

Supporting Information

Aromatic pore surface with multiple adsorption sites for one-step C₂H₄ acquisition from C₂H₆/C₂H₄ mixture

Yongqin Zhu^{a,b}, Zhenyu Ji^{a,b}, Yunzhe Zhou^a, Mingyan Wu^{a,c,d}*

^a State Key Lab of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

^b College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China

^c University of Chinese Academy of Sciences, Beijing, 100049, China

^d *Fujian College, University of Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China.*

*Correspondence and requests for materials should be addressed to M.W. (E-mail: wumy@fjirsm.ac.cn).

Calculation of selectivity via IAST

Single-site Langmuir-Freundlich (SSLF) model was used to fit the adsorption isotherm of C₂H₄ and C₂H₆:

$$N = A_1 \frac{B_1 p^{c_1}}{1 + B_1 p^{c_1}}$$

Where N represents the adsorption capacity of gas, the unit is mmol/g; P represents pressure, the unit is atm; A₁ is the saturated adsorption capacity of different adsorption sites, the unit is mmol/g; B₁ is Langmuir index; c₁ is the Freundlich index.

Then, according to the ideal gas solution adsorption theory (IAST), the adsorption selectivity of C₂H₆/C₂H₄ (1/99, v/v) was calculated:

$$S_{ads} = \frac{x_1/x_2}{p_1/p_2}$$

Calculation of isosteric enthalpy of adsorption (Q_{st})

The isotherms of C₂H₄ and C₂H₆ at 298 K and 273 K are fitted to the Virial equation (Eqn(1)). Then the isovolumetric heat of adsorption (Q_{st}) was calculated by Eqn(2) using the fitting parameters.

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{j=0}^m b_j N^j \quad (1)$$

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

Where P represents pressure, the unit is mmolHg; N represents the adsorption capacity, and the unit is mmol·g⁻¹. T stands for temperature, the unit is K; a and b are adsorption correction coefficients; R represents the ideal gas constant, 8.314 J·mol⁻¹·K⁻¹.

Calculation of Separation Potential

The separation potential (Δq) is a combined metric, which considering both uptake capacity and selectivity. It is defined to quantify mixture separations in fixed bed adsorbers. Δq is defined as $q_1 y_2 / y_1 - q_2^{1-3}$, where the q_1 and q_2 represent the molar loadings within the MOF that is in equilibrium with a bulk gas phase mixture with mole fractions y_1 , and $y_2 = 1 - y_1$. The physical significance of Δq is that it represents the maximum amount of pure gas that can be recovered during the adsorption phase of fixed bed separations.

Computational details

The binding sites for C₂H₄ and C₂H₆ in Ni-3-F were determined through classical molecular simulations. The single X-ray crystallographic structures were subject to geometry optimization through the CASTEP module implemented with the Materials Studio program, using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional and the double numerical plus d-functions (DNP) basis set. The energy, force, and displacement convergence criteria were set as 1×10^{-5} Ha, 2×10^{-3} Ha/Å and 5×10^{-3} Å, respectively. The calculated electrostatic potential for Ni-3-F was mapped onto the Connolly surface with a probe radius of 1.0 Å. Simulated annealing (SA) calculations were performed for a single molecule of C₂H₄ and C₂H₆ through a canonical Monte Carlo (NVT) process, and all MOF atoms were kept fixed at their positions throughout the simulations. The initial configurations were further optimized to ensure a more efficient energy landscape scanning for every MOF-C_xH_x complex, and the optimized configuration having the lowest energy was used as the global minimum for the subsequent analysis and calculation. The static binding energy (at T= 0 K) was then calculated: $\Delta E = E_{\text{MOF}} + E_{\text{gas}} - E_{\text{MOF+gas}}$.

Calculation of C₂H₄ production

$$N_{C_2H_4} = FC_i t_i = \frac{F \times y_{C_2H_4} \times \int_{t_1}^{t_2} \left(\frac{C(t)}{C_0}\right) dt}{m} = \frac{F \times y_{C_2H_4} \times S}{m}$$

F refers to the flow rate of the gas mixture, $y_{C_2H_4}$ refers to the molar fraction of C₂H₄, and m refers to the mass of the adsorbent. S refer to the area of the highlight region in breakthrough curve.

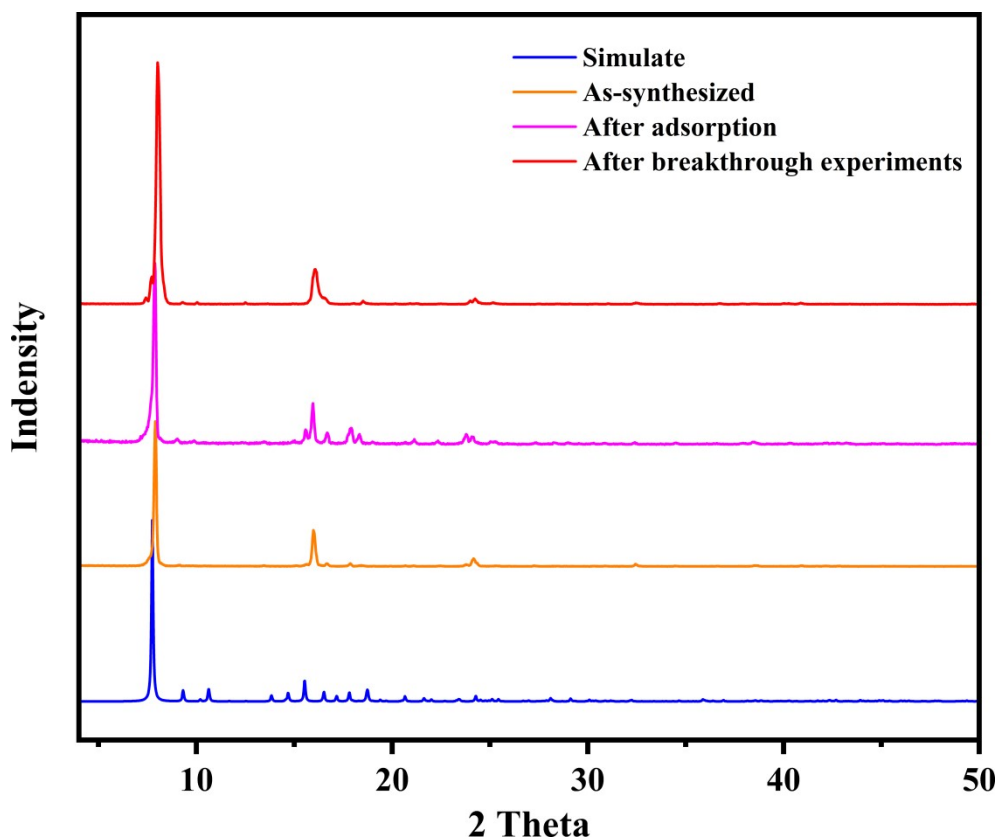


Figure S1. The Powder X-ray diffraction (PXRD) patterns for simulate, as-synthesized, after adsorption and after the breakthrough experiments Ni-3-F.

