as N\textsubscript{2} and CH\textsubscript{4} will not affect the ternary C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} separation very much because of their very weak interactions with the framework, leading to very low uptakes of N\textsubscript{2} and CH\textsubscript{4} at the room temperature. However, some other gas molecules, particularly CO\textsubscript{2}, is expected to significantly affect the C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} separation, because the uptakes of CO\textsubscript{2} are comparable to these C\textsubscript{2} hydrocarbons. Until now, no suitable porous materials have been reported yet for the efficient C\textsubscript{2}H\textsubscript{6}/C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4}/CO\textsubscript{2} separation. Before any porous materials can be realized for this very challenging separation, step-by-step separations by different adsorbents will be necessary to get high purity C\textsubscript{2} hydrocarbons.

**Methods**

**The synthesis.** A mixture of 4-(1H-Tetrazol-5-yl) benzoic acid (TBA, 0.019 g, 0.010 mmol), Th(NO\textsubscript{3})\textsubscript{4} (0.048 g, 0.10 mmol), N,N'-dimethylformamide (DMF, 3.0 mL), and ionic liquid of tetramethylguanidine chloride (0.015 mg, 0.01 mmol) were placed in a 20 ml screw-capped glass capped jar, then five drops of concentrated hydrochloric acid were added to the mixture. The mixture was sealed and heated at 130 °C for 3 days. The reaction system was cooled to 30 °C with about 6 °C min cooling rate. After filtration and washed with excess of N,N'-dimethylacetamide (DMA), colorless block crystals were collected as a pure phase (see PXRD in Fig. 2).

**Gas-adsorption and breakthrough experiments.** The original sample about 100 mg was activated at 60 °C under high vacuum for 12 h in gas adsorption apparatus before the gas adsorption measurement. The BET of the MOFs were performed by nitrogen adsorption and desorption at 77 K using a Belsorp-max.

The single-component isotherms of C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, and C\textsubscript{2}H\textsubscript{6} were collected at 298 and 273 K on a Belsorp-max. The breakthrough separation apparatus consisted of two fixed-bed stainless steel column. One column was loaded with MOF powder (1.9810 g), while the other reactor was used as a blank control group to stabilize the gas flow. The horizontal reactors were placed in a temperature-controlled environment, maintained at 298 K. The flow rates of all gases mixtures were regulated by mass flow controllers, and the effluent gas stream from the column is monitored by a gas chromatography (TCD-Thermal Conductivity Detector, detection limit 0.1%). Prior to each breakthrough experiment, we regenerated the sample by flushing the adsorption bed with helium gas (100 ml per min) for 30 min at 298 K.

**Data availability**

The X-ray crystallographic coordinated for structure reported in this study has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 1969398. This data can be obtained free of charge from the CCDC via https://www.ccdc.cam.ac.uk/structures/. The source data underlying Figs. 2, 4, and 5 and Supplementary Figs. 5, 6, 8, 9, 10a, 10c, and 11 are provided as a Source Data file. And other data, if not included in the article or Supplementary Information or Source Data, are available from the authors on request.

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**Author contributions**

B.C. and F.L. conceived and designed the research, and gave valuable comments on the analysis; LL. carried out the transient breakthrough experiments; R.K. calculated the selectivity and simulated the breakthrough; Z.X. carried out all theoretical calculations and interpretations, created all figures and wrote the draft; X.X., J.X., and Y.F. carried out experiments.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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