

A Water-Resistant Hydrogen-Bonded Organic Framework for Ethane/Ethylene Separation in Humid Environments

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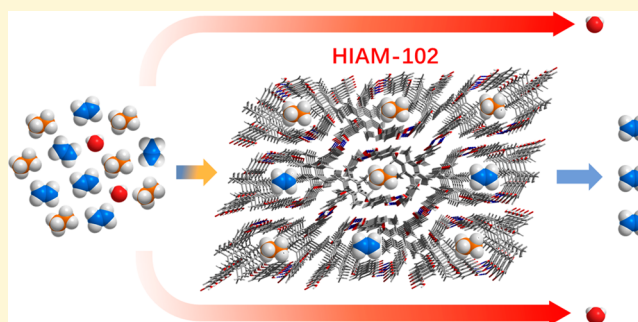


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Supporting Information

ABSTRACT: The separation of ethane (C_2H_6) and ethylene (C_2H_4) represents a crucial process for the production of polymer-grade C_2H_4 , and adsorptive separation holds enormous promise for this industrially important but challenging task. Here, we report a new hydrogen-bonded organic framework (HIAM-102) with suitable channel and superhydrophobicity for preferential adsorption of C_2H_6 over C_2H_4 . HIAM-102 shows a C_2H_6/C_2H_4 IAST selectivity of 1.9 and C_2H_6 uptake of 48.25 cm^3/g at 1 bar and 298 K. Benefitting from the hydrophobic pore surface, it can well-separate C_2H_6 and C_2H_4 under highly humid conditions, as confirmed by experimental column breakthrough measurements. Computational calculations provide additional support for the experimental observations that the nonpolar channel of HIAM-102 interact favorably with C_2H_6 over C_2H_4 .



As one of the most important feedstocks in petrochemical industries, ethylene (C_2H_4) has a wide range of uses for the manufacture of various polymers and other organic chemicals.^{1–3} C_2H_4 is typically produced through the steam cracking of ethane (C_2H_6) and unreacted C_2H_6 (ca. 5%–9% (v/v)) in the product gas needs further purification to obtain polymer-grade ($\geq 99.95\%$) C_2H_4 .^{4,5} However, because of the similar physical and chemical properties of C_2H_6 and C_2H_4 (Table S1 in the Supporting Information), the separation of C_2H_6/C_2H_4 mixtures is currently realized by cryogenic separation with a huge number of trays, which is extremely energy-intensive.^{6,7} To this end, developing new separation techniques with higher energy efficiency is imperative. Among various technologies, adsorptive separation holds particular promise as one of the most economic and operationally feasible separation methods, where highly selective adsorbents are the key to achieve efficient separation.⁸ C_2H_6 -selective adsorbents that preferentially capture C_2H_6 from the mixture to produce pure C_2H_4 directly are ideal, as they avoid multiple adsorption–desorption cycles needed when using C_2H_4 -selective adsorbents.^{9,10} Previous reports^{11–13} have revealed that pores featuring a nonpolar or inert surface wherein dispersion and induction interactions play a domain role are necessary for an C_2H_6 -selective adsorbent, since C_2H_4 has a higher quadrupole moment (1.50×10^{-26} esu cm^2) than ethane

(0.65×10^{-26} esu cm^2), making the interaction force between C_2H_4 and polar surface stronger.

In this context, the emerging hydrogen-bonded organic frameworks (HOFs), which are self-assembled from organic molecules via intermolecular hydrogen-bonding interactions, were considered to have great potential to separate C_2H_6 and C_2H_4 .^{14,15} This is because their metal-free nature enables them with nonpolar pore structures, in contrast to the generally polar pore surfaces of MOFs or zeolites containing metal clusters or metal ions.¹⁶ However, the weak hydrogen-bonding interactions commonly result in fragility of HOFs, and many of them collapse upon dissolution.^{17,18} Therefore, it is very challenging to obtain robust HOFs with permanent porosity, and only a few C_2H_6 -selective HOF adsorbents have been reported until now.^{19–22} In this work, a novel rod-packing HOF material (HIAM-102) with a suitable pore structure for C_2H_6/C_2H_4 separation has been developed. HIAM-102

