Supporting Information

Fine Tuning and Specific Binding Sites with a Porous Hydrogen-Bonded Metal-Complex Framework for Gas Selective Separations

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Gas adsorption measurements

Gas adsorption measurements were performed volumetrically in a Micromeritics ASAP 2050 adsorption apparatus. The adsorption isotherms were obtained at temperatures from 273 K to 298 K and gas pressures from 0 to 826 mmHg. About 150 mg sample was used for the gas adsorption studies. The initial outgassing process was carried out under a vacuum at room temperature for 12 h. The free space of the system was determined by using the helium gas. The degas procedure was repeated on the same sample between measurements for 12 h. Ultrahigh purity grade helium (99.999%), acetylene (>99%), ethylene (99.99%), carbon dioxide (99.99%), and nitrogen (99.99%) were purchased from Jingong Co., Ltd. (China).

The as-synthesized HOF-21 was exchanged with methanol several times and activated at 298 K for 24 h under high vacuum up to 6 μ mHg before BET and gases adsorption studies. The standard BET analysis is typically performed for a pressure range of 0.05 < P/P₀ < 0.3, however, microporous materials show saturation well below the standard range. To choose the pressure range appropriate for a particular adsorbent and to avoid ambiguity when reporting the BET surface area, four consistency should be followed.¹

Experimental data on pure component isotherms for gases including acetylene, ethylene and carbon dioxide were measured at temperatures of 273 K and 298 K while hydrogen was measured at temperature 298 K. The pure component isotherm data were fitted with the dual-site Langmuir- Freundlich isotherm model:

$$\mathbf{N} = A_1 \frac{b_1 p^{c_1}}{1 + b_1 p} + A_2 \frac{b_2 p^{c_2}}{1 + b_2 p}$$

The fitted parameter values are presented in Table S1.

Isosteric heat of adsorption

Zero-coverage isosteric heat of adsorption gives an indication of the strength of the strongest binding sites within the material, which can subsequently be attributed to certain chemical features of the pore surface.² The zero-coverage isosteric heat of adsorption was evaluated by first fitting the temperature-dependent isotherm data to a Virial equation, which can be written as:

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

The isosteric heat of adsorption can then be evaluated using the following expression:

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

The fitted parameter values are presented in Table S2.

Column breakthrough experiments

In a typical experiment, 793.3 mg of HOF-21a (or 687.3 mg of MPM-1-TIFSIX) powder was packed into a column (4.6 mm I.D. × 50 mm). The packed HOF-21 and MPM-1-TIFSIX sorbents were activated in Micromeritics ASAP 2050 adsorption apparatus at 298 K under high dynamic vacuum (6 μ mHg), respectively. Column packing was conducted in glovebox filled with Argon. A helium flow (5 cm³/min) was introduced into the column to further purge the adsorbent. The flow of helium was then turned off while a gas mixture of C₂H₂/C₂H₄ (50:50, *v/v*) at 0.20 cm³/min was allowed to feed into the column. The absolute adsorbed amount of gas *i* (*q_i*) is calculated from the breakthrough curve by the equation:

$$q_i = \frac{F_i \times t_0 - V_{dead} - \int_0^{t_0} F_e \Delta t}{m}$$

where F_i is the influent flow rate of the specific gas (cm³/min); t_0 is the adsorption time (min); V_{dead} is the dead volume of the system (cm³); F_e is the effluent flow rate of the specific gas (cm³/min); and *m* is the mass of the sorbent (g). The separation factor (α) of the breakthrough experiment is determined as

$$\alpha = \frac{q_1}{q_2} \times \frac{y_2}{y_1}$$

where y_i is the molar fraction of gas *i* in the gas mixture.



Figure S1. Comparison of the calculated and experimental PXRD patterns for HOF-21 samples.



Figure S2. (a) Thermogravimetric analysis curves of HOF-21 and (b) Thermogravimetric analysis curves of activated HOF-21a samples at different temperatures.

