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DOI

[10.1002/ange.202411175](https://doi.org/10.1002/ange.202411175)

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Publication date

2024

Document Version

Final published version

Published in

Angewandte Chemie

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[Link to publication](#)

Citation for published version (APA):

Ji, Z., Li, Q., Zhou, Y., Krishna, R., Hong, M., & Wu, M. (2024). Synergistic C₂H₂ Binding Sites in Hydrogen-Bonded Supramolecular Framework for One-Step C₂H₄ Purification from Ternary C₂ Mixture. *Angewandte Chemie*, 136(46), Article e202411175. ⁴
<https://doi.org/10.1002/ange.202411175>, <https://doi.org/10.1002/anie.202411175>

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Gas Separation

Synergistic C₂H₂ Binding Sites in Hydrogen-Bonded Supramolecular Framework for One-Step C₂H₄ Purification from Ternary C₂ Mixture

 Zhenyu Ji⁺, Qing Li⁺, Yunzhe Zhou, Rajamani Krishna, Maochun Hong, and Mingyan Wu*

Abstract: Purification of C₂H₄ from the ternary C₂ hydrocarbon mixture in one step is of critical significance but still extremely challenging according to its intermediate physical properties between C₂H₆ and C₂H₂. Hydrogen-bonded organic frameworks (HOFs) stabilized by supramolecular interactions are emerging as a new kind of adsorbents that facilitate green separation. However, it remains a problem to efficiently realize the one-step C₂H₄ purification from C₂H₆/C₂H₄/C₂H₂ mixture because of the low C₂H₂/C₂H₄ selectivity. We herein report a robust microporous HOF (termed as HOF-TDCPB) with dense O atoms and aromatic rings distributed on the pore surface which provide C₂H₆ and C₂H₂ preferred environment simultaneously. Dynamic breakthrough experiments indicate that HOF-TDCPB can not only obtain high-purity C₂H₄ from binary C₂ mixture, but also firstly realize one-step C₂H₄ purification from ternary C₂H₆/C₂H₄/C₂H₂ mixture, with the C₂H₄ productivity of 3.2 L/kg (>99.999%) for one breakthrough cycle. Furthermore, HOF-TDCPB displays outstanding stability in air, organic solvents and water, which endow it excellent cycle performance even under high-humidity conditions. Theoretical calculations indicate that multiple O sites on pore channels can create synergistic binding sites for C₂H₂, thus affording overall stronger multipoint interactions.

Introduction

Ethylene (C₂H₄), as the foremost olefin as well as the highest volume product in the petrochemical industry, is

widely used to produce polyethylene and other valued products in modern life.^[1] By 2023, annual global C₂H₄ production capacity already exceeds 200 million tons and maintains an annual growth trend.^[2] Presently in the petrochemical industry, C₂H₄ is mainly obtained by pyrolyzing of naphtha steam and dehydrogenation of ethane (C₂H₆), and during these processes, C₂H₆ and acetylene (C₂H₂) are always inevitably produced.^[3] So as to acquire high-purity C₂H₄ for their downstream applications, additional separation processes are necessitated. With the burgeoning progress in advanced porous materials, adsorptive separation technology based on porous adsorbents has been considered as a potential alternative for industrial gas separation and purification.

Recently, several kinds of porous crystalline materials, such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) have been widely explored for separating C₂ gases and some spectacular achievements have been ascended in C₂H₆/C₂H₄ and C₂H₂/C₂H₄ separation progress^[4] Especially, as one kind of rapidly developing organic porous materials, hydrogen-bonded organic frameworks (HOFs), which are mainly stabilized by intermolecular hydrogen-bonding interactions, have been viewed as ideal physical adsorbents, thank to their high crystallinity, easy solution processability, high recyclability.^[5] Additionally, HOFs often exhibit exceptional stability in water, common organic solvents, strong acids and even corrosive gases. For example, the robust HOF UNAM-1 shows remarkable stability in SO₂ and displays reversible adsorption of SO₂ at room temperature.^[6] It has been proved that HOFs constructed by large π -conjugated system usually possess nonpolar channels and can selectively capture C₂H₆ from C₂H₆/C₂H₄ mixture, which can realize one-step C₂H₄ separation from binary C₂H₆/C₂H₄ mixture.^[6] However, since the primary physical properties of C₂H₄ such as molecular size, quadrupole moment and polarizability (4.2 Å, 1.5×10⁻²⁶ esu cm² and 42.52×10⁻²⁵ cm³) all fall between C₂H₂ (3.3 Å, 7.2×10⁻²⁶ esu cm² and 33.3–39.3×10⁻²⁵ cm³) and C₂H₆ (4.4 Å, 0.65×10⁻²⁶ esu cm² and 44.7×10⁻²⁵ cm³),^[8] it is still a formidable challenging to separate intermediate C₂H₄ from ternary C₂ hydrocarbons. As we know, no case of HOF materials has successfully achieved one-step purification of C₂H₄ from C₂H₆/C₂H₄/C₂H₂ mixture up to now. The main reason is that there is lack of efficient C₂H₂ binding sites. Therefore, HOFs generally show poor performance in C₂H₂ adsorption and exhibit low C₂H₂/C₂H₄ selectivity. According to the literatures, multiple oxygen sites in the channels could generate synergetic C–H…O interactions for C₂H₂ molecule and effectively capture C₂H₂ molecules.^[9] Therefore, if we

