Exploiting equilibrium-kinetic synergetic effect for separation of ethylene and ethane in a microporous metal-organic framework

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Physisorption is a promising technology to cut cost for separating ethylene (C2H4) from ethane (C2H6), the most energy-intensive separation process in the petrochemical industry. However, traditional thermodynamically selective adsorbents exhibit limited C2H4/C2H6 selectivity due to their similar physiochemical properties, and the performance enhancement is typically at the expense of elevated adsorption heat. Here, we report highly-efficient C2H4/C2H6 adsorption separation in a phosphate-anion pillared metal-organic framework ZnAtzPO4 exploiting the equilibrium-kinetic synergetic effect. The periodically expanded and contracted aperture decorated with electronegative groups within ZnAtzPO4 enables effective trapping of C2H4 and impedes the diffusion of C2H6, offering an extraordinary equilibrium-kinetic combined selectivity of 32.4. The adsorption heat of C2H4 on ZnAtzPO4 (17.3 to 30.0 kJ mol⁻¹) is substantially lower than many thermodynamically selective adsorbents because its separation capability only partially relies on thermodynamics. The separation mechanism was explored by computational simulations, and breakthrough experiments confirmed the excellent C2H4/C2H6 separation performance of ZnAtzPO4.

INTRODUCTION

As an important feedstock in petrochemical industries, ethylene (C2H4) is one of the highest-yield chemicals in the world with a global production capacity of more than 170 million tons in 2016 (1). C2H4 is usually manufactured by steam cracking and thermal decomposition of naphtha or ethane (C2H6), and the product inevitably contains a certain amount of C2H6 impurity. To obtain polymer-grade C2H4 as the raw material for downstream value-added products, it is necessary to remove the residual C2H6, which is a challenging task due to the very close molecular size of C2H6 (3.81 Å × 4.08 Å × 4.82 Å) and C2H4 (3.28 Å × 4.18 Å × 4.84 Å) and their similar physical properties (2, 3). Industrial separation of C2H4 and C2H6 is generally realized by energy-intensive cryogenic distillation that requires very harsh operation conditions (4), typically at temperature as low as −90° to −15°C and pressure up to 23 bar under a high reflux ratio in distillation towers installed with more than 150 trays (5). The energy used for C2H4/C2H6 and C3H6/C3H8 separation accounts for more than 0.3% of the global energy consumption; therefore, developing energy-efficient methods for C2H4/C2H6 separation is highly demanded and is recognized as one of the most important industrial tasks to change the world’s energy footprint (6).

Adsorption separation enabling efficient gas purification under mild conditions is an energy-saving alternative technology to cryogenic distillation (7–13), and the key lies in developing advanced porous materials (14–16). With regard to C2H4/C2H6 separation, introducing transition-metal ions and unsaturated metal sites into the adsorbents has been widely accepted as a feasible approach (5, 17–21), because they can selectively interact with π-electrons of C2H4 molecules. However, the π-complexation-related materials generally present limited stability, especially in the presence of moisture and sulfides (22), and demand high energy cost for the adsorbents’ regeneration because of their strong affinity to C2H4 (23). Porous materials that are amenable to achieve complete molecular sieving are ideal for C2H4/C2H6 separation (24). However, to precisely control aperture size to a critical range necessary to exclude C2H6 is very challenging, and pores with such limited size typically lead to low diffusion rate and gas uptake. Considering that a practical separation process is simultaneously controlled by effects that arise from thermodynamics and kinetics, adsorbents that can exploit both equilibrium and kinetic selectivity are appealing for gas capture and purification (25, 26) but intractable to design and prepare. Previously, most porous materials reported for C2H4/C2H6 separation are principally based on their discrepant thermodynamic affinity for the guests (27–30). Only a few of zeolites and coordination polymer have been described as suitable substances for kinetic separation (31–33), largely because the analogous dimensions of C2H4 and C2H6 bring critical difficulty to fabricate pores with appropriate sizes that permit the passing of C2H4 while limiting the diffusion of slightly bulkier C2H6 molecules. Moreover, the ultimate efficiencies of reported kinetically selective adsorbents are basically confined by disadvantageous thermodynamic effects, in which case the capacity of C2H6 at the equilibrium state is quite close to or even exceeds that of C2H4 under a wide pressure range. These observations suggest that there is still a broad space to further enhance the separation of C2H4 and C2H6 by developing porous materials with optimal adsorption thermodynamics and kinetics.