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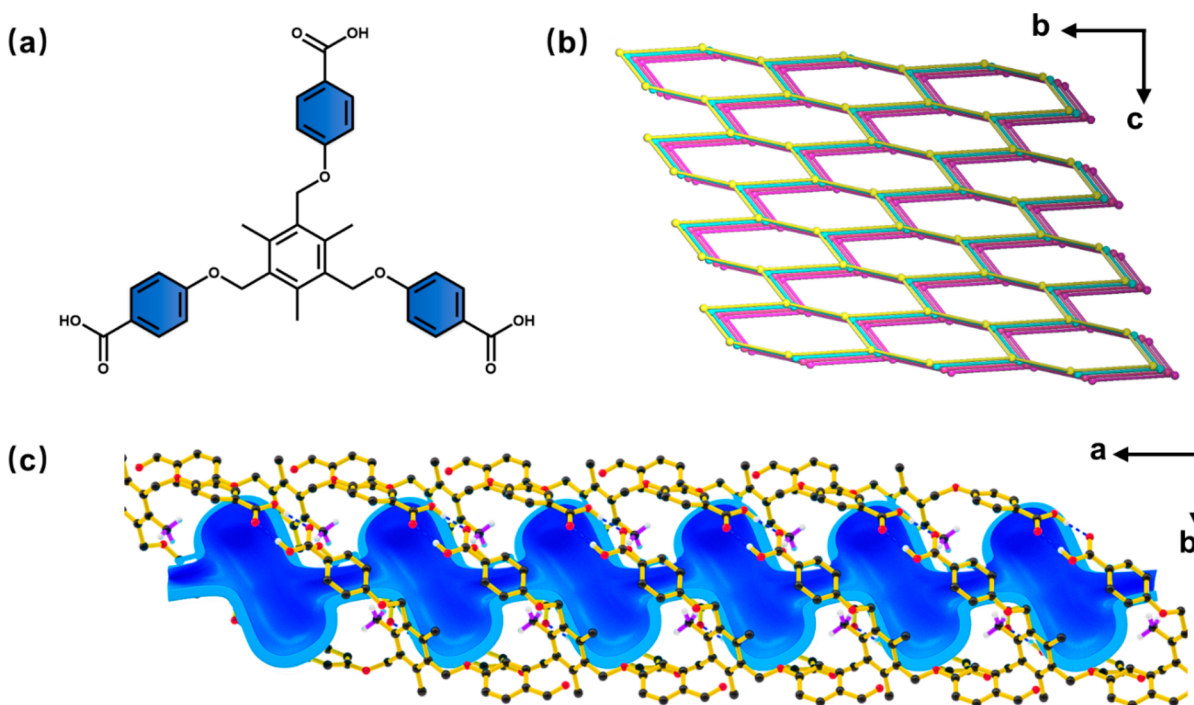


Figure 1. (a) Organic building block used to construct HIAM-102, (b) hcb Shubnikov hexagonal plane net topology structure of HIAM-102, and (c) one-dimensional (1D) channels along the *a*-axis.

exhibits a $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ IAST selectivity of 1.9 and a C_2H_6 uptake of $48.25 \text{ cm}^3/\text{g}$. Its channels are decorated with abundant methyl groups, which endows it with excellent chemical stability and hydrophobicity. It barely adsorbs water up to its saturation pressure. Mixed-gas breakthrough tests under highly humid environments confirmed its $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ separation capability.

The colorless oblique parallelepiped crystals (Figure S1 in the Supporting Information) of HIAM-102 were easily isolated in 60% yield by recrystallization from a hot acetic acid-saturated solution of the organic building block 1,3-bis[4-(carboxyphenyl) oxymethyl]-2,4,6-trimethylbenzene (H_3TBTC), as shown in Figure 1a. (See Supporting Information for synthesis details.) Single-crystal X-ray diffraction (crystal data and structure refinement for HIAM-102 are shown in Table S2 in the Supporting Information) revealed that the structure of HIAM-102 is a three-dimensional porous HOF in which each organic building unit is connected with three neighboring ones by 6 hydrogen bonds involving the carboxyl groups (Figure S2 in the Supporting Information). The O–H \cdots O angle and distance are $169.4^\circ/177.5^\circ/173.7^\circ$ and $2.611/2.701/2.593 \text{ \AA}$, respectively, similar to that of hydrogen bonds for reported HOFs.^{23,24} From a topological perspective, HIAM-102 can be considered as a uninodal three-connected hcb Shubnikov hexagonal plane net, and a three-dimensional (3D) rod-packing network is further constructed through plane polycatenation via interlayer $\pi\cdots\pi$ stacking of adjacent aromatic rings (Figure 1b), leaving one-dimensional (1D) open channels. The methyl groups on the benzene core of H_3TBTC divide the channel of HIAM-102 into arrays of interconnected pockets $\sim 4.6 \text{ \AA}$ in diameter at the neck sites, which is close to the kinetic diameter of C_2H_6 (see Figure 1c, as well as Figure S3 in the Supporting Information). The methyl groups decorating the channel surface lead to the

hydrophobic character of the material, making it resistant to water, which will be discussed later.