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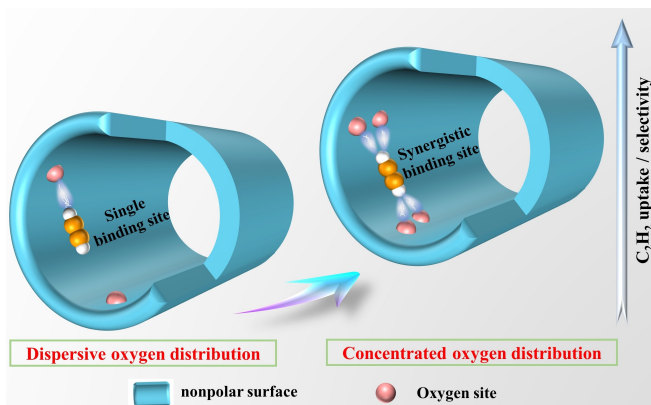
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employ an organic building unit with multiple carboxylic acids and large aromatic system to construct a HOF with both the high-density oxygen atoms and the aromatic rings dispersing on the pore surface. This HOF can not only maintain the high affinity for C_2H_6 , but can also exhibit favorite adsorption for C_2H_2 , thus enabling the one-step purification of C_2H_4 from ternary $C_2H_6/C_2H_4/C_2H_2$ mixtures (Scheme 1).

With the above consideration, we herein employ a hexacarboxylic acid organic ligand 1,3,5-tri(3,5-di(4-carboxyphenyl-1-yl)phenyl-1-yl)-benzene (H_6TDCPB) and construct a microporous hydrogen-bonded organic framework (HOF-TDCPB). Benefiting from its large π -conjugated system and multi-fold interpenetrated framework, HOF-TDCPB exhibits exceptional stability and water resistance. More importantly, on account of the abundance of aromatic rings and the high-density carboxylate oxygen atoms distributed on its pore surface, as envisaged HOF-TDCPB shows both higher adsorption capacity for C_2H_6 and C_2H_2 over C_2H_4 in the temperature range of 273 to 298 K. Furthermore, at 298 K per mole of HOF-TDCPB could absorb 2.1 mole C_2H_2 molecules, which is the highest value among all reported HOFs. And the C_2H_2 storage density for HOF-TDCPB could also reach a very high value of 0.23 g/cm³, outperforming most of HOF materials similarly. Dynamic breakthrough studies indicate that HOF-TDCPB could not only obtain the polymer-grade pure C_2H_4 from C_2H_6/C_2H_4 and C_2H_2/C_2H_4 in one step respectively, but also could directly acquire the polymer-grade pure C_2H_4 from the $C_2H_6/C_2H_4/C_2H_2$ mixture, which realizes the first report in HOF materials for one-step C_2H_4 purification from ternary C2 mixtures. Modeling studies indicate that concentrated distribution of oxygen atoms on the pore wall of HOF-TDCPB can form synergistic sites for C_2H_2 molecules, which endows it preferential C_2H_2 adsorption.



Scheme 1. The strategy of engineering synergistic binding sites for C_2H_2 molecule in hydrogen-bonded organic framework for construction of C_2H_2/C_2H_6 -selective adsorbent.

Results and Discussion

HOF-TDCPB can be obtained as colorless needle-shaped crystals by simple organic steam diffusion method (See SI). X-ray crystallography reveals that HOF-TDCPB crystallizes in the trigonal $R\bar{3}c$ space group and has a distinctive 3D framework. In the crystal structure of HOF-TDCPB, H_6TDCPB is C_3 -symmetric with six equivalent non-planar windmills-like cantilevers and each H_6TDCPB molecule is interconnected with six neighboring H_6TDCPB molecules through six pairs of intermolecular dimeric $-COOH\cdots HOOC-$ hydrogen bonds (Figure 1a). The $O\cdots O$ distances and $O-H\cdots O$ angles are in the range of 2.5–2.6 Å and 172.6–175.8° respectively (Table S2). In H_6TDCPB , the inner three adjacent benzene rings present a torsion angle of 45.9° in the same direction with the central benzene ring, which endows H_6TDCPB with a distorted octahedral conformation (Figure S2). Topologically, if simplifying the H_6TDCPB as a six-connected node, the framework of HOF-TDCPB can be classified as the *pcu* topology (Figure 1b). Such *pcu* hydrogen bonded-networks are also found in HOF-76^[10] and CPHAT-1,^[11] and they both exhibit excellent stability. Furthermore, in the structure of HOF-TDCPB, eight identical frameworks interpenetrate with each other through the $\pi\cdots\pi$ interactions between adjacent layers, resulting in a narrow 1D channel with layer-by-layer stacked aromatic rings around the pore walls. And this nonpolar pore environment facilitates preferential binding of C_2H_6 molecules.^[11] The pore size of HOF-TDCPB along the *c*-axis calculated by *Zeo++* package^[13] is approximate 5.0 Å (Figure 1d–1f) and the total solvent-accessible volume is estimated to be 24.9% of the whole crystal volume according to *PLATON* analysis.^[14] It is noteworthy that despite the multifold interpenetration and the lower porosity, all carboxylic acid groups in HOF-TDCPB are distributed in the channels, resulting in a high density of oxygen atoms on the pore surface. The calculated surface oxygen atoms density could reach 2.2×10^{-5} mol/m², much exceeding HOF-76 (1.1×10^{-5} mol/m²), ZJU-HOF-1 (1.3×10^{-5} mol/m²), CPDBC-1 (0.6×10^{-5} mol/m²), HOF-TCPB (0.6×10^{-5} mol/m²) and HOF-NBDA (1.7×10^{-5} mol/m²) (Table S3), which presents HOF-TDCPB more potential hydrogen bond receptors for C_2H_2 . More intuitively, according to electrostatic potential (ESP) analysis in Figure S3, the densely distributed carboxylic acid O atoms possess even more negative static electricity, which may provide multiple binding sites to preferentially and more strongly interact with the positive H atoms of C_2H_2 . Combining customized pore chemistry and suitable pore size, we speculate that HOF-TDCPB may capture C_2H_6 and C_2H_2 simultaneously from ternary C2 mixture.