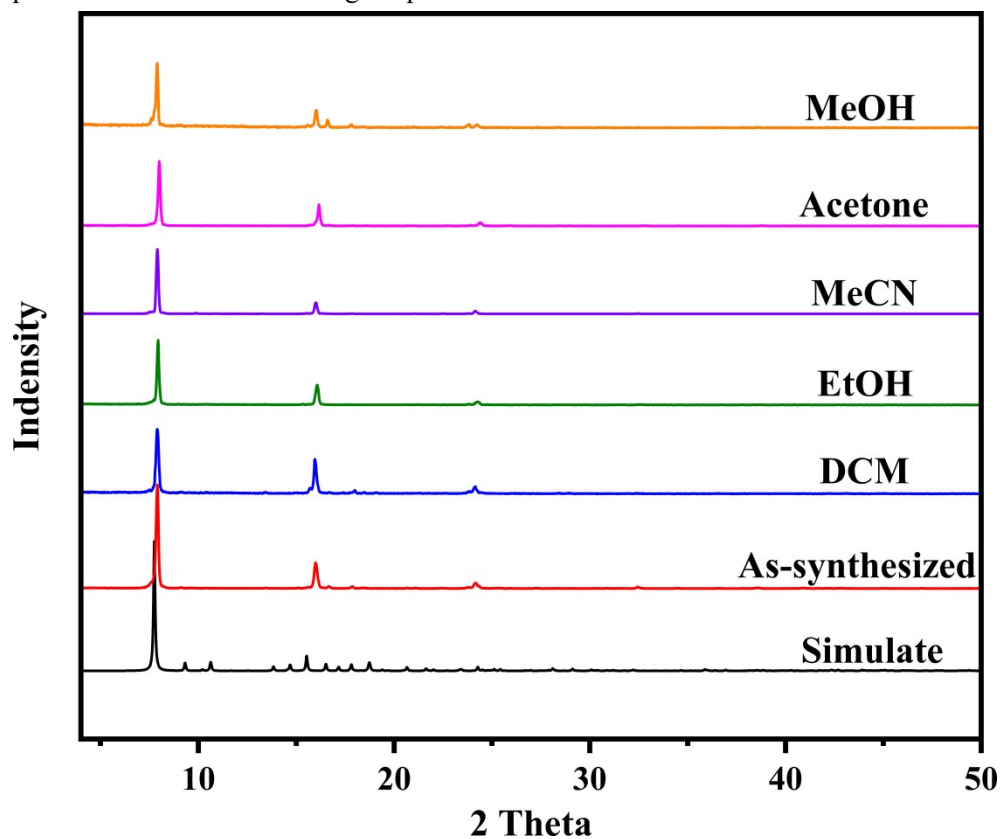


Figure S2. PXRD patterns of Ni-3-F after soaking in different solvents.

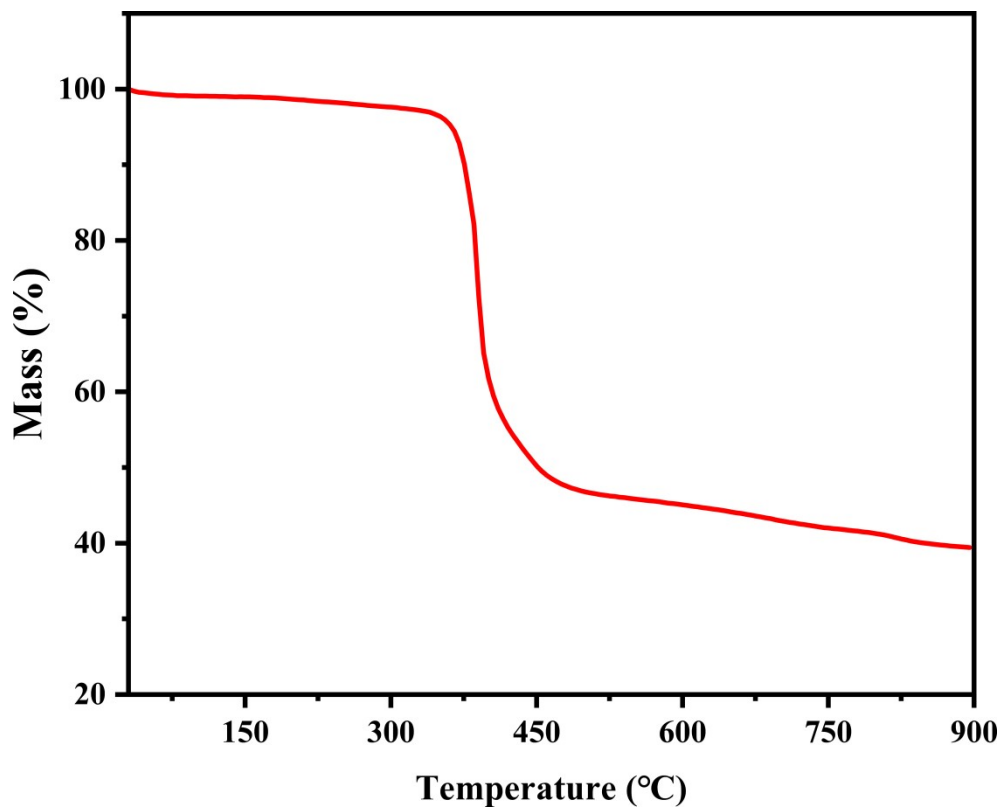


Figure S3. TGA curves of Ni-3-F.

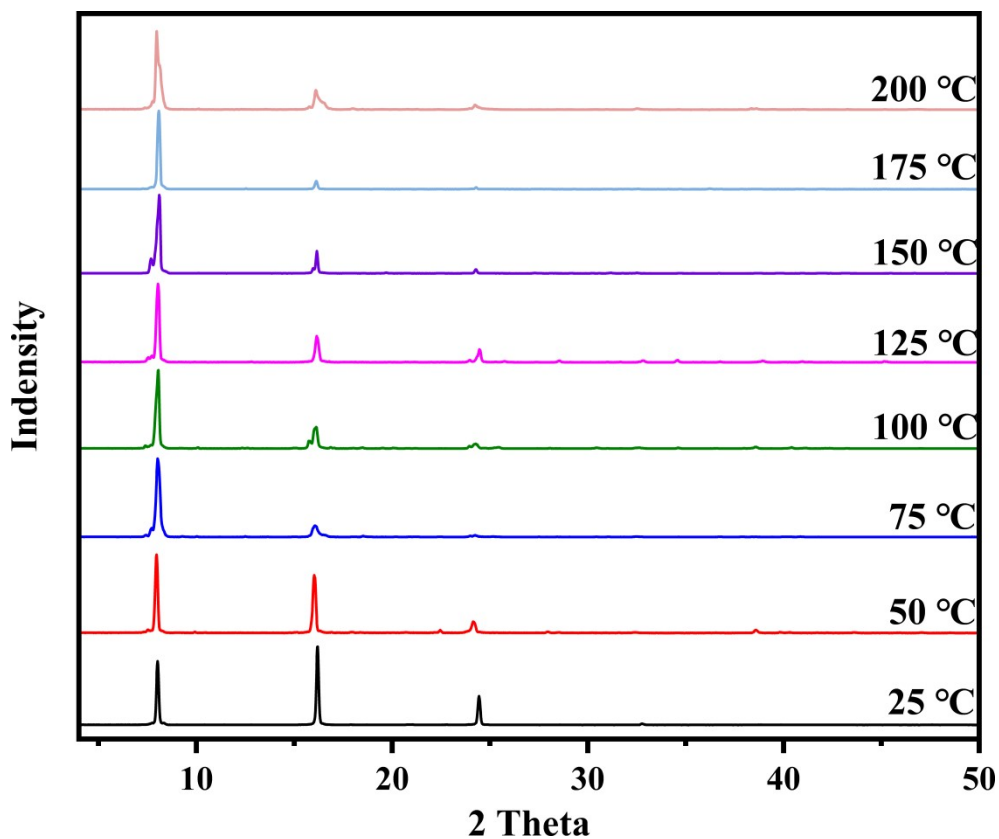


Fig. S4. VT-PXRD patterns of Ni-3-F measured in the air atmosphere.