Here, we reveal the high-efficient separation of C2H4 and C2H6 in a phosphate-anion (PO4³⁻) pillared metal-organic framework (MOF) {Zn3(Atz)3(PO4)j}∞ (ZnAtzPO4; Atz = 3-amino-1,2,4-triazole) by exploiting synergetic effect of equilibrium and kinetics. The material features periodically expanded and contracted pore decorated by electronegative groups, which provides sufficient binding sites for...
ZnAtzPO₄ and effectively impedes the diffusion of C₂H₆, inducing an outstanding recognition ability to C₂H₄ over C₂H₆. The equilibrium-kinetic combined selectivity (32.4), as well as C₂H₄ capacity of ZnAtzPO₄, outperforms those of the state-of-the-art materials. The extraordinary performance was achieved along with ultralow adsorption heat (17.3 kJ mol⁻¹ for C₂H₄ at zero loading), and gas molecules adsorbed on the material can be easily removed at ambient temperature, indicating the promising prospect of the material for industrial application. DFT-D (dispersion-corrected density functional theory) calculations and molecular dynamics (MD) simulations were used to give insights into the unique separation mechanism, and breakthrough experiments for the C₂H₄/C₂H₆ (50:50, v/v) mixture were carried out to confirm the excellent performance of ZnAtzPO₄.

RESULTS
Pore structure and C₂H₄/C₂H₆ adsorption property
ZnAtzPO₄ was prepared by hydrothermal reaction of phosphoric acid, zinc carbonate basic, and Atz in a mixture of water, methanol, and aqueous ammonia under 180°C for 2 days (34). The structure of ZnAtzPO₄ contains two-dimensional cationic layers (fig. S1), which are fabricated by Zn²⁺ cations and deprotonated Atz ligands in both tridentate and bidentate coordination modes. The organic ligands only connect to Zn⁷⁺ cations via nitrogen atoms contained in the triazole rings, and the amino groups are all free of coordination. The layers are further pillared by PO₄³⁻ anions, resulting in the final porous framework of ZnAtzPO₄. As shown in Fig. 1A and fig. S1, the channel of ZnAtzPO₄ is decorated by intruding amino groups from bidentate-coordinated Atz ligands (highlighted by rose), which are arranged in an antiparallel manner along a, and abundant electro-negative oxygen atoms from PO₄³⁻ anion pillars alongside the channel. The pillars adopt a staggered fashion, periodically contracting and expanding the cross section of the channel (Fig. 1B); therefore, the channel can be vividly described as iterant pocket-like space interconnected by narrow bottleneck structure. The pocket-like space each contains two symmetric passages (Fig. 1C) with the same size of 4.94 Å, which is enough to accommodate both C₂H₄ and C₂H₆ guests. In contrast, the neck is much narrower (3.82 Å, distance between N…N; Fig. 1D), which is quite close to the minimum dimension of C₂H₆ (3.81 Å) but apparently larger than that of C₂H₄ (3.28 Å). We anticipated that this delicate pocket-like structure would facilitate C₂H₄ trapping, but the narrow bottleneck would probably set a barrier for C₂H₆ to diffuse in the channel of ZnAtzPO₄.