As for its strong intermolecular supramolecular interactions and multiple interpenetrations within the framework, we firstly investigated the stability of HOF-TDCPB. As depicted in Figure 2a and S5, after exposing the sample in air for 6 months or immersing them in 12 M HCl and some common organic solvents for 7 days, it can maintain the good crystallinity. In addition, thanks to its large π -conjugate building skeleton, HOF-TDCPB also exhibits

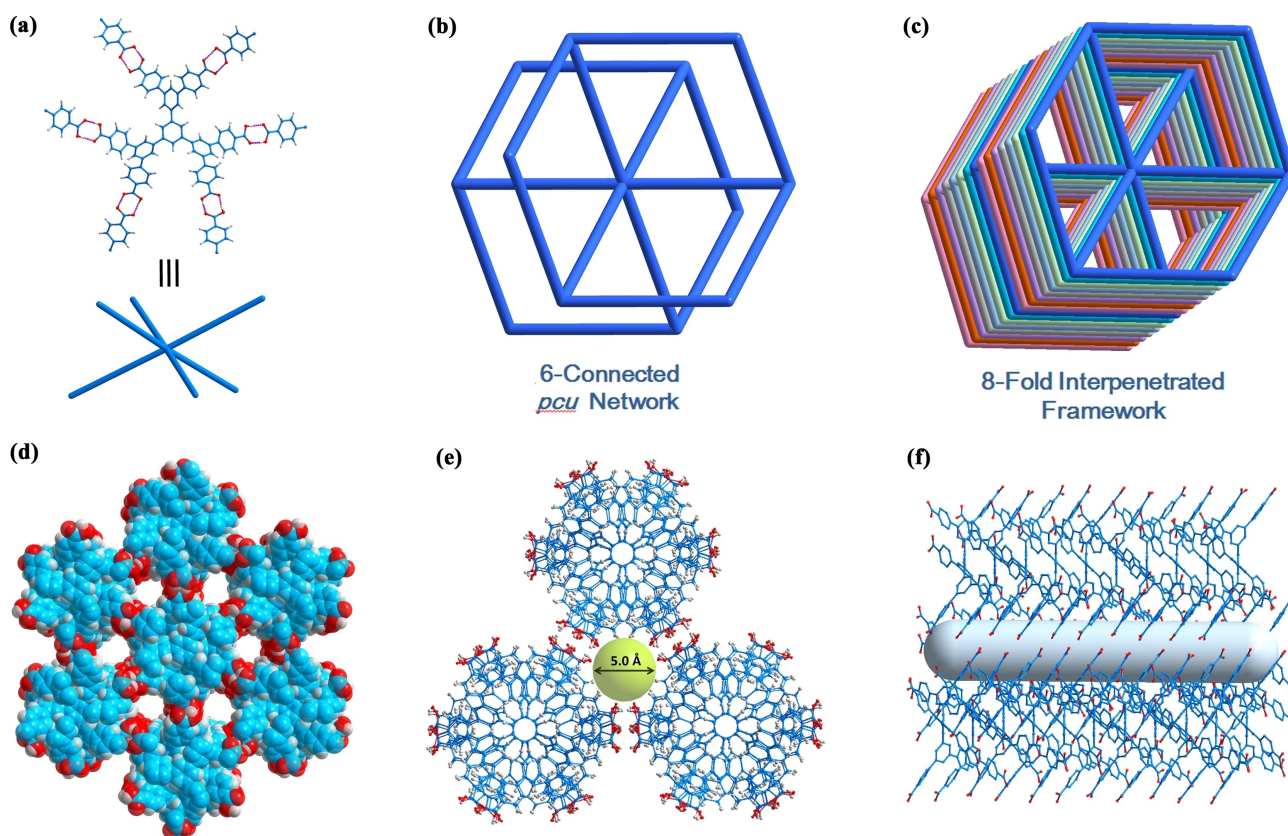


Figure 1. Crystal structure of HOF-TDCPB. (a) View of the connection of adjacent building blocks and simplified six-connected nodes. (b) Augment to *pcu* network. (c) The 8-fold interpenetrated framework. (d) Representation of the porous framework of HOF-TDCPB from *c* axis. (e) One-dimensional (1D) channels viewed along *c*-axis and (f) *a*-axis, revealing a moderate size of ca. 5.0 Å in diameter.

