

Gas Separation

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A Rod-Packing Hydrogen-Bonded Organic Framework with Suitable Pore Confinement for Benchmark Ethane/Ethylene Separation

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Abstract: For the separation of ethane from ethylene, it remains challenging to target both high C_2H_6 adsorption and selectivity in a C_2H_6 -selective material. Herein, we report a reversible solid-state transformation in a labile hydrogenbonded organic framework to generate a new rod-packing desolvated framework (ZJU-HOF-1) with suitable cavity spaces and functional surfaces to optimally interact with C_2H_6 . ZJU-HOF-1 thus exhibits simultaneously high C_2H_6 uptake (88 cm³g⁻¹ at 0.5 bar and 298 K) and C_2H_6/C_2H_4 selectivity (2.25), which are significantly higher than those of most top-performing materials. Theoretical calculations revealed that the cage-like cavities and functional sites synergistically "match" better with C_2H_6 to provide stronger multipoint interactions with C_2H_6 than C_2H_4 . In combination with its high stability and ultralow water uptake, this material can efficiently capture C_2H_6 from 50/50 C_2H_6/C_2H_4 mixtures in ambient conditions under 60 % RH, providing a record polymer-grade C_2H_4 productivity of 0.98 mmolg⁻¹.

Introduction

Ethylene (C_2H_4) is a key feedstock for many chemicals and polymers in the chemical industry and is primarily derived from naphtha or ethane cracking.^[1,2] However, steam

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crackers do not produce pure $C_2H_4~({\geq}\,99.95\,\%,~polymer$ grade), in which ethane (C_2H_6) is inevitably existed as a major byproduct. The separation of C₂H₆ from C₂H₄ is thereby a critical process to yield polymer-grade C₂H₄ for polymer production. At present, it is mainly accomplished by means of cryogenic distillation under harsh conditions (typically at 5-28 bar and 180-258 K), which represents one of the most energy-intensive processes. The energy consumption for such separation is estimated to be about 7.3 GJ per tonne of ethylene.^[3,4] To replace traditional cryogenic distillation, adsorptive separation technologies based on porous materials attract particular interest because of their great potential to provide tremendous energy savings.^[5] Such separation can be implemented by either ethane- or ethylene-selective adsorbents; however, ethane-selective materials are more desired because of the simplicity of being able to produce ethylene directly at the outlet.^[6,7]

Since ethane has a higher polarizability than ethylene, dispersion and induction interactions would make major contributions in C₂H₆-selective adsorbents;^[8] so an adsorbent material with a pore structure enriched with nonpolar/inert surfaces (e.g., featuring aromatic or aliphatic moieties) may favor the preferential adsorption of C₂H₆ over C₂H₄. In this regard, the emerging hydrogen-bonded organic frameworks (HOFs) are of particular interest to be developed as C₂H₆selective adsorbents.^[9,10] HOFs are formed from purely organic building blocks through intermolecular hydrogen bonds (H-bonds).^[11-14] This metal-free nature endows HOFs with native nonpolar/inert pore surfaces to directly produce the desired C₂H₆-selective materials. Owing to the soft and flexible H-bonds, HOFs hold some inherent advantages such as high solution processability, easy purification, and facile regeneration and healing by simple recrystallization. Moreover, HOF materials can be highly crystalline that benefits not only structural determination but also the investigation of structure-property relationship. These attractive merits make the exploitation of porous HOFs as C₂H₆-selective adsorbents become very attractive. However, the major drawback of HOFs is their structural fragility because of the weak nature of H-bonds, making their frameworks oftentimes collapse upon removal of solvent molecules.^[15] It is also very difficult to precise control over pore size and functional sites in HOFs to strongly interact with gas molecules,^[9,10] which has always limited their separation performance. It is therefore not surprising that the research on robust HOFs for gas separation is still at the comparatively early stage.^[16,17] To date, only few porous HOFs have been established for the important hydrocarbon separations with quite limited separation per-

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formance.^[18–20] Despite a great challenge, we recently succeeded in realizing a robust HOF material (HOF-76a) for selective separation of C_2H_6/C_2H_4 .^[18] While this material exhibits a moderate C_2H_6/C_2H_4 selectivity, the large one-dimensional pores and the lack of strong C_2H_6 adsorption sites lead to a weak binding affinity and thus poor C_2H_6 uptake, largely delimiting the productivity of the desired C_2H_4 product.