Inspired by the eligible structure of ZnAtzPO₄, we further analyzed its thermodynamic and kinetic adsorption characteristics for C₂H₄ and C₂H₆ by measuring single-component adsorption isotherms and time-dependent gas uptake profiles. From the adsorption isotherms shown in Fig. 2A, ZnAtzPO₄ has a C₂H₄ uptake of 1.92 mmol g⁻¹ at 298 K and 1 bar, equivalent to 3.04 mmol cm⁻³ (table S1). The adsorption capacity of C₂H₄ is higher than C₂H₆ in the whole pressure range, indicative of its preferable thermodynamic affinity for C₂H₄. The C₂H₄/C₂H₆ uptake ratio reached 1.85 at 1 bar, exceeding that of some excellently performing equilibrium-based porous materials for C₂H₄/C₂H₆ separation, such as HKUST-1 (1.19) (35), zeolite 5A (1.42) (36), and PAF-1-SO₃Ag (1.82) (5). As the temperature reduced to 273 K, the gas uptake ratio further increased to 2.04, and the amount of C₂H₄ captured attained 2.41 mmol g⁻¹. Meanwhile, kinetic studies suggested that the material exhibited much faster adsorption rate for C₂H₄ than C₂H₆. As shown in Fig. 2B, the adsorption of C₂H₄ reached equilibrium within about 40 min at 298 K and about 45 min at 273 K, with the capacities consistent to those taken from adsorption isotherms. After a continuous recording for 150 min, the amount of C₂H₄ adsorbed on the sample still has not reached that under the equilibrium state and persists climbing up gradually. Fitting the data with micropore diffusion model gave a kinetic selectivity of 36.6 at 298 K and up to 140.7 at 273 K (table S1), highlighting the potential of ZnAtzPO₄ to separate the C₂H₄/C₂H₆ mixture through a unique equilibrium-kinetic synergetic effect, which has rarely been observed in MOFs (37). To objectively compare the separation performance of ZnAtzPO₄ with other adsorbents ever reported for C₂H₄/C₂H₆ separation, we further calculated the equilibrium-kinetic combined selectivity (38) based on their diffusivities and Henry’s constants for C₂H₄ and C₂H₆ gases. As shown in Fig. 2C and table S1, ZnAtzPO₄ displays a dramatic combined selectivity reaching up to 32.4 at 273 K. At ambient temperature, the selectivity is calculated as 12.4, higher than those of other kinetically selective adsorbents measured under similar conditions, like ITQ-29 (~1.31), Si-CHA (~1.31), and ITQ-55 (~6.4) (31, 32).

To evaluate the strength of interactions between ZnAtzPO₄ and C₂H₄/C₂H₆ gases, the isosteric heat of adsorption (Qₑ) was calculated for C₂H₄ and C₂H₆ based on their adsorption isotherms under three different temperatures using the Clausius-Clapeyron equation (fig. S2).
The material exhibits moderate $Q_{st}$ for $\text{C}_2\text{H}_4$, with the value varying from 17.31 to 29.98 kJ mol$^{-1}$. It is worth mentioning that the maximum value of $Q_{st}$ for $\text{C}_2\text{H}_4$ is remarkably lower than those of UTSA-280 (35.0 kJ mol$^{-1}$) (24), zeolite 5A (37 kJ mol$^{-1}$) (36), Co-gallate (44 kJ mol$^{-1}$) (3), and many other adsorbents containing transition-metal ions and unsaturated metal sites, such as Mg-MOF-74 (42.6 kJ mol$^{-1}$) (39), Fe-MOF-74 (47.5 kJ mol$^{-1}$) (20), PAF-1-SO$_3$Ag (106 kJ mol$^{-1}$) (5), and (Cr)-MIL-101-SO$_3$Ag (120 kJ mol$^{-1}$) (21) (Fig. 2D). The moderate heat of adsorption reveals the possibility to regenerate this material under mild conditions; thereby, oligomerization of $\text{C}_2\text{H}_4$ that may happen under the catalysis of open metal sites could be avoided. For equilibrium-based adsorbents, the effective adsorption separation of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ principally relies on the discrepancy between the affinities of the gases to the adsorbent; here, usually high isosteric heat is required for the preferentially adsorbed guest to achieve desirable selectivity. In the case of ZnAtzPO$_4$, the excellent selectivity achieved under the modest $Q_{st}$ largely owns its way to exploit the synergistic effect of equilibrium and kinetics, which means that the separation capability of ZnAtzPO$_4$ is only partially reliant on thermodynamics. The kinetic characteristics of ZnAtzPO$_4$ also contribute to maximize the purification performance, without affecting the adsorption heat.