excellent water stability which can be certified by the well matched PXRD patterns with the fresh sample after soaking HOF-TDCPB in water for 30 days or boiling water for 7 days. Water vapor adsorption shows that HOF-TDCPB hardly adsorb water molecules even reaching the saturated vapor pressure which can also indicate its water resistance (Figure S6). What is more, thermogravimetric analysis experiment (TGA) and variable-temperature PXRD (VT-PXRD) were also performed to illustrate the thermal stability of HOF-TDCPB (Figure S7 and S8). TGA experiment shows that there is no significant weight loss up to 360 °C. And then, no obvious changes in the PXRD patterns are observed even at 200 °C in air atmosphere, implying that the framework remains at such high temperature. And such exceptional thermal stability and solvent stability are rarely seen in the hydrogen-bonded organic frameworks.^[15] More importantly, HOF-TDCPB can be regenerated by simple recrystallization, which can effectively reduce its synthetic costs (Figure S9). Above characteristics of HOF-TDCPB indicate it can be served as potential adsorbent in the actual industrial environment.

Based on the moderate pore size and outstanding stability of HOF-TDCPB, we next tested its gas adsorption properties. Firstly, we employed the N₂ adsorption experiment at 77 K to investigate the porosity. As shown in Figure S9, HOF-TDCPB could absorb 148.8 cm³ g⁻¹ N₂ at

77 K and 1 bar. The corresponding Brunauer–Emmett–Teller (BET) surface area is 530.0 m² g⁻¹. The calculated pore size is 5.2 Å (Figure S12), much close to the value (5.0 Å) obtained from the crystal structure. Excitingly, after treatment with some harsh conditions, HOF-TDCPB samples show no obvious decrease on the N₂ uptakes at 77 K (Figure S18–S19). The particularly stable structure and naturally special pore environment of HOF-TDCPB prompt us to investigate its gas adsorption performance on C₂ hydrocarbons. For HOF-TDCPB, not only it is expected to adsorb more C₂H₆ than C₂H₄, but also it shows superior adsorption of C₂H₂. As depicted in Figure 2b and 2c, the uptakes of HOF-TDCPB for C₂H₆, C₂H₄ and C₂H₂ are 46.8 cm³ g⁻¹, 43.9 cm³ g⁻¹ and 59.7 cm³ g⁻¹ respectively at 273 K and 100 kPa. The maximum adsorption of C₂H₄ by HOF-TDCPB is less than those of both C₂H₂ and C₂H₆, which implies that the framework may show stronger affinity for C₂H₂ and C₂H₆ than C₂H₄. At 298 K, the uptakes of HOF-TDCPB for C₂H₆, C₂H₄ and C₂H₂ could reach 37.9 cm³ g⁻¹, 35.5 cm³ g⁻¹ and 46.0 cm³ g⁻¹ at 100 kPa. After five-cycle adsorption tests for C₂H₆, C₂H₄ and C₂H₂, the adsorption capacities show no obvious change (Figure S20–S22). And the saturated uptakes of HOF-TDCPB on C₂H₆, C₂H₄, and C₂H₂ still remain in the order of C₂H₂ > C₂H₆ > C₂H₄. Furthermore, at low pressure region, the adsorption isotherms for C₂H₆ and C₂H₂ as well increase more sharply