The powder X-ray diffraction (PXRD) pattern of the as-synthesized HIAM-102 matches well with the simulated one, as shown in Figure S4 in the Supporting Information, demonstrating that the material was phase pure and well-crystallized. The HOF material is thermally robust and can be directly activated by heating at 120°C (see Figures S5 and S6 in the Supporting Information). To verify the chemical stability of HIAM-102, PXRD patterns were collected on samples immersed in several organic solvents (acetonitrile, ethanol, dichloromethane, and acetone), acid aqueous solutions (pH 1), and basic aqueous solutions (pH 12), and the results show that HIAM-102 remains intact in these solutions (see Figure S7 aqueous). It is noteworthy that HIAM-102 also possesses excellent water stability, confirmed by the unchanged PXRD patterns before and after the samples were soaked in water for three weeks (see Figure S8 in the Supporting Information).

As a result of the restricted pore aperture of HIAM-102, N_2 was barely adsorbed at 77 K. Instead, CO_2 adsorption at 273 K was performed to evaluate the porosity and pore size of HIAM-102 (Figure 2a). Its surface area and pore volume were calculated to be $191.05 \text{ m}^2/\text{g}$ and $0.10 \text{ cm}^3/\text{g}$, respectively, using the Dubinin–Astakhov method and the pore size was centered at 4.6 \AA established by the Horvath–Kawazoe method, well matching the pore aperture measured from crystal structure. Single-component adsorption isotherms of C_2H_6 and C_2H_4 for HIAM-102 were collected at 278, 288, and 298 K and up to 1 bar, as shown in Figure 2b, as well as Figure S9. HIAM-102 adsorbs $48.25 \text{ cm}^3/\text{g}$ of C_2H_6 at 1 bar and 298 K, higher than that of C_2H_4 ($44.39 \text{ cm}^3/\text{g}$) under identical conditions, showing a notable ethane-selective behavior. To evaluate the separation ability for $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ mixtures, ideal adsorbed solution theory (IAST) was used to determine the adsorption selectivity and the dual-site Langmuir–Freundlich