The TGA analysis of HOF-21 under a nitrogen flow reveals a mass loss of 6.62% between 50 and 110 °C. This is attributed to the loss of guest molecules from the framework. A mass loss of 3.84% between 110 and 210 °C due to the loss of two water molecules that is coordinated to the paddle wheel center (calc. mass loss 3.64%). The loss of adenines happens at temperature over 210 °C. Additionally, it can be found from Fig. 2b that HOF-21a samples degassed at temperature below 353 K show no loss of two water molecules that is coordinated to the paddle wheel center.



Figure S3. CO₂ isotherm at 196 K and N₂ isotherm at 77 K collected on HOF-21a.



BET surface area for the activated HOF-21 at 298 K :

 $S_{BET} = \frac{1}{22414 \times (0.01346 + 0.0000220406)} \times 6.023 \times 10^{23} \times 0.170 \times 10^{-18}$ $= 339 \ m^2/g$

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Figure S4. Comparison of CO₂ isotherms at 196 K collected on the room temperature-activated HOF-21a (parent material), collapsed HOF-21 (green), salt-treated HOF-21 (red) and water-treated HOF-21 (orange) after activation at 423 K.



HOF-21 sample activated under 423 K :

$$S_{BET} = \frac{1}{22414 \times 1} \times 6.023 \times 10^{23} \times 0.170 \times 10^{-19} = 4.57 m^2/g$$



HOF-21 sample activated under 423 K and then soaked in pure water for 48 h :

 $S_{BET} = \frac{1}{22414 \times (0.01583 + 0.0000353964)} \times 6.023 \times 10^{23} \times 0.170 \times 10^{-19}$ $= 288m^2/g$



HOF-21 sample activated under 423 K and then soaked in (NH₄)₂SiF₆ aqueous solution for 48 h :

$$S_{BET} = \frac{1}{22414 \times (0.01436 + 0.0000454008)} \times 6.023 \times 10^{23} \times 0.170 \times 10^{-19}$$
$$= 317m^2/g$$



Figure S5. CO₂ isotherms at 196 K collected on room temperature-activated MPM-1-TIFSIX (parent material), 473 K-activated (green), and salt-treated MPM-1-TIFSIX (red) and water-treated MPM-1-TIFSIX (orange) after activation at 473 K.



Figure S6. Comparison of PXRD patterns of MPM-1-TIFSIX between the calculated and those for the as-synthesized, collapsed, and soaked in water and $(NH4)_2 TiF_6$ aqueous solution.

Adsorbates	A ₁ (mmol/g)	b ₁ (kPa ⁻¹)	c ₁	A ₂ (mmol/g)	b ₂ (kPa ⁻¹)	c ₂
C ₂ H ₂ (273K)	1.591262	1.334531	1.074642	2.005099	0.030995	0.71109
C ₂ H ₂ (298K)	1.496942	0.408414	0.939489	2.384335	0.010531	0.71485
C ₂ H ₄ (273K)	0.77763	0.028953	1	1.136573	0.723643	1
C ₂ H ₄ (298K)	1.281654	0.003424	1	0.996413	0.15917	1
N ₂ (298K)	0.070669	0.035951	1.056077	0.688071	0.000841	1.3581

Table S1. Equation parameters for the Dual-site Langmuir-Freundlich isotherm model of HOF-21a.

Table S2. Coefficients a_i (i = 0, 1, 2, 3, 4, 5) for fitting the temperature-dependent isotherm data of 273 K and 298 K on C₂H₂ to the Virial equation of HOF-21a and MPM-1-TIFSIX

Adsorbent	a ₀	a ₁	a ₂	a ₃	a ₄	a ₅
HOF-21a	-4315.01	-2.68	-1.09	-2.52e-4	-2.52e-04	4.24e-07
MPM-1- TIFSIX	-3574.71	3.54	-0.092	1.97e-04	-6.74e-07	1.82e-09

References

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2. Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T. H.; Long, J. R., Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* 2012, 112 (2), 724-81.