Besides, ZnAtzPO$_4$ presents great stability to air and moisture. After the sample was exposed to humid atmosphere (298 K, 70% humidity) for 4 weeks, no obvious change in its powder x-ray diffractometry (PXRD) pattern could be observed as compared to the as-synthesized sample (fig. S3). $\text{C}_2\text{H}_4$/C$_2$H$_6$ adsorption isotherms and time-dependent gas uptakes measured on the sample revealed that, after such treatment, their sorption properties still remained almost unchanged (fig. S3). Furthermore, thermal gravimetric analysis (TGA) indicates that this material exhibits excellent thermal stability, with the decomposition temperature approaching 420°C (fig. S4). These results qualify ZnAtzPO$_4$ as a promising candidate for industrial separation of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$.

**Exploring separation mechanism by computational method**
To gain insights into the unusual equilibrium-kinetic synergetic effect of ZnAtzPO$_4$ to effectively adsorb $\text{C}_2\text{H}_4$, first-principles DFT-D calculations were conducted to explore the preferential binding sites. The computational results demonstrate that ZnAtzPO$_4$ provides two distinct binding sites for $\text{C}_2\text{H}_4$ (Fig. 3, A and B). The capacious pocket-like space each contains two symmetric apertures (Fig. 1C), and they offer identical binding site (site I) to the olefin and can be reckoned as molecule traps. In this site, $\text{C}_2\text{H}_4$ molecule interacts with the channel mainly through weak hydrogen bonding interactions (Fig. 3A). It locates close to the pillaring PO$_4^{3-}$ anions and bonds to the surrounding oxygen atoms from three different pillars via C–H…O hydrogen bonds. The shortest C–H…O bond has a length of 2.65 Å, while the others are longer and range from 2.90 to 3.16 Å. In addition, the C$_2$H$_4$ guest also strengthens its interaction with ZnAtzPO$_4$ by forming C–H…N hydrogen bonds with nitrogen atom coming from both amino group and triazole ring of the

**Fig. 2. Single-component gas adsorption properties.** (A) Single-component adsorption isotherms of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ on ZnAtzPO$_4$ under 298 and 273 K. (B) Time-dependent gas uptake profiles of $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ at 0.4 bar and different temperatures. (C) Equilibrium-kinetic combined selectivity ($\text{C}_2\text{H}_4$/C$_2$H$_6$) and $\text{C}_2\text{H}_4$ uptake of ZnAtzPO$_4$, ITQ-29, Si-CHA, and ITQ-55. Data for ITQ-55 were collected at 303 K, and those for ITQ-29 and Si-CHA were collected at 301 K. (D) Highest value of $Q_{st}$ calculated for $\text{C}_2\text{H}_4$ on ZnAtzPO$_4$, UTSA-280, zeolite 5A, Mg-MOF-74, Co-gallate, Fe-MOF-74, PAF-1-SO$_3$Ag, and (Cr)-MIL-101-SO$_3$Ag.
Atz ligands, with lengths of 2.54 to 3.16 Å. The second binding site (site II, Fig. 3B) for C$_2$H$_4$ is near the center of the bottleneck structure, which joins two adjacent pockets. The mechanism for C$_2$H$_4$ to interact with the adsorbent in this site is quite different from that in site I (Fig. 3A), where the molecular interactions are mainly dominated by hydrogen bonds. In site II, there is only one quite weak C–H…O bond formed between C$_2$H$_4$ and the PO$_4$$^{3–}$ pillar, with the length being 3.05 Å. Because of the specific chemical environment, the adsorbate is mainly stabilized by supermolecular N–H…C interactions with hydrogen atoms of the intruding amino groups from the bidentate-coordinated Atz ligands, and their lengths are in the range of 2.94 to 3.18 Å. The fact that there is a lack of strong hydrogen bond (C–H…O/N < 2.3 Å) (2) in sites I and II proves that the adsorbate merely interacts with the pore through weak intermolecular interactions, consistent to the quite modest value of $Q_a$ as has been calculated. Furthermore, the DFT-D study on C$_2$H$_4$ reveals that unlike C$_2$H$_4$, the C$_2$H$_6$ molecule can only approach the binding site in the capacious pocket-like space (fig. S5). The molecular dimension of C$_2$H$_6$ is comparable to the size of the bottleneck structure, and it induces a steric hindrance to prevent the bottleneck to expose the second binding site to C$_2$H$_4$. The distinct modes between C$_2$H$_4$ and C$_2$H$_6$ to interact with the pore may be the reason that endows ZnAtzPO$_4$ with the excellent thermodynamic selectivity.