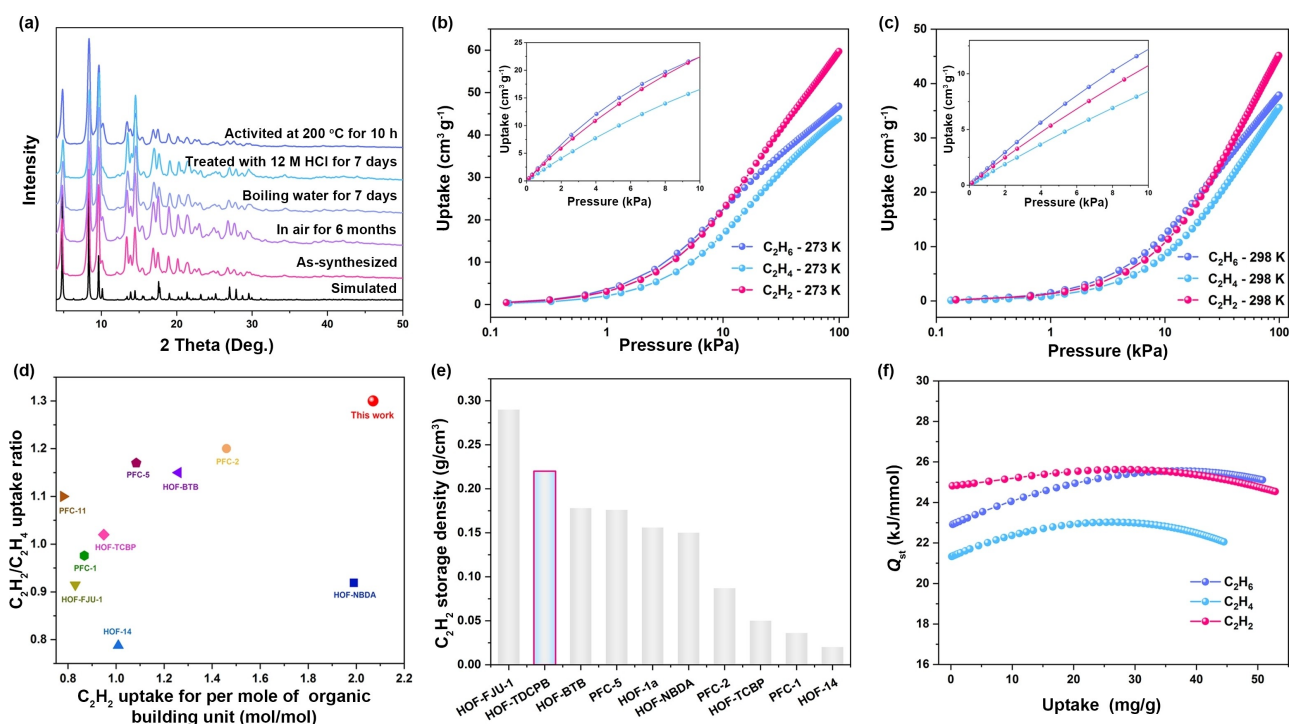


Figure 2. (a) The PXRD patterns of HOF-TDCPB under different conditions. (b) C_2H_6 , C_2H_4 , and C_2H_2 adsorption isotherms of HOF-TDCPB at 273 K and (c) 298 K. (d) Comparison of C_2H_2 -selective HOFs of their C_2H_2 uptake for per mole organic building unit and C_2H_2/C_2H_4 uptake ratio. (e) Comparison of storage densities of C_2H_2 for HOF-TDCPB and other HOFs (1 atm and 298 K). (f) Q_{st} of HOF-TDCPB for C_2H_6 , C_2H_4 and C_2H_2 respectively.

than C_2H_4 , which is completely consistent with the characterization of C_2H_2/C_2H_6 -selective adsorbent.^[16] What is more, for HOF-TDCPB, per mole organic building unit can absorb 2.1 mole C_2H_2 molecules,^[5c] which is the highest value among all reported HOFs to date (Figure 2d). The uptake ratio of C_2H_2/C_2H_4 reaches 1.3, surpassing most of HOF materials, such as PFC-5 (1.2),^[17] HOF-BTB (1.2),^[18] and HOF-NBDA (1.0)^[19] (Table S4). More significantly, benefited from abundant electronegative oxygen sites on the pore wall, the storage density of C_2H_2 for HOF-TDCPB can reach 0.23 g/cm^3 , just below the highest reported value of 0.29 g/cm^3 for HOF-FJU-1. And above results together indicate that HOF-TDCPB exhibits higher affinity for C_2H_2

and C_2H_6 and can be used as a potential C_2H_2/C_2H_6 -selective adsorbent.

In order to further assess the different interactions of C_2H_6 , C_2H_4 and C_2H_2 , the heat of adsorption (Q_{st}) was calculated with the adsorption isotherms at 273 K and 298 K. As shown in Figure 2f, the Q_{st} for C_2H_2 (24.8 kJ mol^{-1}) and for C_2H_6 (22.9 kJ mol^{-1}) at zero coverage are both higher than that for C_2H_4 (21.3 kJ mol^{-1}), which also proves that HOF-TDCPB shows a stronger interaction with C_2H_2 and C_2H_6 than C_2H_4 . To gain precise insight into the binding sites for C_2H_6 , C_2H_4 and C_2H_2 in HOF-TDCPB, we performed theoretical calculations using Grand Canonical Monte Carlo (GCMC) method. As depicted in Figure 3,

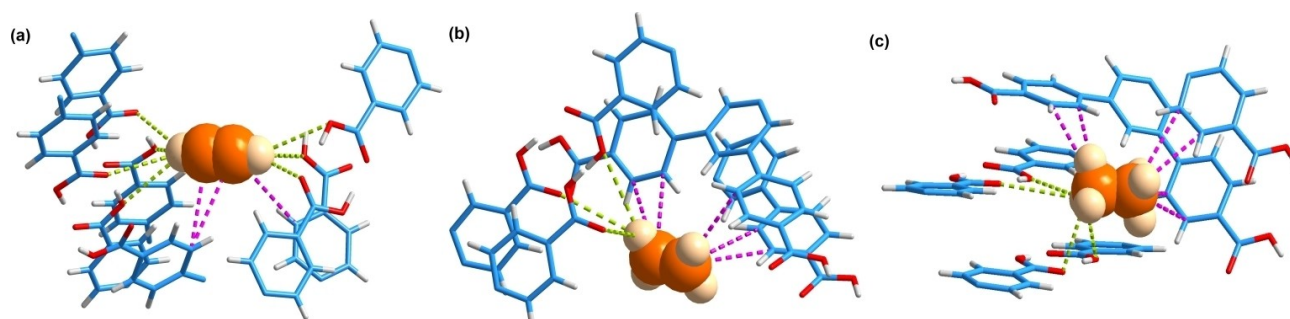


Figure 3. The calculated preferential adsorption sites for (a) C_2H_2 , (b) C_2H_4 and (c) C_2H_6 in HOF-TDCPB. The C–H...O hydrogen bonds are shown in dashed green lines and the C–H... π interactions between gas molecule and the pore surface are shown in dashed purple lines. For clarity, C_2H_2 , C_2H_4 and C_2H_6 molecules are in space-filling model.