A chemical separation benefits from both uptake capacity and adsorption selectivity and can be most efficient when a material excels in both aspects; however, it is very difficult to target a material with both high values (so-called tradeoff).^[21] To realize both high gas selectivity and adsorption uptake for C₂H₆/C₂H₄ separation, an ideal adsorbent should have suitable pore/cavity sizes and functional surfaces to simultaneously enforce the preferential adsorption of C₂H₆ over C₂H₄ but without sacrificing moderate pore volumes or surface areas to take up large amount of C₂H₆ molecules. However, from the structural point of view, there commonly exists a trade-off between pore dimensions and pore volumes in porous materials.^[22,23] For example, pore dimensions that match with small gas molecules often correlate to small pore volumes, which in turn result in low uptakes. Conversely, high pore volumes typically stem from large pores, which cannot discriminate the molecules with similar sizes. It is still a daunting challenge for the community to design and realize ideal adsorbents to meet the above mentioned criteria, especially for the immature HOFs. Herein, we report a unique rod-packing HOF material (ZJU-HOF-1, Figure 1) featuring the suitable cavity sizes (4.6 Å) and functional surfaces, which can meet those mentioned criteria for benchmark C_2H_6/C_2H_4 separation. The activated ZJU-HOF-1 shows a relatively high BET surface area of 1465 m²g⁻¹ to secure enough pore spaces for high C₂H₆ uptake. Owing to the rod-packing configuration and threefold interpenetration, ZJU-HOF-1 features numerous small cage-like cavities decorated by multipoint functional sites that match better with the size/shape of C2H6 molecule and thus facilitate closer contacts with C2H6. This unique pore confinement thus results in a rare combination of simultaneously high C_2H_6 uptake (88 cm³g⁻¹ at 0.5 bar and 298 K) and C₂H₆/C₂H₄ selectivity (2.25) observed in ZJU-HOF-1. Importantly, this material is also chemically stable and shows an ultralow water uptake at 60 % RH to avoid coadsorption of water. Breakthrough experiments confirmed that ZJU-HOF-1 exhibits the record-high C_2H_4 productivity of 0.98 mmolg⁻¹ (or 21.9 Lkg⁻¹) for both dry and humid (60 % RH) C_2H_6/C_2H_4 mixtures at 298 K and 1.01 bar, a value higher than that of $Fe_2(O_2)(dobdc)$ (0.86 mmol g⁻¹), the benchmark material for C_2H_6/C_2H_4 separation in MOFs.



Figure 1. a) The structure of TMBTI. b) The single network constructed by TMBTI molecules. c) A rod-shaped H-bonded chain formed by *meta*benzenedicarboxylic motifs along the *c* axis. d) The threefold-interpenetrated structure of JLU-SOF3. e) The modeled structure of ZJU-HOF-1 upon activation, revealing an obvious structural transformation between JLU-SOF-3 and ZJU-HOF-1. f) The *acs* topology of ZJU-HOF-1 (red dotted lines represent H-bonds). The CCDC number can be found in the Supporting Information.

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Results and Discussion

The hexacarboxylate ligand 2,4,6-trimethylbenzene-1,3,5trivlisophthalate (TMBTI) was simply prepared through a multistep reaction procedure (Scheme S1, Supporting Information). Slow evaporation of an ethyl ether solution into a THF solution of TMBTI in two weeks afforded the colorless stick-like crystals. During our exploration of the activated ZJU-HOF-1, the structure of the as-synthesized HOF (JLU-SOF3) was independently reported for different properties.^[13c] Single crystal X-ray diffraction analysis revealed that JLU-SOF3 crystallizes in a hexagonal $P\bar{6}2c$ space group with a hydrogen-bonded 3D network (Figure 1). Due to the steric hindrance of methyl groups, the dihedral angle of each outer phenyl ring relative to the center phenyl ring in TMBTI molecule is about 90° (Figure 1a). This feature enables the adjacent meta-benzenedicarboxylate motifs from different TMBTI to form 1D infinite rod-shaped H-bonding chains along the c axis (Figure 1c), which are further linked by the center phenyl ring to construct the 3D rod-packing framework (Figure 1b). The O-H…O distance and angle are 2.610/2.599 Å and 174.7°, respectively. If the TMBTI is considered as a six-connected node, JLU-SOF3 possesses the acs $\{4^{9}6^{6}\}$ topology (Figure S7). Closer inspection of the structure reveals that six discrete TMBTI molecules form a six-membered ring in a hexagon pore conformation with a large window size of 22.7 Å. This large pore nature of single network can lead to interpenetration, wherein three identical frameworks interpenetrate each other through the ring-like window along the *c* axis (Figure 1 d).