The diffusion behaviors of C$_2$H$_4$ and C$_2$H$_6$ in the pore of ZnAtzPO$_4$ were further investigated by performing MD simulations to reveal the kinetic characteristics. The simulations demonstrate that, when each cell of ZnAtzPO$_4$ contains two gas molecules, the diffusivities of single-component C$_2$H$_4$ and C$_2$H$_6$ are $2.07 \times 10^{-10}$ m$^2$ s$^{-1}$ and $7.17 \times 10^{-12}$ m$^2$ s$^{-1}$ under 298 K. The ideal kinetic selectivity is calculated as 29 and agrees well with the experimental measurement (~36). For the equimolar C$_2$H$_4$/C$_2$H$_6$ gas mixture, the diffusivities of C$_2$H$_4$ and C$_2$H$_6$ are $1.12 \times 10^{-10}$ m$^2$ s$^{-1}$ and $7.47 \times 10^{-12}$ m$^2$ s$^{-1}$, respectively. Although the adsorption kinetics of C$_2$H$_4$ in the mixture declines as compared to its single component maybe due to the steric effect of slow-diffusing C$_2$H$_6$, the material still exhibits a prominent kinetic selectivity of 15. The results also indicate that after introducing C$_2$H$_6$ molecules to the channel of ZnAtzPO$_4$, the bottleneck exhibits obvious transient structural transformations to adapt to the sluggish passing of C$_2$H$_6$, and the aperture size prominently increases to 4.1 Å, about 0.3 Å larger than that without gas molecules (Fig. 3C). Snapshots (fig. S6) show that the expansion of the bottleneck-like window is mainly facilitated by slight rotation of the bidentate-coordinated Atz ligands that intrude amino groups to the channel. On the contrary, study on the diffusion of C$_2$H$_4$ reveals that after inserting the gas molecule to the channel, no obvious change in the aperture size of the bottleneck was observed, and its probability distribution is quite consistent to that of an empty host (Fig. 3C). These results suggest that the diffusion of C$_2$H$_4$ in the channel strongly relies on the flexibility of ZnAtzPO$_4$, considering that the size of the bottleneck (3.82 Å) at the ground state is so close to the extreme size (3.81 Å) to allow the passing of C$_2$H$_6$, setting a barrier for its penetration. The much smaller dimension of C$_2$H$_4$ (3.28 Å) allows it to travel along the pore more freely, without the necessity to expand the narrow windows, which thereby induces the marked kinetic selectivity of ZnAtzPO$_4$.

**Breakthrough experiments**

It is worth emphasizing that removal of C$_2$H$_6$ from C$_2$H$_4$ is yet a technical challenge in industry. To further probe the validity of the equilibrium-kinetic synergetic effect for C$_2$H$_4$/C$_2$H$_6$ separation, breakthrough experiments for a C$_2$H$_4$/C$_2$H$_6$ (50:50, v/v) gas mixture were performed on a stainless column packed with the ZnAtzPO$_4$ material at 273 K and 1 bar. As shown in Fig. 4A, the component of C$_2$H$_6$ broke through the column quickly after 26 min, whereas C$_2$H$_4$ was retained in the adsorption bed for nearly 70 min. The retention time for C$_2$H$_4$ is two times more than that of C$_2$H$_6$. Moreover, the elution of C$_2$H$_4$ was accompanied by a remarkable roll-up phenomenon of C$_2$H$_6$, meaning that the C$_2$H$_6$ molecules that have already been adsorbed can be largely displaced by the olefin, indicative of the excellent competition ability of C$_2$H$_4$ over C$_2$H$_6$ on the binding sites of ZnAtzPO$_4$. After the concentration of eluting gas remained unchanged, the amount of C$_2$H$_4$ adsorbed into the column reached 1.80 mmol g$^{-1}$, equivalent to 6.7 times that of C$_2$H$_6$ (0.27 mmol g$^{-1}$) (fig. S7), highlighting the great efficiency of ZnAtzPO$_4$ for actual C$_2$H$_4$/C$_2$H$_6$ adsorption separation. Besides, recycling measurements reveal that ZnAtzPO$_4$ can retain its separation capability with the breakthrough time being almost unchanged within five cycles (Fig. 4B and fig. S7). After simple desorption procedure manipulated by purging the material with inert gas (He) at ambient temperature, the column was well regenerated and reserved similar breakthrough curve (fig. S7), benefitting from the very modest adsorption heat as has been calculated. This further presents ZnAtzPO$_4$ as a brilliant...
microporous material for industrial separation of C$_2$H$_4$ and C$_2$H$_6$. By exploiting the equilibrium-kinetic synergetic effect, we successfully achieved the high-efficient C$_2$H$_4$/C$_2$H$_6$ adsorption separation with ZnAtzPO$_4$. With the solid empirical evidence, we believe that it would bring a new train of thoughts and tactics for the splitting of close-boiling light hydrocarbons.