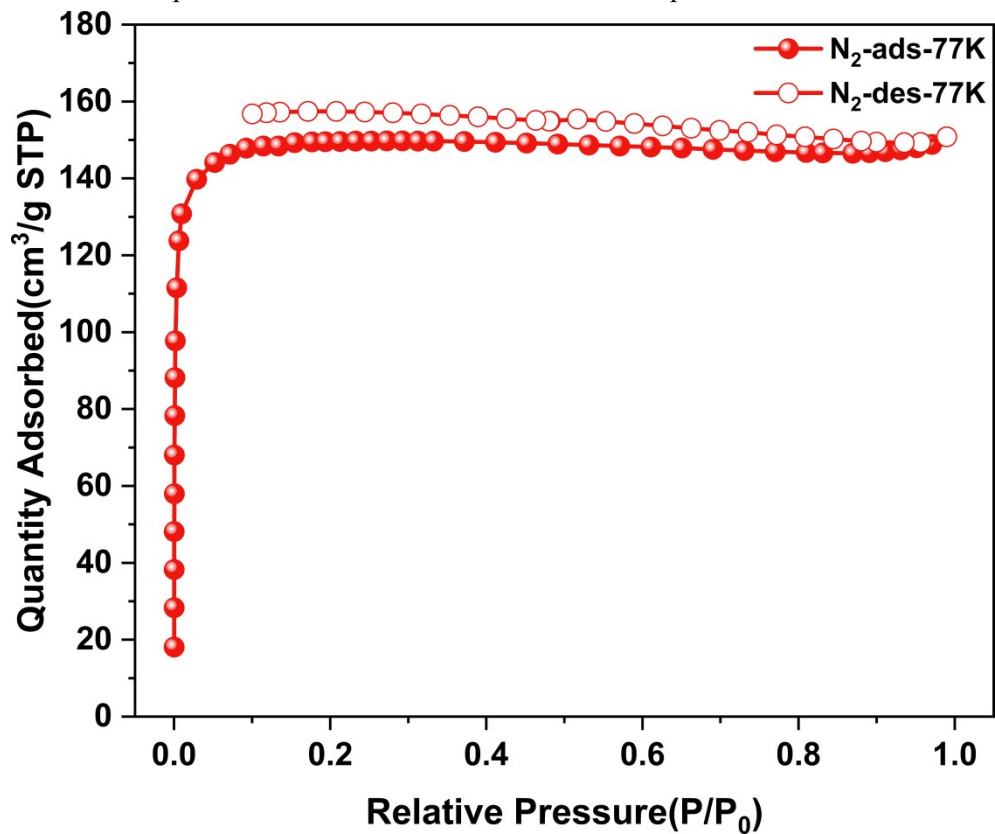


Figure S5. N₂ isotherms at 77 K of Ni-3-F.

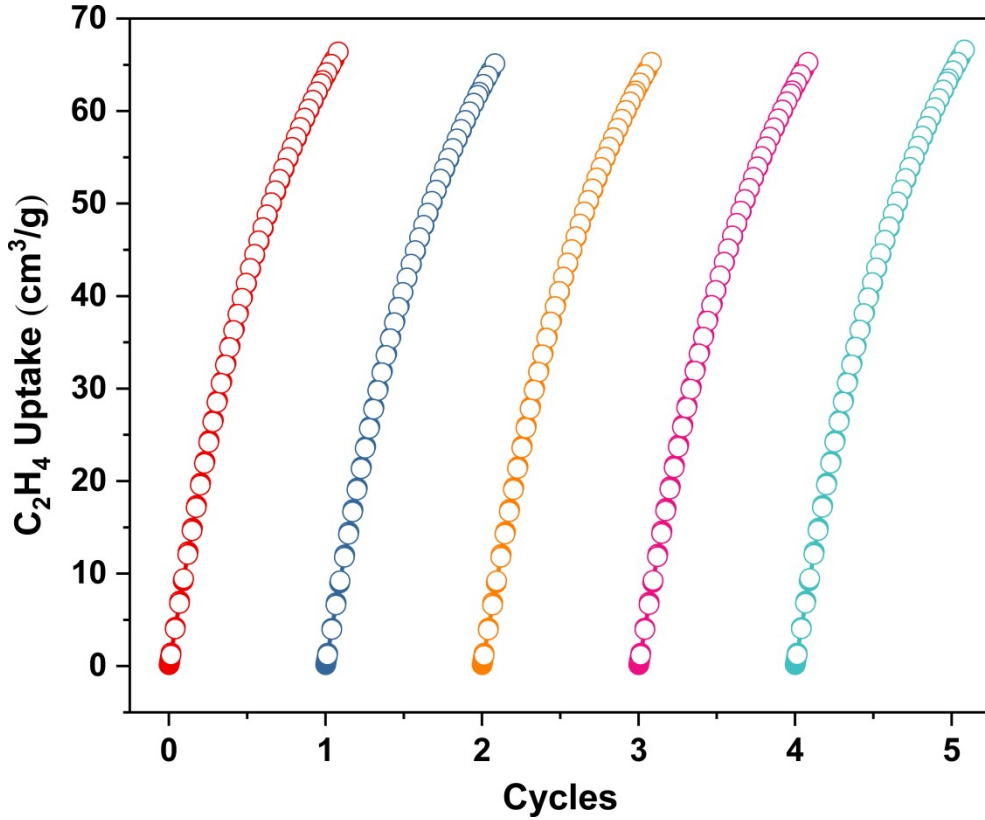


Figure S6. Five cycles C₂H₄ adsorption isotherms at 298 K.