When the as-synthesized sample was desolvated in high vacuum to generate the activated sample (ZJU-HOF-1), we found that there exist obvious changes in the PXRD patterns between JLU-SOF3 and ZJU-HOF-1 (Figure S8). This clearly indicates that a structural transformation occurs during this activation, however, which was ignored in the reported literature. Great efforts have been made to elaborately

investigate the new structure of the activated ZJU-HOF-1. Despite extensive attempts, we were not able to obtain highquality single crystals of ZJU-HOF-1 for single-crystal X-ray diffraction studies (Figure S9) and thus structural determination was conducted by powder diffractometry. On the basis of the PXRD data, we first identified a new symmetry of hexagonal $P\bar{6}c2$ space group for ZJU-HOF-1 crystal. With the symmetry and the overall network connection known, we thus modeled its structure straightforwardly and further optimized the structure based on DFT calculations (see Supporting Information for more details).^[24] The structure model is shown in Figure 1e, which has different unit cell parameters with JLU-SOF3 (Table S4). The simulated PXRD pattern of this structural model agrees excellently with the experimental data (Figure S10), strongly supporting its validity. Detailed structure information of ZJU-HOF-1 is provided in Tables S3 and S4.

To further probe the structural transformation from JLU-SOF3 to ZJU-HOF-1, the nudged elastic band calculations were performed to find the minimum energy path of the structural transition. An animation consisting of structure snapshots along the minimal energy path shows clearly how the JLU-SOF3 framework evolves to the structure of ZJU-HOF-1 (see the movie in the Supporting Information). During this process, the different nets are obviously smoothing along the *ab* plane to make the center phenyl rings of TMBTI molecules from adjacent nets coincide with each other, accompanying a slight rotation (15°) along the c axis for every monomer molecular. This transformation induces a slight structure contraction (5.43% by volume), leading to a new symmetry and uniform pores in ZJU-HOF-1 (Figure 2a). The framework of ZJU-HOF-1 still holds a threefold interpenetration with the same acs topology (Figure 1 f and Figure S10, Supporting Information). The O-H-O distance (2.564 Å) on the rod-shaped H-bonded chains along the c axis is slightly shorter than that in ZJU-HOF-1 (Figure 2c). As depicted in Figure 2b, ZJU-HOF-1 exhibits open triangular-



Figure 2. a) The threefold-interpenetrated structure of ZJU-HOF-1. b) The triangular pore channel (7.0 Å) and three intercrossed small pockets around the corners of the triangular-like channel. c) View of the small pockets stacked along the c axis, with a diameter of 4.6 Å. d) Depiction of one pocket constructed by two stacked phenyl rings and four carboxylate groups (C, dark gray; O, red; H, white).

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like pore channels with a diameter of 7.0 Å along the *c* axis, which are large enough for both C_2H_4 and C_2H_6 molecules to enter the pores. Due to the rod-packing configuration and threefold interpenetration, there produces numerous small cage-like pockets around the corner of the triangular channels (Figure 2 b,c). Each of such small pockets is constructed by two stacked phenyl rings and four carboxylate groups with a diameter size of 4.6 Å (Figure 2 d), which matches better with the larger C_2H_6 molecule (4.4 Å) than C_2H_4 (4.1 Å). These optimized pocket sizes and pore surfaces of functional O atoms thus exhibit the potential to provide more suitable pore confinement effects toward C_2H_6 molecule.

The chemical stability and structural transformation between JLU-SOF3 and ZJU-HOF-1 were investigated at different conditions, monitored by PXRD patterns. As revealed in Figures S12 and S13, the framework of JLU-SOF3 can gradually transform to ZJU-HOF-1 under removal of solvent molecules upon air exposure, heating or vacuum degassing. Conversely, the framework of ZJU-HOF-1 can be reversibly converted to JLU-SOF3 when soaking the sample into the Et₂O or H₂O solution (Figure S14). To examine the chemical stability, the as-synthesized samples were treated in water, HCl (pH 1) and NaOH (pH 10) solutions at room temperature (RT). After two days, the framework can retain its structural integrity as evidenced by PXRD patterns and SEM images (Figures S15 and S16), revealing its highly chemical stabilities.