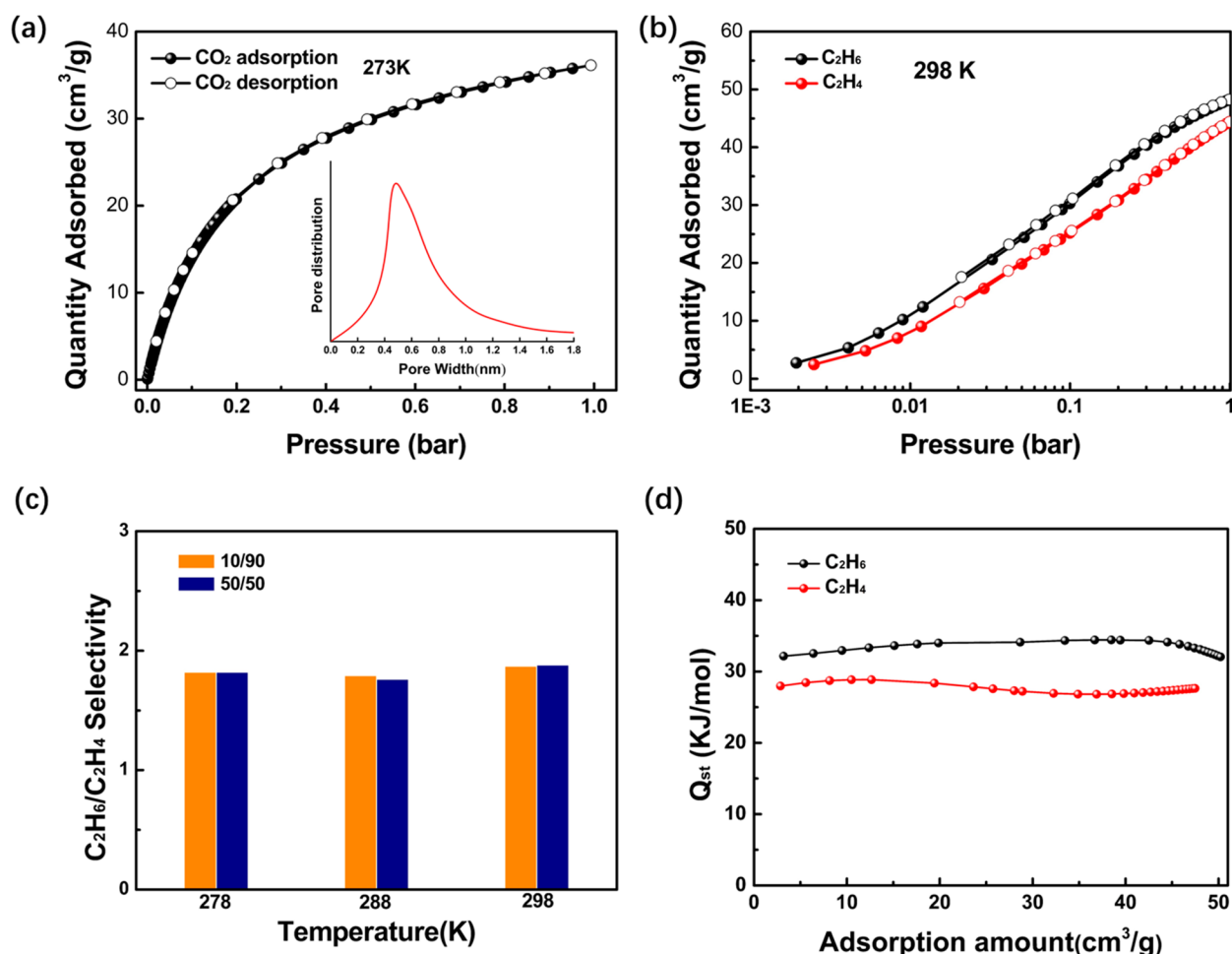


Figure 2. (a) CO₂ adsorption–desorption isotherms at 273 K (inset shows the pore distribution), (b) C₂H₆/C₂H₄ adsorption–desorption isotherms at 298 K, (c) IAST selectivity of C₂H₆/C₂H₄, and (d) adsorption heat of C₂H₆/C₂H₄ on HIAM-102.

fitting parameters are shown in Table S3 in the Supporting Information. The calculated selectivity at 298 K and 1 bar was 1.9, which is comparable to the benchmark HOFs for C₂H₆/C₂H₄ separation.^{19–22} The isosteric heat of adsorption (Q_{st}) for HIAM-102 was determined based on single-component adsorption isotherms obtained at 278, 288, and 298 K, using the Clausius–Clapeyron equation (Figure 2d). The Q_{st} value of C₂H₆ at zero coverage was 32.1 kJ/mol, which is higher than that of C₂H₄ (27.9 kJ/mol), suggesting that C₂H₆ has a relatively stronger interaction with the adsorbent than C₂H₄.

In practical application, water is an unavoidable component in feed gas. Most of the reported porous adsorbents, including zeolites, MOFs, and HOFs, are either structurally water-sensitive or prone to adsorbing water simultaneously and thus their separation capability would be largely lost under practical humidity conditions. Thus, adsorbents with hydrophobic pores are more favored for gas separation in the real world.^{21,25} HIAM-102 shows high hydrophobicity, evidenced by the negligible adsorption quantity of H₂O near saturation pressure, which was only 11.7 cm³/g, making it promising for gas adsorption and separation in a humid environment (see Figure 3d).

The volumetric adsorption capacity and ethane/ethylene selectivity of HIAM-102 is among the best HOFs reported for the separation of ethane and ethylene (see Figure S10 in the Supporting Information). Considering its hydrophobicity and

water resistance, HIAM-102 holds particular promise for the separation of the two gases, especially under humid conditions.^{19–22} The experimental breakthrough experiments for C₂H₆/C₂H₄ (50/50 and 10/90; v/v) were conducted on HIAM-102 at 298 K and 1 bar in dry and humid environments to evaluate its gas-separation performance. As shown in Figure 3a, with a feed of 10/90 mixture gas, which is closer to the proportion in industrial applications, C₂H₄ eluted before C₂H₆ with a retention time difference of 7.1 min, because of its preferential adsorption of C₂H₆ over C₂H₄. During this time duration, highly pure ethylene (99.99%+) can be produced directly from the outlet of the column with 5.3 L/kg in a single breakthrough cycle under dry atmosphere (Figure S11 in the Supporting Information). In order to simulate the humid environment in a practical process, feed gases with relative humidity (RH) values of 54% and 87% were used (see Figure 3a, as well as Figure S12 in the Supporting Information) and the mixture can be well-separated under both conditions, showing no notable loss in retention time difference (6.8 min) and ethylene productivity (5.2 L/kg; see Figure S13 in the Supporting Information) under 87% RH, compared to the results observed under dry conditions. The breakthrough curve in a humid environment showed longer breakthrough time, revealing that the adsorption dynamics was impacted by water. This should be attributed to the increased dependence on molecular mass transfer caused by saturation of water on the