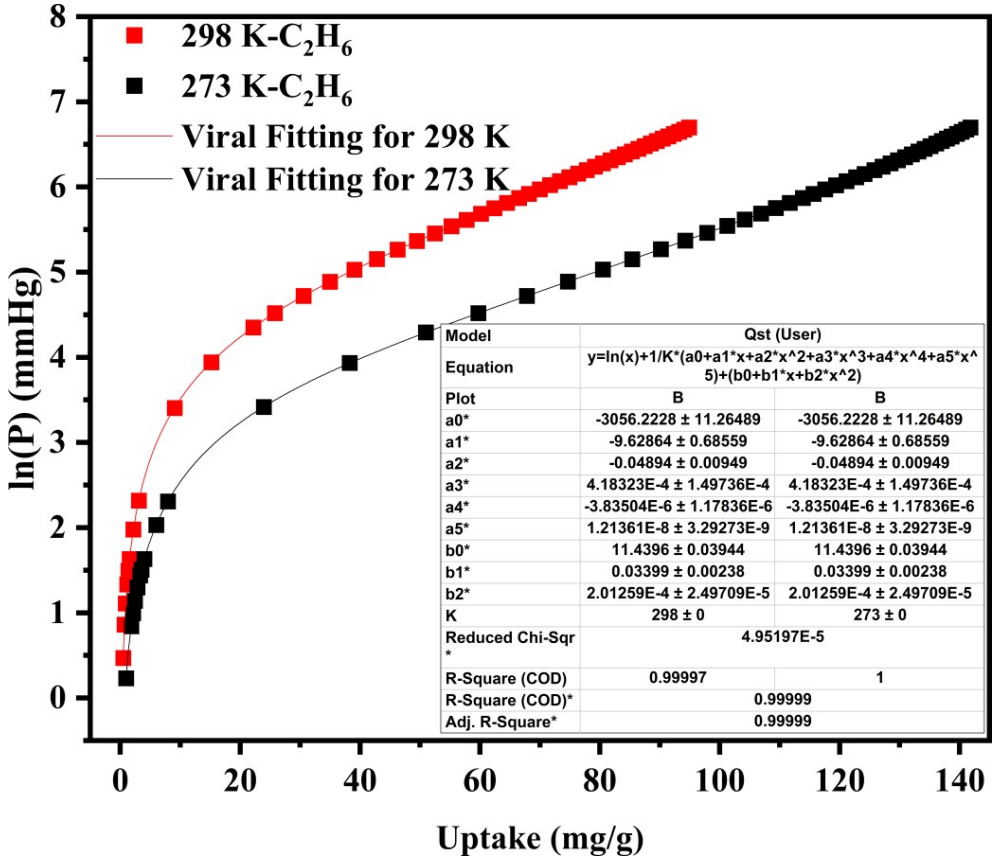


Figure S7. Fitting curve and calculated fitting parameters of C₂H₆.

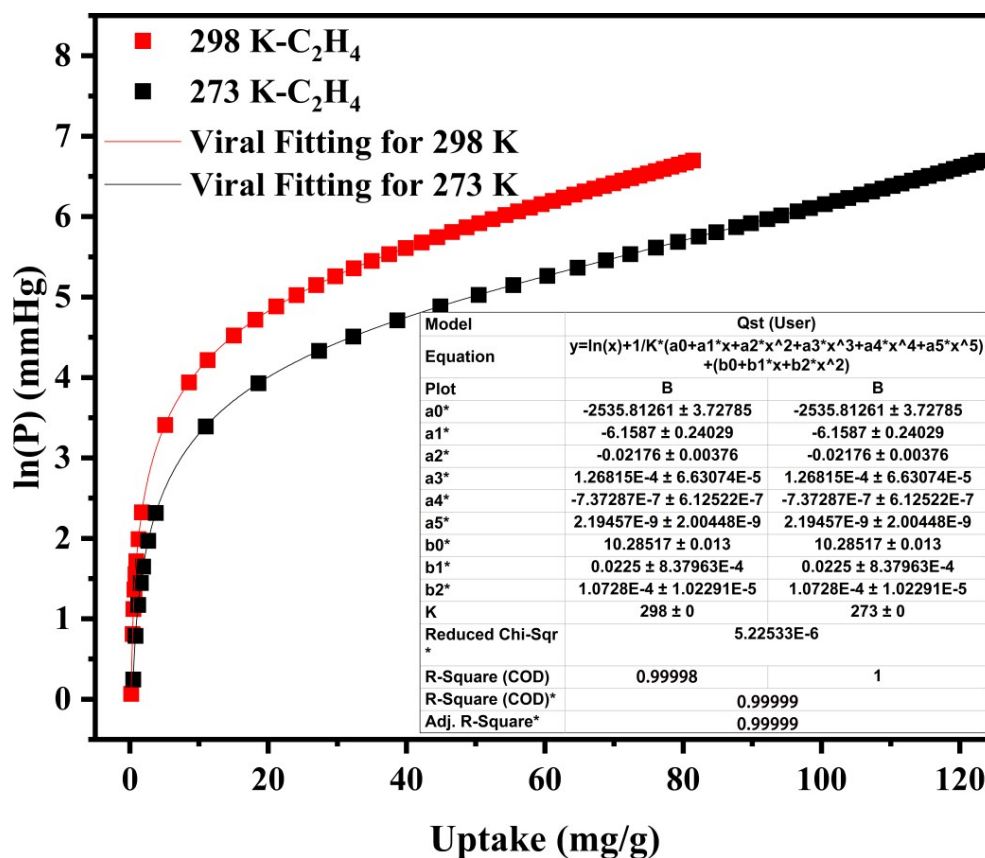


Figure S8. Fitting curve and calculated fitting parameters of C₂H₄.

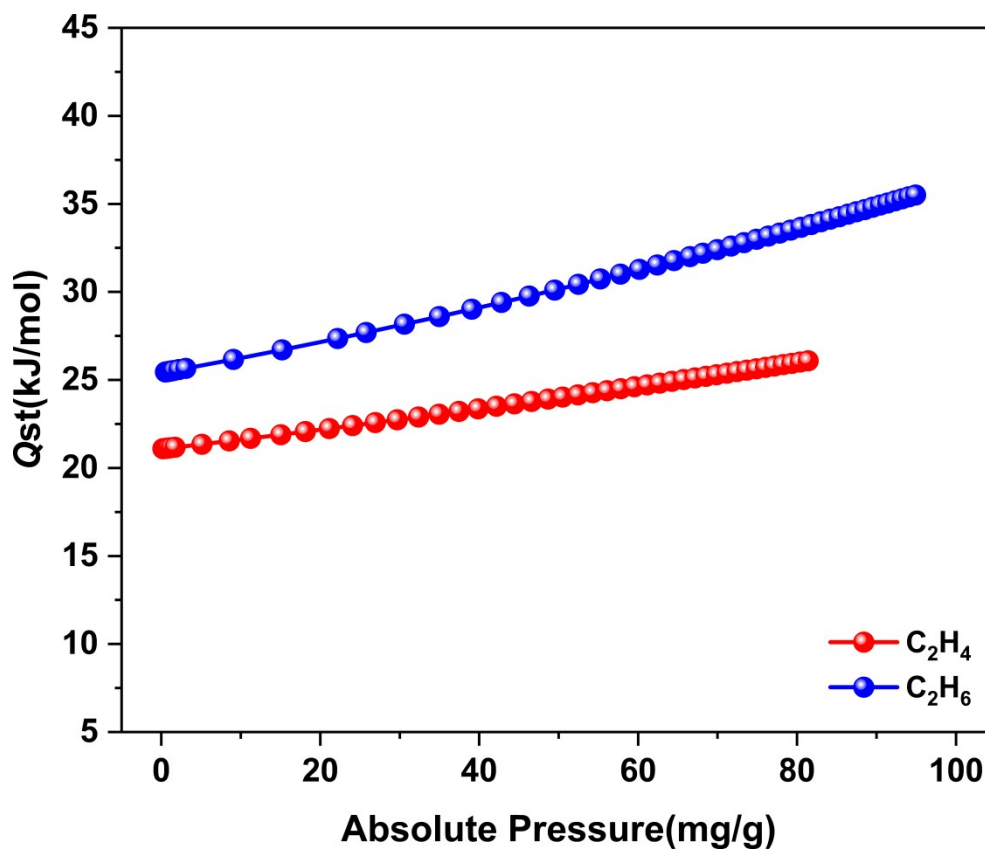


Figure S9. The calculated Q_{st} of Ni-3-F for C_2H_6 (blue) and C_2H_4 (red) respectively.