The permanent porosity of ZJU-HOF-1 was established by nitrogen (N_2) gas sorption experiments at 77 K. As shown in Figure 3a, ZJU-HOF-1 can adsorb a large amount of N_2

(386 cm³g⁻¹) at 77 K and 1 bar. The BET surface area and pore volume of ZJU-HOF-1 were calculated to be moderate high of 1465 m²g⁻¹ and 0.60 cm³g⁻¹, respectively. The pore size distribution, determined by the Horvath–Kawazoe model, shows two types of pores in the range of 5–9 Å, consistent well with the results obtained from the crystal structure. After immersing in water, HCl and NaOH solutions for 2 days, the reactivated ZJU-HOF-1 samples show no obvious decrease on N₂ uptakes at 77 K (Figure S19).

Single-component adsorption isotherms of C₂H₆ and C₂H₄ for ZJU-HOF-1 were examined at both 273 K and 298 K up to 1 bar. As shown in Figures 3b and S20, ZJU-HOF-1 shows an obviously preferential adsorption of C2H6 over C2H4 at both temperatures. The uptake amount of C_2H_6 (109 cm³g⁻¹) at 298 K and 1 bar is notably higher than that of C₂H₄. When compared with HOF-76a, ZJU-HOF-1 exhibits a much steeper and higher C₂H₆ uptake in the whole range of 1 bar (Figure 3c). At a partial pressure of 0.5 bar for $50/50 \text{ C}_2\text{H}_6/$ C_2H_4 separation, ZJU-HOF-1 displays an extremely high C_2H_6 uptake of 88 cm³g⁻¹, 2.3 times higher than that of HOF-76a $(38 \text{ cm}^3 \text{g}^{-1})$,^[18] indicating its significantly enhanced C₂H₆ capture capacity (Figure 3c). This can be well explicated by the experimental isosteric heat of adsorption (Q_{st}) , wherein the initial $Q_{\rm st}$ value of C₂H₆ for ZJU-HOF-1 (31.5 kJ mol⁻¹) is much higher than the 22.8 kJ mol⁻¹ observed in HOF-76a (Figure S21). Further, we also investigated the time-dependent ads/desorption kinetics profiles of ZJU-HOF-1 at 298 K. As shown in Figure S23, ZJU-HOF-1 exhibits similar adsorption kinetics for C₂H₆ and C₂H₄ with fast diffusion rates and the adsorbed molecules can be completely removed under



Figure 3. a) N₂ adsorption isotherms of ZJU-HOF-1 at 77 K. Inset shows pore size distribution for ZJU-HOF-1. b) Adsorption isotherms of C_2H_6 and C_2H_4 for ZJU-HOF-1 at 298 K. c) Comparison of C_2H_6 adsorption isotherms for ZJU-HOF-1 and HOF-76a at 298 K. d) C_2H_6/C_2H_4 IAST selectivity of ZJU-HOF-1 as compared with HOF-76a at 298 K. e) The C_2H_6 location observed by DFT calculations. f) Comparison of each pore cavity for the preferential C_2H_6 and g) C_2H_4 adsorption site (O, red; C, dark gray; H, white).

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a high vacuum quickly, which are probably attributed to its comparably large pore channels.

Ideal adsorbed solution theory (IAST) was employed to estimate the adsorption selectivity of ZJU-HOF-1 for C₂H₆/ C₂H₄ mixtures at 298 K. As indicated in Figure 3d, ZJU-HOF-1 exhibits a high C_2H_6/C_2H_4 selectivity of up to 3.2 at low pressure and 298 K for C_2H_6/C_2H_4 (50/50) mixtures. With the increase of pressure, it gradually decreases down to 2.25 at 1 bar. This value is notably higher than that of HOF-BTB (1.4) and HOF-76a (2.0).^[18] It is worth to note that high C_2H_6 uptake capacity is also very important to determine the C₂H₆/ C_2H_4 separation performance. As shown in Figure S25, ZJU-HOF-1 exhibits an extremely high C2H6 uptake $(3.2 \text{ mmol g}^{-1})$ from an equimolar mixture of C_2H_6/C_2H_4 as a function of IAST selectivity, far exceeding that of HOF-76a $(1.62 \text{ mmol g}^{-1})$ and HOF-BTB $(1.67 \text{ mmol g}^{-1})$. When we put gas uptake and selectivity as concurrent objectives, ZJU-HOF-1 shows a rare balance of both very high C_2H_6/C_2H_4 selectivity and C_2H_6 adsorption from C_2H_6/C_2H_4 mixtures, outperforming most of MOF materials reported (Figure S25).