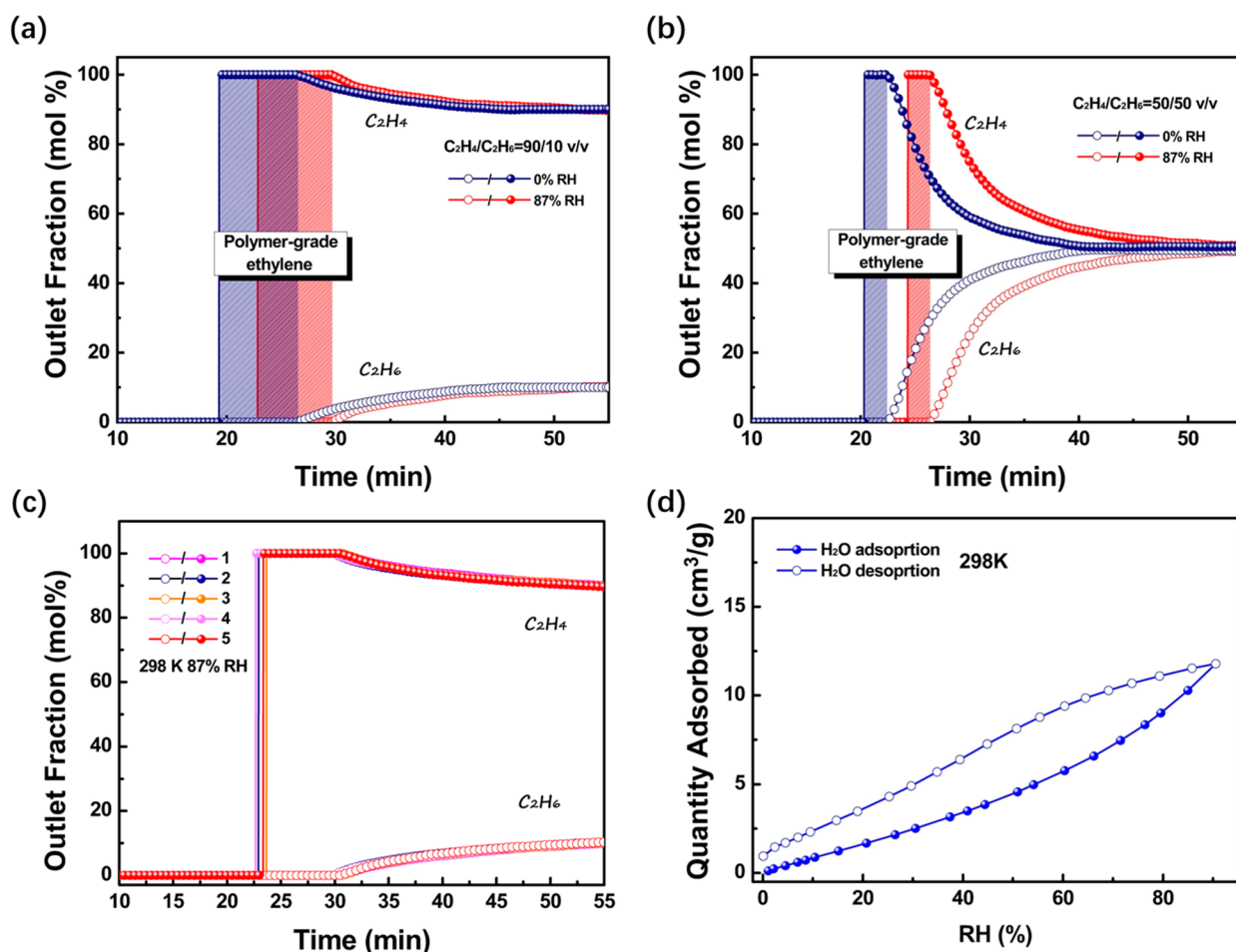


Figure 3. (a) Dynamic breakthrough curves for C_2H_6/C_2H_4 (50/50 and 10/90; v/v), under a dry atmosphere, (b) dynamic breakthrough curves for C_2H_6/C_2H_4 (50/50 and 10/90; v/v) under 87% RH atmosphere, (c) 5 cycles of dynamic breakthrough curves C_2H_6/C_2H_4 (10/90; v/v) under 87% RH atmosphere, and (d) water vapor adsorption and desorption isotherms at 298 K.