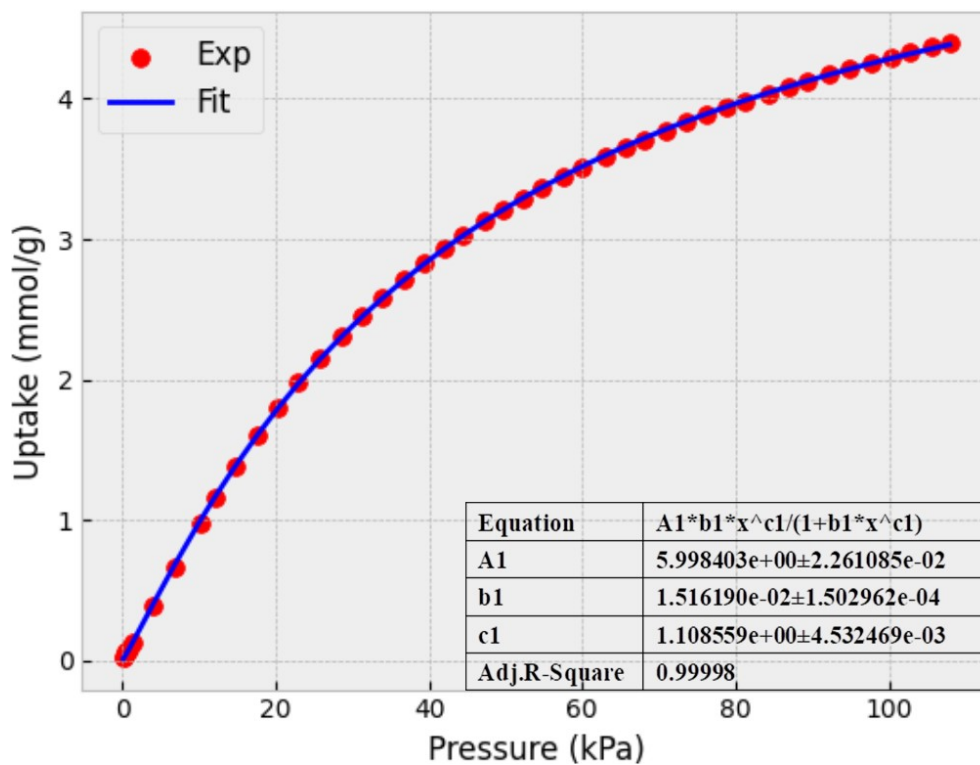


Figure S10. C_2H_4 adsorption isotherms fitting by SSLF model at 273 K.

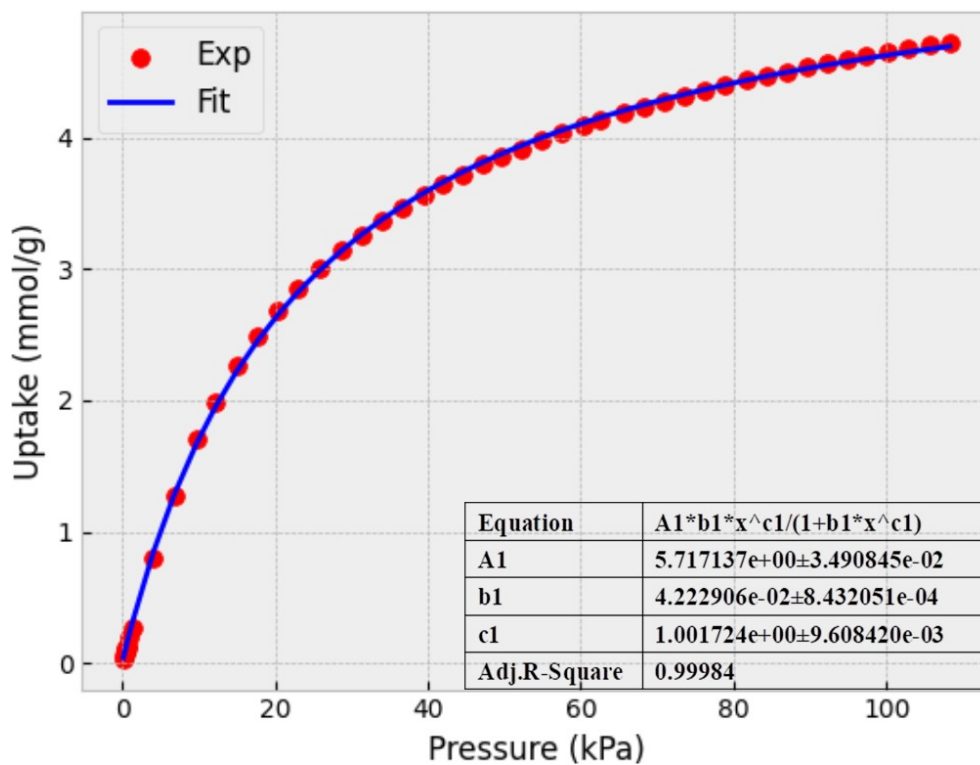


Figure S11. C_2H_6 adsorption isotherms fitting by SSLF model at 273 K.

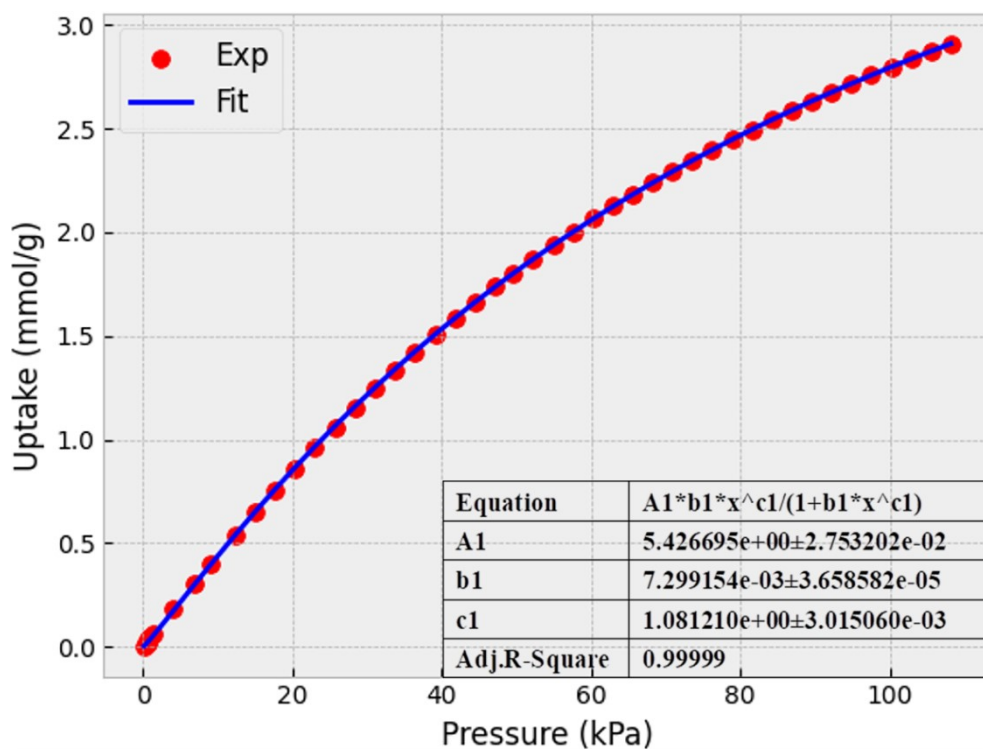


Figure S12. C₂H₄ adsorption isotherms fitting by SSLF model at 298 K.