To elucidate the origin of the observed high C_2H_6 uptake and selectivity, we performed detailed modeling studies using first-principles dispersion-corrected density functional theory (DFT-D) method on ZJU-HOF-1. We found that, for both C_2H_4 and C_2H_6 molecules, the primary adsorption sites are located at the small cage-like pockets within the corner of the triangular pore channels (Figure 3 e). The lowest-energy gas binding sites are shown in Figure 3 f.g. For clarity, we only showed one pocket site that can trap one gas molecule. Within each unit cell, there exist 6 such binding sites, which are crystallographically equivalent (Figure S26). The calculated

static binding energies for C₂H₆ and C₂H₄ are 34.4 and 31.7 kJ mol⁻¹, respectively. The stronger C_2H_6 -framework interactions are fully consistent with our experimental observations. This is partly because the nonplanar C_2H_6 molecule has more number of H atoms and sterically "matches" better to the pocket size/shape than the planar C_2H_4 molecule. As a consequence, each C_2H_6 molecule interacts with two stacked phenyl rings and four oxygen atoms originated from four carboxylic groups to form two C-H··· π interactions (H··· π , 3.226 and 4.060 Å) and seven C-H…O interactions (H…O, 2.605-4.060 Å; Figure S27). In contrast, the C_2H_4 molecule shows only one C-H··· π interaction with one phenyl ring (H $\cdots\pi$, 3.212 Å) and five C–H \cdots O interactions (H···O, 2.552-3.811 Å). Evidently, the higher binding energy of C₂H₆ can be mainly attributed to the suitable size and functional surfaces of the pockets that match better with C_2H_6 , thus leading to the more number of C-H··· π and C-H-O interactions with the framework. A full occupancy of these binding sites would correspond to 4.91 mmol g^{-1} gas uptake, which is very close to the experimental C₂H₆ uptake (4.82 mmolg⁻¹) at room temperature and 1 bar. In contrast, the much lower C_2H_4 uptake at room temperature and 1 bar suggests that only part of the binding sites are populated due to the weaker binding affinity with the framework. All of these results can explain the observed high C₂H₆ adsorption and separation performance at 1 bar qualitatively.

Transient breakthrough simulations were firstly conducted to preliminarily evaluate the feasibility of using ZJU-HOF-1 in a fixed bed for separation of C_2H_6/C_2H_4 (50/50 and 10/90) mixtures. As shown in Figure 4a, efficient separation



Figure 4. a) Simulated breakthrough curves for C_2H_6/C_2H_4 (50/50 and 10/90) separation (C_A/C_0 , outlet concentration/feed concentration). b) Experimental breakthrough curves for dry and wet C_2H_6/C_2H_4 (50/50) mixtures at 298 K and 1.01 bar. c) Recyclability of ZJU-HOF-1 in multiple mixed-gas column breakthrough tests. d) Comparison of C_2H_4 productivity in volume per unit mass of adsorbents. e) Experimental breakthrough curves for a 50/50 mixture at 298 K and 5 bar. f) Water vapor adsorption isotherm of ZJU-HOF-1 at 296 K.