all three C₂ molecules could interact with carboxylate O atoms and phenyl rings of HOF-TDCPB through multiple supramolecular interactions. However, their interaction modes are much differentiated. For the C₂H₂ molecule, the optimal binding site occurs at the corner of the channel. As demonstrated in Figure 3a, C₂H₂ molecule could form seven C–H...O hydrogen bonds with seven carboxylic groups (H...O separations: 2.66 Å, 2.99 Å, 3.03 Å, 3.42 Å, 3.54 Å, 3.80 Å and 3.80 Å), creating a firmly synergistic C₂H₂ binding site. Such synergistic oxygen binding sites for H atoms of C₂H₂ molecules could distinctly strengthen the C₂H₂ uptakes.^[9b,20] Furthermore, three benzene rings around the C₂H₂ molecule also assist three C–H... π interactions (C...C separations: 3.93 Å, 4.12 Å and 4.20 Å). And all these combined interactions could provide HOF-TDCPB a relatively stronger binding site for C₂H₂. Relative to C₂H₂, C₂H₄ molecule is slightly tilted on the pore wall and it mainly interacts with the skeleton through C–H... π interactions. As depicted in Figure 3b, only one H atom of C₂H₄ interacts with adjacent carboxylic acid to produce three C–H...O interactions (H...O separations: 3.66 Å, 3.69 Å and 3.79 Å). And five C–H... π interactions (C...C separations: from 3.72 Å, 3.78 Å, 3.80 Å, 3.90 Å and 4.06 Å) are observed to generate more interactions between C₂H₄ molecule and framework. Given that C₂H₆ molecule, the strongest binding site is similar to C₂H₄. Six C–H... π interactions (C...C separations: 3.68 Å, 3.75 Å, 3.84 Å, 3.87 Å, 3.89 Å and 4.03 Å) and four additional C–H...O interactions (H...O separations: 3.01 Å, 3.38 Å, 3.65 Å and 3.73 Å) are found between the framework and C₂H₆ molecule (Figure 3c). Notably, relative to C₂H₄, C₂H₂ molecule can form more C–H...O interactions with HOF-TDCPB and the H...O separations between C₂H₂ and framework are much shorter (Table S5), which indicate that synergistic oxygen sites in HOF-TDCPB are effective in enhancing the affinity for C₂H₂ molecules. Similar phenomenon is also observed for C₂H₆. The calculated static binding energy for these C₂ gases follows the order of C₂H₂ (40.3 kJ/mol) > C₂H₆ (37.6 kJ/mol) > C₂H₄ (35.9 kJ/mol), which are consistent well with the trend of the experimental Q_{st} values observed in HOF-TDCPB. Furthermore, in situ FTIR experiments with corresponding C₂ gas loadings as well confirmed the interactions between C₂H₂/C₂H₄/C₂H₆ and HOF-TDCPB (Figure S26–S28). These results comprehensively indicate that HOF-TDCPB possess preferential adsorption for C₂H₆ and C₂H₂ rather than C₂H₄.

To evaluate the potential separation ability of HOF-TDCPB for C₂H₂/C₂H₄ and C₂H₆/C₂H₄, an ideal adsorbed solution theory (IAST) calculation was employed on the base of the single-component C₂H₆, C₂H₄ and C₂H₂ adsorption isotherms at 298 K. As demonstrated in Figure S32, for different ratios of C₂H₆/C₂H₄ mixture (1/1, 1/9, and 1/15), the IAST selectivities are 1.50, 1.52 and 1.52 respectively. And the IAST selectivity for C₂H₂/C₂H₄ with ratio of 1/99 (v/v) is 1.51 (Figure S33). The C₂H₆/C₂H₄ and C₂H₂/C₂H₄ selectivities are comparable to those of most reported C₂H₂/C₂H₆-selective adsorbents, such as NKCOF-62 (1.30 and 1.37),^[21] NPU-1 (1.40 and 1.32),^[22] HIAM-111 (1.23 and 1.62)^[23], CAU-23 (1.50 and 1.54)^[24] and FJI–W-66a (2.31 and 1.40).^[25]

As for the HOF materials that have been reported, as given in Figure S38–S39, even though they demonstrate excellent C₂H₆/C₂H₄ selectivities, poor C₂H₂ selectivities prevent any of them from achieving one-step purification of C₂H₄ from ternary C₂ hydrocarbon mixture. These results suggest that HOF-TDCPB realizes high selectivity of HOF materials for both C₂H₆ and C₂H₂ relative to C₂H₄ and possesses the feasibility to purify C₂H₄ from C₂H₂ and C₂H₆ in practical applications.