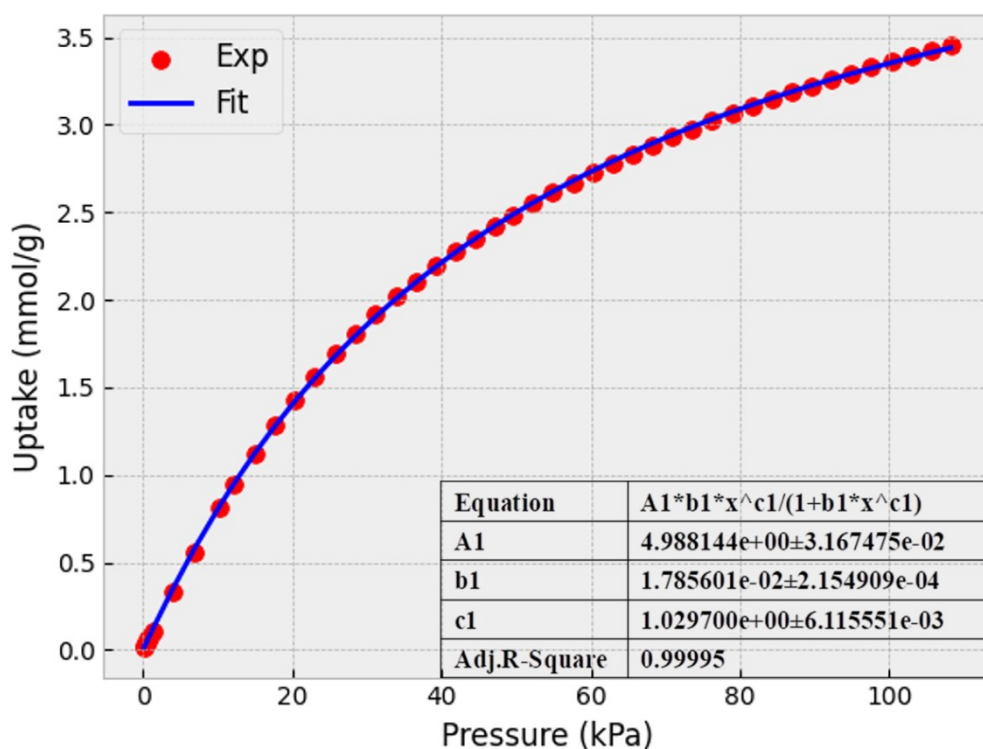


Figure S13. C₂H₆ adsorption isotherms fitting by SSLF model at 298 K.

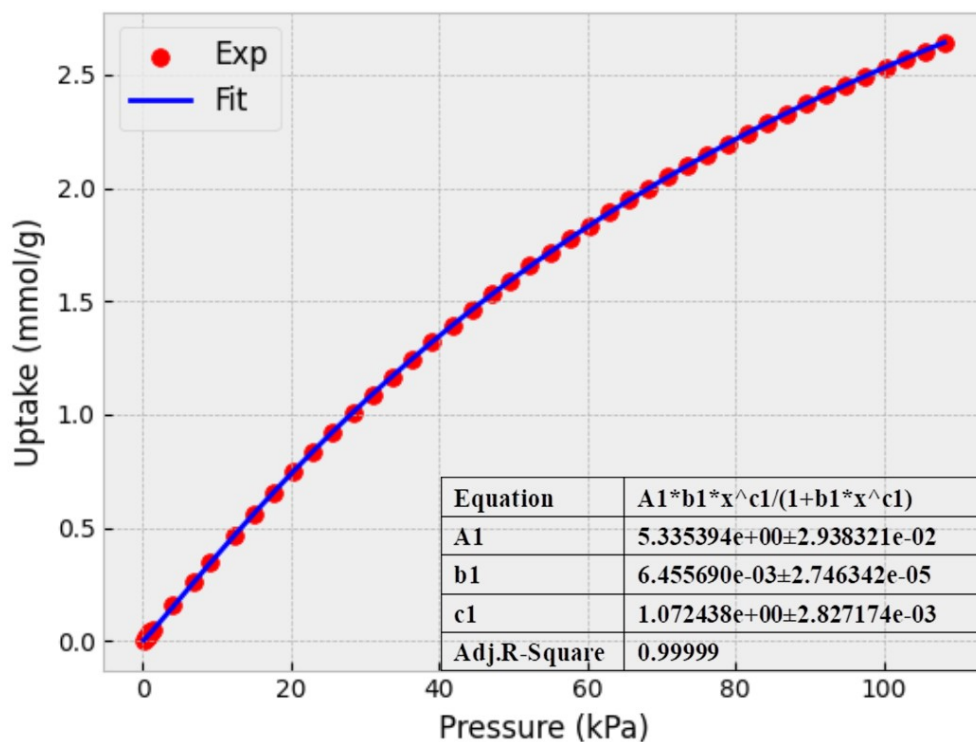


Figure S14. C₂H₄ adsorption isotherms fitting by SSLF model at 303 K.

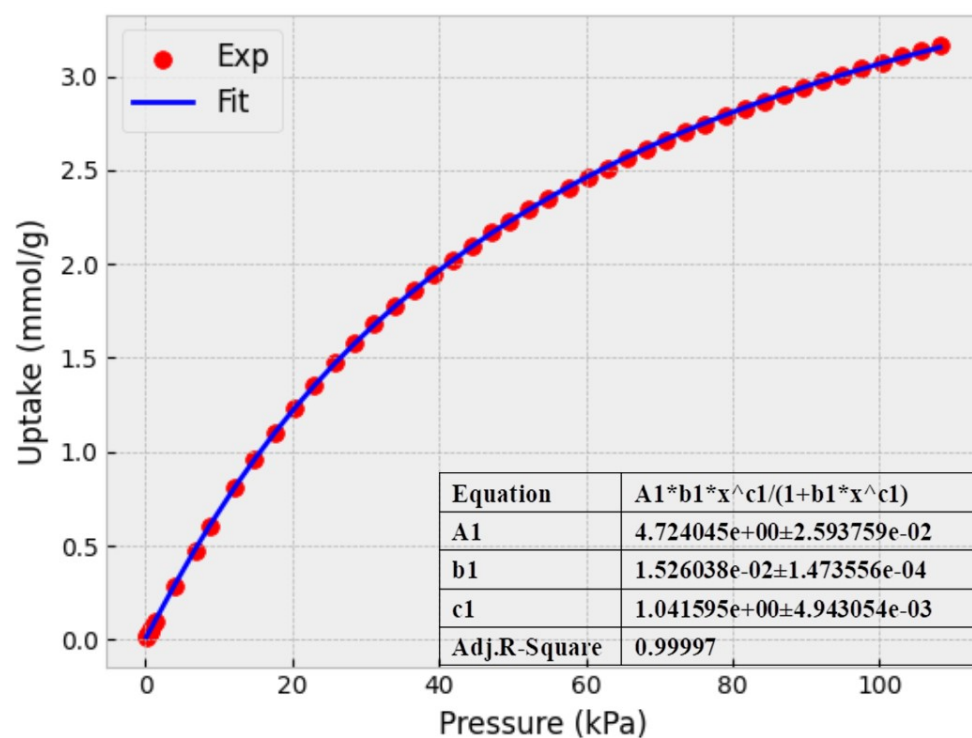


Figure S15. C₂H₆ adsorption isotherms fitting by SSLF model at 303 K.