DISCUSSION
In summary, we reported the separation of C$_2$H$_4$/C$_2$H$_6$ in a phosphate-anion pillared microporous MOF, which exhibits a unique equilibrium-kinetic combined selectivity to the olefin and is attractive for practical separation. The equilibrium-kinetic synergetic effect of ZnAtzPO$_4$ mainly originates from its delicate pore structure, featuring periodically expanded and contracted cross section. Its minimum aperture size approaches the limit for C$_2$H$_4$ to pass through, and the diffusion of C$_2$H$_6$ depends on transient structural transformations of the neck-like structure, which seriously slows down the diffusion rate of the paraffin. On the other hand, the pore of ZnAtzPO$_4$ is decorated with abundant electronegative functional groups that are amenable to construct stable interaction network with C$_2$H$_4$ and trap the olefin efficiently. Computational methods were applied to explore the binding sites of the guest molecules and further verify the faster adsorption kinetics of C$_2$H$_4$. Moreover, recycling breakthrough experiment for the C$_2$H$_4$/C$_2$H$_6$ gas mixture (50:50, v/v) was carried out, and it confirmed the outstanding capability of ZnAtzPO$_4$ for adsorption of C$_2$H$_4$ under modest Q$_m$, because the separation process only partially relies on thermodynamics. As a glaring merit, the material can be regenerated under mild conditions with less energy consumption. In brief, this work not only provides a porous material with impressive C$_2$H$_4$ purification performance but also brings a new strategy for developing the next-generation materials for energy-efficient gas separation.

MATERIALS AND METHODS
Experimental design
Chemicals
All the chemicals were obtained from commercial resources and used as received without any further purification. Methanol (anhydrous, 99%) was purchased from Sigma-Aldrich. Phosphoric acid [85 weight % (wt %)], ammonium hydroxide (30 wt %), and 3-amino-1,2,4-triazole (96%) were purchased from Macklin. 3Zn(OH)$_2$·2ZnCO$_3$ was purchased from Strem Chemicals.

Synthesis of (Zn$_3$(Atz)$_3$(PO$_4$))$_n$ (ZnAtzPO$_4$)
Samples of ZnAtzPO$_4$ were synthesized according to the literature report (34) with minor modifications. A mixture containing 0.035 g of phosphoric acid, 0.1 g of 3Zn(OH)$_2$·2ZnCO$_3$, 0.4 g of 3-amino-1,2,4-triazole, 2 ml of H$_2$O, and 2 ml of methanol was added to a Teflon tube, then sealed and placed in an oven with a temperature of 180°C for 48 hours, and cooled to room temperature naturally. The colorless precipitation was collected by filtration, then washed with methanol, and dried in air. Last, the product was heated at 60°C under high vacuum for 2 hours and then at 100°C for another 12 hours to obtain the activated sample of ZnAtzPO$_4$.

Characterization methods
PXRD data were collected on a SHIMADZU XRD-600 diffractometer (Cu K$_\alpha$ = 1.540598 Å) with an operating power of 40 kV, 30 mA, and a scan speed of 4.0°/min. The range of 2θ was from 5° to 50°. TGA data for activated sample of ZnAtzPO$_4$ were recorded on an apparatus of TGA Q500 V20.13 Build 39, from room temperature to 800°C, with a ramp of 10°C/min under N$_2$ atmosphere.