In order to evaluate the practical performance of HOF-TDCPB for the purification of C₂H₄, dynamic breakthrough experiments were carried out. Firstly, binary gas mixture was employed for testing the separation ability for HOF-TDCPB. As depicted in Figure 4a–4c, HOF-TDCPB can efficiently capture the C₂H₆ from the C₂H₆/C₂H₄ gas mixture with the ratios of 1/15, 1/10, 5/5. Detailed inspection of these separation curves, C₂H₄ always breaks through the fixed bed while C₂H₆ is thoroughly adsorbed by HOF-TDCPB. The gas chromatography results testify that C₂H₄ with purity up to 99.999 % can be collected from the outlet (the detection limit of the instrument is 10 ppm). The retention times of pure C₂H₄ for C₂H₆/C₂H₄ (1/15, 1/10, 5/5) on HOF-TDCPB could reach 35.9 min, 40.0 min and 31.1 min respectively. The corresponding high-purity C₂H₄ yields are respectively assigned to 3.5 L/kg, 2.6 L/kg and 1.0 L/kg. These results suggest that HOF-TDCPB retains a C₂H₆ preferred pore environment like reported HOFs. Furthermore, in view of the fact that HOF-TDCPB also possesses a high affinity for C₂H₂, the separation performance for C₂H₂/C₂H₄ (1/99) mixture has been also investigated. As demonstrated in Figure 4d, C₂H₄ elutes through the adsorption bed at ca. 64.6 min and the C₂H₂ stays undetected in the fixed bed until 92.6 min. During this time, 18.5 L/kg high purity of C₂H₄ can likewise be collected.

Motivated by the confirmed separation performance of binary mixture for HOF-TDCPB, we further assessed the

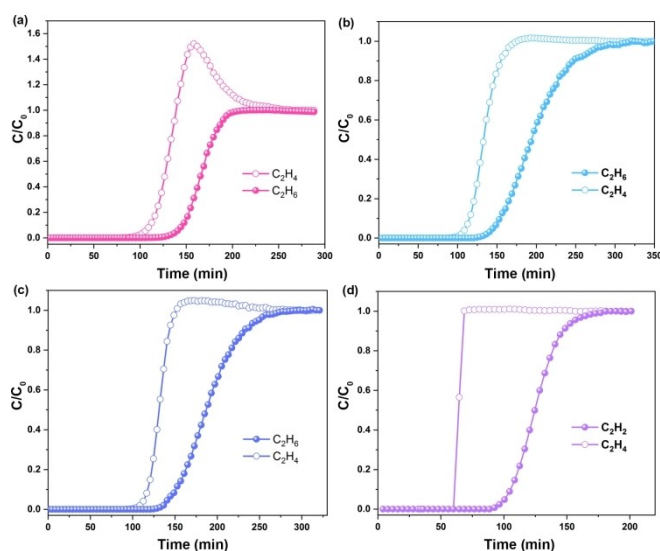


Figure 4. Breakthrough curves of HOF-TDCPB for C₂H₆/C₂H₄ and C₂H₂/C₂H₄ at 298 K. (a) 5/5, v/v, (b) 1/9, v/v and (c) 1/15, v/v for C₂H₆/C₂H₄ with He as balance gas. (d) 1/99, v/v for C₂H₂/C₂H₄.

C_2H_4 purification capacity from ternary C2 mixture gases. As can be seen in Figure 5a, HOF-TDCPB can efficiently separate the $C_2H_6/C_2H_4/C_2H_2$ (5/5/5, v/v/v) mixture under ambient condition. The C_2H_4 can be certainly detected before C_2H_6 and C_2H_2 , and the order of gas outflow at the outlet is C_2H_4 , C_2H_6 and C_2H_2 , which is coincident with the uptake capacity (C_2H_2 : $46.0 \text{ cm}^3 \text{ g}^{-1}$, C_2H_6 : $37.9 \text{ cm}^3 \text{ g}^{-1}$, C_2H_4 : $35.5 \text{ cm}^3 \text{ g}^{-1}$) and adsorption heats (C_2H_2 : 24.8 kJ mol^{-1} , C_2H_6 : 22.9 kJ mol^{-1} , C_2H_4 : 21.3 kJ mol^{-1}). After one breakthrough test, 0.8 L/kg polymer-grade C_2H_4 could be directly obtained. Moreover, additional ratios of $C_2H_6/C_2H_4/C_2H_2$ (6/3/6, 2/10/10, 3/10/3) gas mixtures were also adopted to further measure the ability of HOF-TDCPB to purify C_2H_4 from the ternary mixture. As described in Figure 5b–5c, HOF-TDCPB can preferentially capture C_2H_6 and C_2H_2 in different $C_2H_6/C_2H_4/C_2H_2$ ratios, realizing the efficient C_2H_4 purification. In sharp contrast, HOFs that lack effective C_2H_2 adsorption sites are unable to purify C_2H_4 from ternary C2 mixture (Figure S40). Among these different ratios of ternary C2 mixtures, the maximum productivity of 3.2 L/kg for high-purity C_2H_4 can be recovered from $C_2H_6/C_2H_4/C_2H_2$ (3/10/3) mixture in a single breakthrough step, which is comparable to some benchmark adsorbents, such as Zn-(BDC)(H_2 BPZ) (4.6 L/kg),^[26] PCP-FDCA (4.5 L/kg)^[19] and LIFM-YYY-6 (3.1 L/kg).^[27] Excitingly, this is the first case