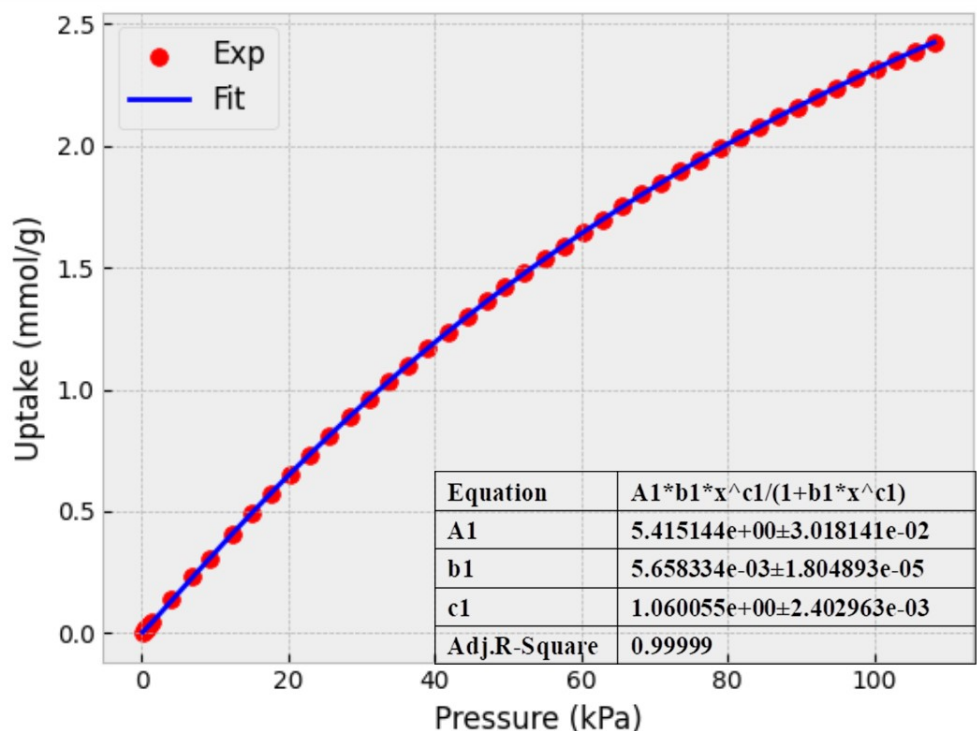


Figure S16. C₂H₄ adsorption isotherms fitting by SSLF model at 308 K.

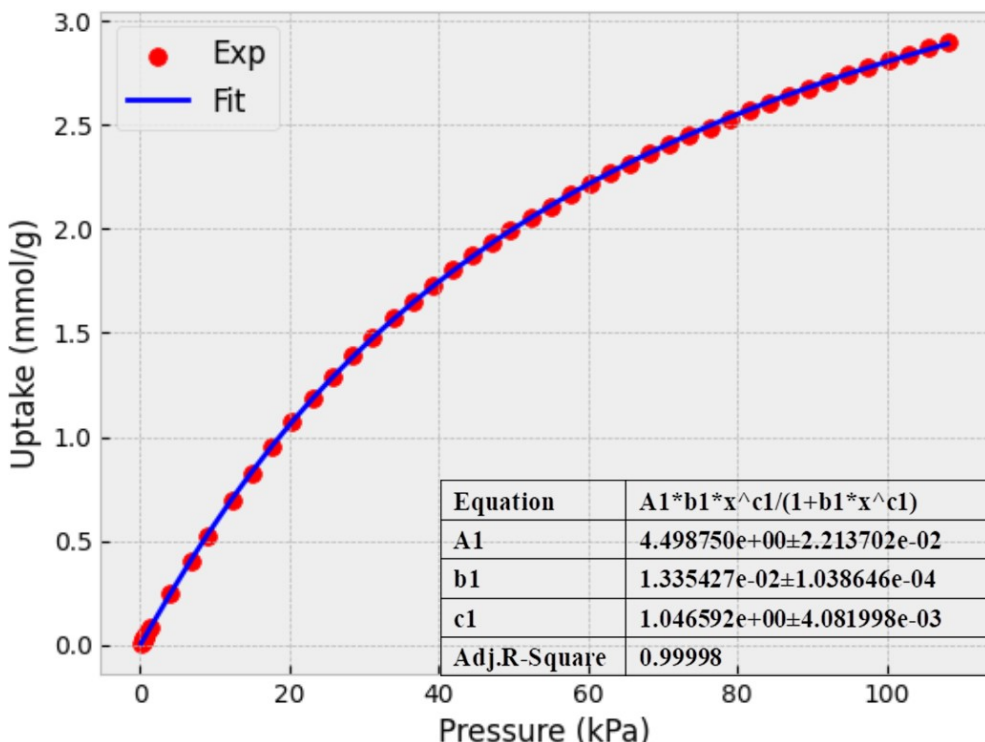


Figure S17. C₂H₆ adsorption isotherms fitting by SSLF model at 308 K.

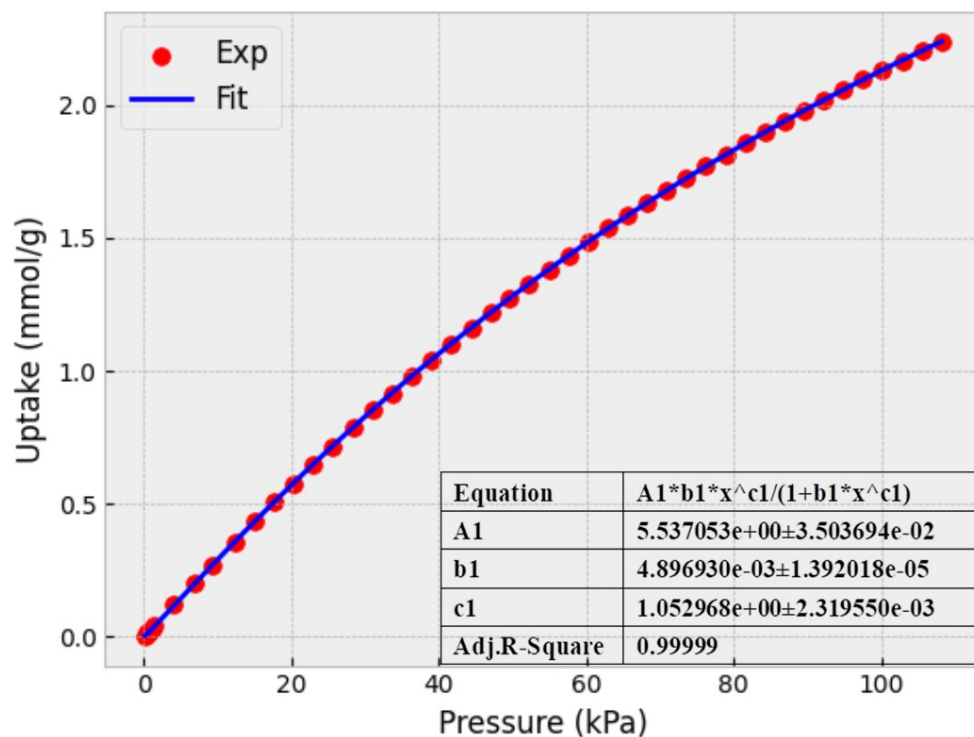


Figure S18. C₂H₄ adsorption isotherms fitting by SSLF model at 313 K.