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can be realized by ZJU-HOF-1 for both 50/50 and 10/90 $C_{2}H_{c}$ C₂H₄ mixtures, wherein C₂H₄ breakthrough occurs first and then C₂H₆ passes through the fixed bed after a longer time (τ_{break}) . Next, experimental breakthrough studies were performed in a packed column of ZJU-HOF-1 for actual C₂H₆/ C₂H₄ (50/50 and 10/90) mixtures with a total flow of 1.25 mLmin⁻¹ at 298 K. Figure 4c reveals that complete separation of C₂H₆ from C₂H₄ can be realized in ZJU-HOF-1. Ethylene was first eluted at 74 min to yield a pure gas with an undetectable amount of C2H6 (the detection limit of the instrument is 0.01%), whereas the adsorbent retained C₂H₆ until 92 min. During this breakthrough process, pure C2H4 production (>99.95%) from the outlet effluent for a given cycle was calculated to be 0.98 mmol g^{-1} (21.9 Lkg⁻¹, Figure 4 d), three times higher than HOF-76a (0.32 mmol g^{-1} or 7.2 Lkg^{-1} ^[18] and even outperforming that of the best MOF $Fe_2(O_2)(dobdc)$ (0.86 mmol g⁻¹ or 19.3 L kg⁻¹).^[7a] The C₂H₄ productivity of ZJU-HOF-1 can be further improved to 1.02 mmol g^{-1} at a high pressure of 5 bar (Figure 4e). It is worth to note that $Fe_2(O_2)(dobdc)$ shows a high regeneration energy ($Q_{st} = 66.8 \text{ kJ mol}^{-1}$), and is not stable in air/moisture and requires harsh handling under inert conditions, which largely hampers its real-world applications. In strong contrast, ZJU-HOF-1 shows highly chemical stability and low regeneration energy $(31.5 \text{ kJ mol}^{-1})$. This HOF can be easily regenerated to recover its separation capacity by the sweeping He gas at 323 K for 60 min, as evidenced by multiple breakthrough tests over five continuous cycles (Figure 4c).

In industrial C_2H_6/C_2H_4 separation, the feed gases typically contain water vapor, which could have negative effects on the uptake capacity and separation performance for many physisorbents. In this regard, many metal-containing materials such as MOFs and zeolites are sensitive to humidity or show high water uptake to result in competitive adsorption,^[25] thus suffering from gas sorption capacity reduction or structure decomposition under high humidity.^[7a,21a] To effectively avoid the effect of water vapor, ideal adsorbents would have not only high water stability but also low water uptake to minimize the co-adsorption of water. As shown in Figure 4 f, thanks to the hydrophobic nature of HOFs,^[9a] we found that the water amount adsorbed in ZJU-HOF-1 is very low up to 60% RH, with a negligible uptake of only 0.011 gg^{-1} . This could be highly favorable for C2H6/C2H4 separation under high humidity conditions. The breakthrough experiments on a wet C_2H_6/C_2H_4 mixture with 60 % humidity confirm that the presence of water vapor has no effect on the separation capacity of ZJU-HOF-1 (Figure 4b), further rendering it an ideal adsorbent for C₂H₄ purification under real industrial conditions.

Conclusion

In summary, we have realized the reversible solid-state transformation of a labile HOF material to result in a rodpacking desolvated structure (ZJU-HOF-1). This structural transition gives rise to the optimized pore confinement with suitable cavity spaces and functional surfaces in ZJU-HOF-1 for benchmark C_2H_6/C_2H_4 separation. The moderate high surface area and unique pore architecture of ZJU-HOF-1 lead to a rare combination of both high C₂H₆ uptake capacity and excellent C_2H_6/C_2H_4 selectivity, both of which are higher than most of C_2H_6 -selective materials. As revealed by DFT calculations, the suitable cage-like cavities and functional surfaces have collaborative roles for the preferential binding of C₂H₆ over C₂H₄. On account of the remarkable uptake and excellent selectivity, ZJU-HOF-1 exhibits the record polymer-grade C₂H₄ productivity of 0.98 mmol g^{-1} (or 21.9 Lkg^{-1}) from 50/50 dry and humid (60 $\%\,$ RH) $C_2 H_6 / C_2 H_4$ mixtures at ambient conditions, even higher than the state-of-the-art Fe2(O2)(dobdc) reported so far. Combined with its extraordinary chemical stability and ultralow water uptake at high humidity, ZJU-HOF-1 embodies a new benchmark material that has the potential to be applied for C₂H₆/C₂H₄ separation in real-world applications. This work here not only reports the benchmark HOF material for C_2H_6/C_2H_4 separation, but also provides some guidance to design new porous HOFs with suitable pore confinement to address some other important and challenging gas separations.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: ethane capture \cdot ethylene purification \cdot gas separation \cdot hydrogen bonds \cdot microporous materials

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