outer adsorbent layer.²⁶ We also studied the breakthrough performance with equimolar gas mixture on HIAM-102, and the results show that high-purity ethylene gas can be obtained in both dry and humid environments (Figure 3b). Note that this is the first example that C_2H_6/C_2H_4 separation is achieved in such an extremely humid environment.^{21,25,27,28} Benefitting from the low adsorption heat, HIAM-102 can be easily regenerated to recover its separation capacity by the He gas purging at 333 K for 1 h, and five consecutive breakthrough cycles under 87% RH (Figure 3c) revealed no loss of separation efficiency, indicating that the adsorbent is highly durable.

To further investigate the guest–host interaction and gain mechanistic insights, we performed ab initio calculations (see the Supporting Information for details). We started by loading C_2H_6 and C_2H_4 at various positions within the framework to determine the optimum binding site. The calculations suggest that both the C_2 hydrocarbons have a preferential binding spot locked between the hydrogen-bonded framework formed by the benzene carboxylic of the adjacent building blocks, as shown in Figure 4. The calculated binding energy for C_2H_6 is 57 kJ/mol, which is stronger than the 51 kJ/mol calculated for C_2H_4 . This stronger binding for C_2H_6 is in perfect agreement with our experimental adsorption results. Our induced charge density calculations also point toward the same direction, i.e., stronger interaction of C_2H_6 with the framework (see Figure

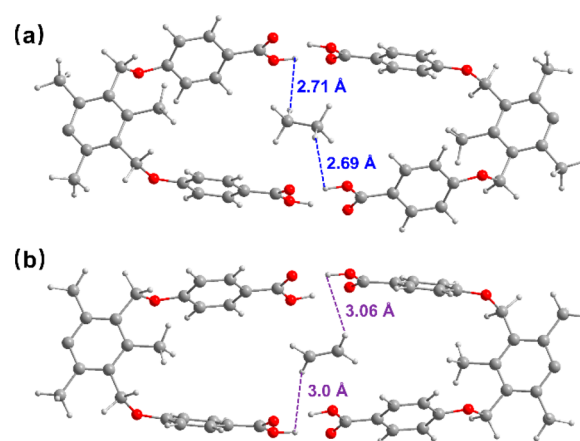


Figure 4. Optimized configuration of (a) C_2H_6 and (b) C_2H_4 in the channel of HIAM-102, from computational calculations.

S14 in the Supporting Information). C_2H_6 has a shorter distance from the framework, which is the reason for its stronger binding. It is found that the main interaction is via $H@C_2H_6/C_2H_4$ with the $-COOH$ of the HOF. The average $H@C_2H_6$ and $O@framework$ separation is ~ 2.79 Å, whereas the average $H@C_2H_4$ and $O@framework$ separation is as high as ~ 3.47 Å. The closest H (C_2H_6) to H (carboxylic acid) distance is 2.69 Å, while the value for C_2H_4 is 3.0 Å. This

shorter distance of C₂H₆ from the framework is the reason for its stronger interaction and, consequently, favorable binding.

In summary, we have developed an efficient HOF adsorbent for C₂H₆/C₂H₄ separation. HIAM-102 possesses a hcb structure topology with 1D channels decorated by methyl groups. HIAM-102 shows relatively high C₂H₆ uptake capacity (48.25 cm³/g), C₂H₆/C₂H₄ selectivity (1.9), and hydrophobicity with a low H₂O adsorption (11.7 cm³/g). Mixture breakthrough tests in humid environments (54% and 87% RH) confirmed the excellent C₂H₆/C₂H₄ separation performance of HIAM-102, which was unaffected by water vapor in the feed gas. This study may shed light on the design of HOFs with high gas separation efficiency under humid conditions.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.2c00370>.

Full details for experimental procedures, single-crystal X-ray crystallography, gas sorption and stability tests, breakthrough experiments, DFT calculation data, and crystallographic data for HIAM-102 (CCDC No. 2151662) (PDF)

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Notes

The authors declare no competing financial interest.

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