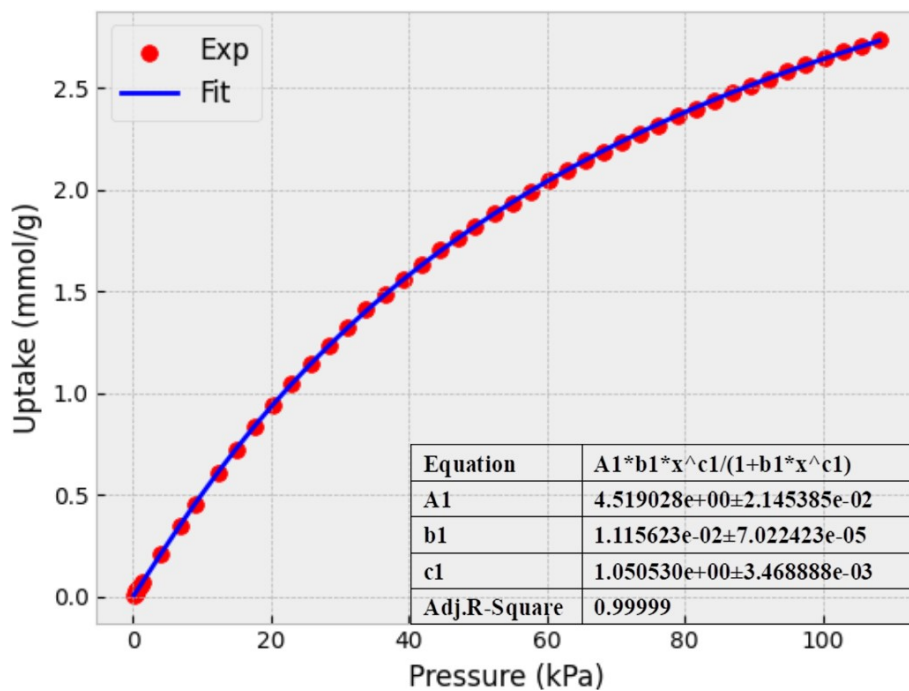


Figure S19. C₂H₆ adsorption isotherms fitting by SSLF model at 313 K.

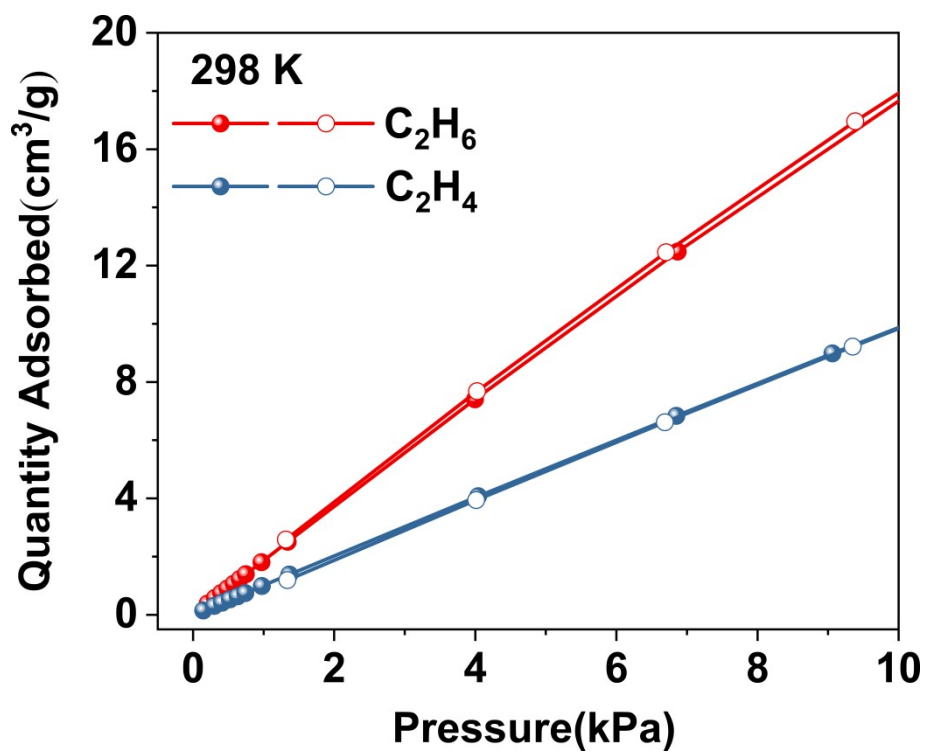


Figure S20. The comparison of C₂H₆ and C₂H₄ isotherms of Ni-3-F at 298 K in the 0-10 kPa pressure range.

Table S1. Crystal data and structure refinements for Ni-3-F.

Compound	Ni-3-F
CCDC	2369828
Empirical formula	C ₂₄ H ₁₂ F ₂ N ₂ NiO ₄
Formula weight	489.05
Temperature (K)	100
Crystal system	orthogonality
Space group	Pnna
Unit cell dimensions (Å, deg)	a = 17.2804 (4), α = 90
	b = 12.1294 (3), β = 90
	c = 15.2030 (3), γ = 90
Volume (Å ³)	3186.56
Z	8
Density (calculated) (g/m ³)	1.024
Absorption coefficient (mm ⁻¹)	1.191
F ₀₀₀	1000
θ for data collection (deg)	4.664 to 76.419
Reflections collected	11649
Goodness-of-fit on F ²	0.985
Final R indexes [I > 2sigma(I)]	R ₁ =0.0639, wR ₂ =0.1899
Final R indexes [all data]	R ₁ =0.0678, wR ₂ =0.1940
Largest diff. peak / hole / (e Å ⁻³)	0.948 / -0.407

Table S2. Summary of adsorption capacity of C₂H₆ and C₂H₄, IAST (C₂H₆/C₂H₄ (1/99)) and separation potential (C₂H₆/C₂H₄ (1/99)) at different temperatures.

Temperatures	C ₂ H ₆ Uptake (cm ³ /g)	C ₂ H ₄ Uptake (cm ³ /g)	IAST	Separation potential (mmol/g)
273 K	105.89	98.58	1.86	3.64
298 K	77.44	65.13	1.80	2.21
303 K	70.93	59.13	1.76	1.90
308 K	64.98	54.28	1.72	1.64
313 K	61.39	50.11	1.69	1.45

References

- (1) PRAUSNITZ, A. L. M. a. J. M. Thermodynamics of Mixed-Gas Adsorption. *AIChE journal* **1965**, *11*, 121-130.
- (2) Krishna, R. Metrics for Evaluation and Screening of Metal–Organic Frameworks for Applications in Mixture Separations. *ACS Omega* **2020**, *5*, 16987-17004.
- (3) Krishna, R. Screening metal–organic frameworks for mixture separations in fixed-bed adsorbers using a combined selectivity/capacity metric. *RSC Advances* **2017**, *7*, 35724-35737.