Kinetic adsorption measurement
The time-dependent adsorption profiles of C$_2$H$_4$ and C$_2$H$_6$ were measured on Intelligent Gravimetric Analyzer (IGA-100, HIDEN). About 100 mg of ZnAtzPO$_4$ was first loaded to the sample chamber and activated at 100°C under high vacuum for 4 hours. After being cooled to specific temperature, the chamber was backfilled with He, until the pressure reached 0.4 bar. Upon the analysis started, a single-component gas of C$_2$H$_4$ or C$_2$H$_6$ was introduced into the chamber at a rate of 35 ml/min. The mass of the sample loaded with gas molecules was continuously recorded for 150 min.

Statistical analysis
The equilibrium-kinetic combined selectivity (S$_{ij}$) is defined as (38)

$$S_{ij} = \alpha_{ij} \times \beta_{ij}^{0.5}$$  \hspace{1cm} (1)
In Eq. 1, $\alpha_{ij}$ represents the separation selectivity based on thermodynamic equilibrium alone and can be calculated from the ratio of Henry’s constants (Eq. 2). $\beta_{ij}$ represents the kinetic selectivity based on diffusion rates of the gas molecules and can be obtained from the ratio of diffusion time constants (Eq. 3)

$$\alpha_{ij} = H_i / H_j$$

$$\beta_{ij} = D_i' / D_j'$$

In Eq. 3, $D_i' / D_j'$ can be further derived from the following micropore diffusion model (Eq. 4), where $m_i$ is the gas uptake at time $t$, $m_\infty$ is the gas uptake at equilibrium, $D_i$ is the intracrystalline diffusivity of gas molecules in porous media, and $r_i$ is the radius of the equivalent spherical particle. $D_i'$ can be obtained from the square of the slope ($m_i / m_\infty$) plotted against $t^2$ multiplied by $\pi/36$.

$$\frac{m_i}{m_\infty} \approx \frac{6 \cdot D_i r_i}{r} \left(1 - \frac{m_i}{m_\infty} < 0.3\right)$$

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/15/eaaz4322/DC1

**REFERENCES AND NOTES**

1. L. Li, R.-B. Lin, R. Krishna, H. Li, S. Xiang, H. Wu, J. Li, W. Zhou, B. Chen, Ethane/ethylene separation in a metal-organic framework with iron-oxo peroxide sites. Science 362, 443–446 (2018).

2. P.-Q. Liao, W.-X. Zhang, J.-P. Zhang, X.-M. Chen, Efficient purification of ethene by an ethene-trapping metal-organic framework. Nat. Commun. 6, 8697 (2015).

3. Z. Bao, J. Wang, Z. Zhang, H. Xing, Q. Yang, Y. Yang, H. Wu, R. Krishna, W. Zhou, B. Chen, Q. Ren, Molecular sieving of ethane from ethylene through the minimum molecular dimension differentiation in gallate-based metal-organic frameworks. Angew. Chem. Int. Ed. Engl. 57, 16020–16025 (2018).

4. M. Rungra, C. Zhang, W. J. Koros, L. Xu, Membrane-based ethylene-ethane separation: The upper bound and beyond. Adv. Chem. 59, 3475–3489 (2013).

5. B. Li, Y. Zhang, R. Krishna, K. Yao, Y. Han, Z. Wu, D. Ma, Z. Shi, T. Pham, B. Space, J. Liu, P. K. Thallapally, J. Liu, M. Chrizhanovsk, S. Ma, Introduction of $ε$-complexation into porouromatic framework for highly selective adsorption of ethylene over ethane. J. Am. Chem. Soc. 136, 8654–8660 (2014).

6. D. S. Sholl, R. P. Lively, Seven chemical separations to change the world. Science 340, 13554–13562 (2011).

7. Z. Zhang, Q. Yang, X. Cui, L. Yang, Z. Bao, Q. Ren, H. Xing, Single-molecule propyne trap: Highly efficient removal of propyne from propylene on zeolite 5A. Science 358, 1068–1071 (2017).

8. N. Hedin, G. J. Demartin, W. J. Roth, K. G. Strohmaier, S. C. Reyes, PFG NMR self-diffusion and anionic nets demonstrating ion exchange, adsorption and luminescent properties. Chem. Commun. 47, 6425–6427 (2011).