of a single HOF adsorbent for one-step C_2H_4 purification from the ternary mixture of $C_2H_2/C_2H_6/C_2H_4$. More importantly, HOF-TDCPB shows excellent reusability in C_2H_4 purification. As shown in Figure 5e and Figures S43–S50, after five-cycle breakthrough experiments of all gas substrates, HOF-TDCPB can maintain its separation performance with the separation time almost unchanged. In view of the unavoidable moisture in the industrial environment and excellent water ability of HOF-TDCPB, the dynamic breakthrough experiments under humidity environment was measured at 298 K, as shown in Figure 5f and Figures S51–S58. It can be found that the breakthrough curves at 86% and 100% RH are almost consistent with the situation in dry conditions, rationally implying that water vapor hardly influences the separation performance of HOF-TDCPB.

Conclusion

In summary, we herein employ a hexacarboxylic acid organic ligand to construct a microporous hydrogen-bonded organic framework with a customized pore size and pore environment. Benefiting from the abundance of aromatic rings and high-density oxygen sites distributed on its pore surface, HOF-TDCPB presents a higher affinity for C_2H_6 and C_2H_2 simultaneously and shows the potential to purify C_2H_4 in one step from ternary C2 mixture. Dynamic breakthrough experiments revealed that HOF-TDCPB could not only obtain the polymer-grade pure C_2H_4 from C_2H_6/C_2H_4 and C_2H_2/C_2H_4 in one step, but also could directly acquire the polymer-grade pure C_2H_4 from the $C_2H_6/C_2H_4/C_2H_2$ mixture. And it is noteworthy that HOF-TDCPB is the first example in HOFs for one-step purification of C_2H_4 from a ternary C2 mixture by optimising the pore environment. And we think this work will be very helpful to designedly synthesize microporous HOF materials for C_2H_4 purification in the future.

Acknowledgements

This work is supported by NSFC (22271282) and the Self-deployment Project Research Program of Haixi Institutes, Chinese Academy of Sciences with the grant number of CXZX-2022-JQ04. Additionally, this work is also supported by Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (No. 2021ZR120) and NSF of Fujian Province (No. 2021J01517 and 2020J06034).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

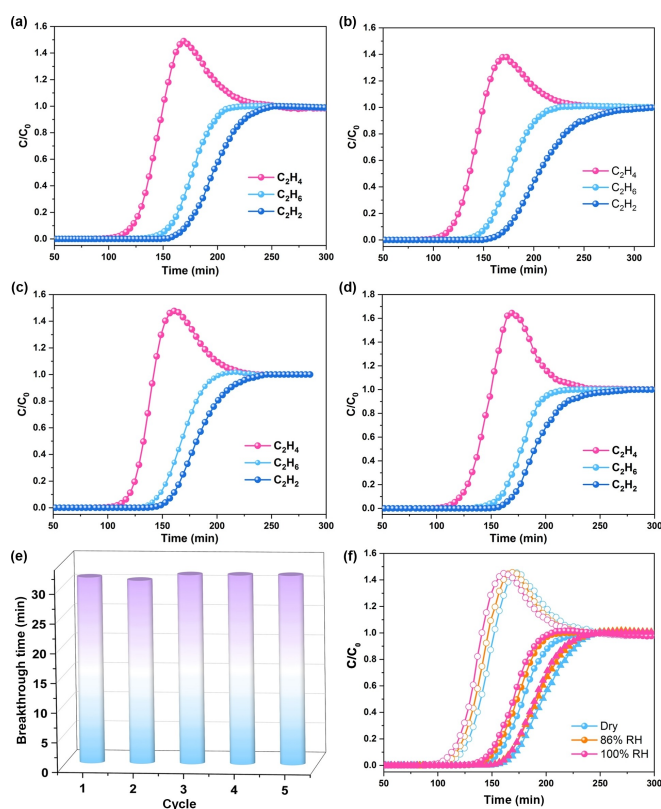


Figure 5. Breakthrough curves of HOF-TDCPB at 298 K for different volume ratio $C_2H_6/C_2H_4/C_2H_2$ mixtures with He as balance gas. (a) 5/5/5; (b) 6/3/6; (c) 2/10/10; (d) 3/10/3. (e) and (f) The cycling breakthrough tests and breakthrough experiments under different relative humidity for $C_2H_6/C_2H_4/C_2H_2$ (3/10/3, v/v) mixture at 298 K.

Keywords: hydrogen-bonded organic framework · synergistic binding site · ethylene purification · ternary C2 mixture · humid environment

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Manuscript received: June 13, 2024

Accepted manuscript online: August 5, 2024

Version of record online: October 8, 2024