9. H.-Y. Bu, M.-L. Tong, H.-C. Chang, S. Kitagawa, S. R. Batten, A neutral 3D copper coordination polymer showing 1D open channels and the first interpenetrating NB-type network. Angew. Chem. Int. Ed. 43, 192–195 (2004).

10. A. Cadiau, Y. Belmabhkhot, K. Adil, P. M. Bhatt, R. S. Pillai, A. Shikurnenko, C. Martinneau-Corcos, G. Maurin, M. Ediaoudi, Hydrosynthetically stable fluorinated metal-organic frameworks for energy-efficient dehydration. Science 356, 731–735 (2017).

11. L. Li, R.-B. Lin, X. Wang, W. Zhou, L. Jia, J. Li, B. Chen, Kinetic separation of propylene over propane in a microporous metal-organic framework. Chem. Eng. J. 354, 977–982 (2018).

12. R.-B. Lin, L. Li, H.-L. Zhou, H. Wu, C. He, S. Li, R. Krishna, J. Li, W. Zhou, B. Chen, Molecular sieving of ethylene from ethane using a rigid metal–organic framework. Nat. Mater. 17, 1128–1133 (2018).

13. P. Nugent, Y. Belmabhkhot, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Ediaoudi, M. J. Zavorotukh, Porous materials with optimal adsorption thermodynamics and kinetics for CO2 separation. Nature 495, 80–84 (2013).

14. Y. Wang, N.-Y. Huang, X.-W. Zhang, H. He, R.-K. Huang, Z.-M. Ye, Y. Li, D.-D. Zhou, P.-Q. Xiao, X.-M. Chen, J.-P. Zhang, Selective aerobic oxidation of a metal-organic framework boosts thermodynamic and kinetic propylene/propane selectivity. Angew. Chem. Int. Ed. Engl. 58, 7692–7696 (2019).

15. R.-B. Lin, H. Wu, L. Li, X.-L. Tang, Z. Li, J. Gao, H. Cui, W. Zhou, B. Chen, Boosting ethene/ethylene separation within isoreticular ultramicroporous metal-organic frameworks. J. Am. Chem. Soc. 140, 12940–12946 (2018).

16. Y. Wang, S. Yuan, Z. Hu, T. Kundu, J. Zhang, S. B. Peh, Y. Cheng, J. Dong, D. Yuan, H.-C. Zhou, D. Zhao, Pore size reduction in zincium metal–organic frameworks for ethylene/ethane separation. ACS Sustainable Chem. Eng. 7, 7118–7126 (2019).

17. Z. Bao, G. Chang, H. Xing, R. Krishna, Q. Ren, B. Chen, Potential of microporous metal–organic frameworks for separation of hydrocarbon mixtures. Energ. Environ. Sci. 9, 3612–3614 (2016).

18. S. Yang, A. J. Ramirez-Cuesta, R. Nevbio, V. Garcia-Sakai, P. Manuel, S. K. Callear, S. C. Campbell, C. C. Tang, M. Schroder, Supramolecular binding and separation of hydrocarbons within a functionalized porous metal–organic framework. Nat. Chem. 7, 121–129 (2015).

19. P. J. Bereciuma, A. Cantin, A. Corma, J. L. Jordi, M. Palomino, F. Rey, S. Valencia, E. W. Corcoran, P. Kortunov, P. I. Ravikovitch, A. Burton, C. Yoon, Y. Wang, C. Paur, J. Guzman, A. R. Bishop, G. L. Casy, Control of zeolite framework topology and pore and topology for separation of ethane and ethylene. Science 358, 1068–1071 (2017).

20. N. Mofarahi, S. M. Salehi, Pure and binary adsorption isotherms of ethylene and ethane on zeolite 5A. Adsorption 19, 101–110 (2013).

21. Z. Bao, S. Alnemrat, L. Yu, I. Vasiliev, Q. Ren, X. Lu, S. Deng, Kinetic separation of carbon dioxide and methane on a copper metal-organic framework. J. Colloid Interface Sci. 357, 504–509 (2011).
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