Supporting Information

Reticular chemistry guided function customization: a case study of constructing low-polarity channel for efficient C_3H_6/C_2H_4 separation

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1. Calculation procedures of selectivity from IAST

The measured experimental data is excess loadings (q^{ex}) of the pure components C_3H_6, C_2H_6 and C_2H_4 for **ZJNU-401**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT} \quad \text{(S1)}$$

Here Z is the compressibility factor. The Peng-Robinson equation was used to estimate the value of compressibility factor to obtain the absolute loading, while the measure pore volume is also necessary.

In order to perform the IAST calculations, the single-component isotherm was fitted by the dual-site Langmuir-Freundlich (DSLF) adsorption model to correlate the pure-component equilibrium data and further predict the adsorption of mixtures. The DSLF model is described as:

 (S2)

Here p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol kg^{-1}), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol kg^{-1}), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), n_1 and n_2 are the deviations from an ideal homogeneous surface. To investigate the separation of binary mixtures, the adsorption selectivity is defined by

$$S_{ij} = \frac{x_1 / x_2}{y_1 / y_2} \quad \text{(S3)}$$

x_1 and x_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of x_1 and x_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

2. Theory calculations

Adsorption sites

The fixed loading task in Sorption module based on metropolis Monte Carlo method in MS 2020 was employed to determine the adsorption sites of acethylene, ethane and ethylene molecule at MOF of **ZJNU-401**. The Universal Force Field (UFF)[1] parameters were employed to describe the interaction between adsorbates and MOF. In present sorption process, the Metropolis algorithm was used to accept or reject a configurational move of considered molecules. 1000000 steps of Metropolis Monte Carlo calculations were carried out with the initial equilibration period of 100000 steps.

Binding energy

Binding energy between adsorbates (namely, ethane, ethylene and propylene) and MOF was calculated for low energy structure obtained from adsorption site calculation. All calculation was carried out by Forcite module with Universal Force Field (UFF)[2] parameters in Materials Studio (MS) 2020. After geometry optimization, the binding energies E_b were calculated according to the following equation[3]:

$$\Delta E = E_{\text{total}} - E_{\text{MOF}} - E_{\text{adsorbate}}$$

Where E_{total} is the total energy of the MOF structure with adsorbate adsorption, E_{MOF} is the energy of the isolated MOF and $E_{adsorbate}$ is the energy of one adsorbate, namely, ethane, ethylene or propylene.

3. Experimental Section

3.1 Materials and Measurements

All materials were purchased commercially and used without re-treatment processed. Powder X-ray diffraction (PXRD) data were operated on a Rigaku D/max-2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 298 K and collected data at a range of 3-40^{o} (2θ). The thermal gravimetric analysis (TGA) was carried out on

TGA Q500 at a range of 308 to 1073 K in the air atmosphere. With accompanying graphite-monoChromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Apex II CCD diffractometer, the Single crystal X-ray diffraction analysis was recorded at room temperature (CCDC: 2365428). The further crystallographic data of **ZJNU-401** was listed in the supporting information. Gas adsorption measurement was recorded on Autosorb iQ adsorption apparatus. 60 mg of sample of **ZJNU-401** was immersed in dehydrated methanol with frequent exchanges for 4 days, and degassed under vacuum at 373 K for 10 h. N_2 adsorption and desorption experiments were carried out at 77 K to characterize the pore environment. C_2H_4, C_2H_6 and C_3H_6 adsorption and desorption experiments carried out at 273/298/308 K. The temperature at 77 K was maintained with liquid nitrogen and other temperatures were controlled by a circulating water bath. Breakthrough experiments were performed at a commercial testing company.

4. Supporting Figures

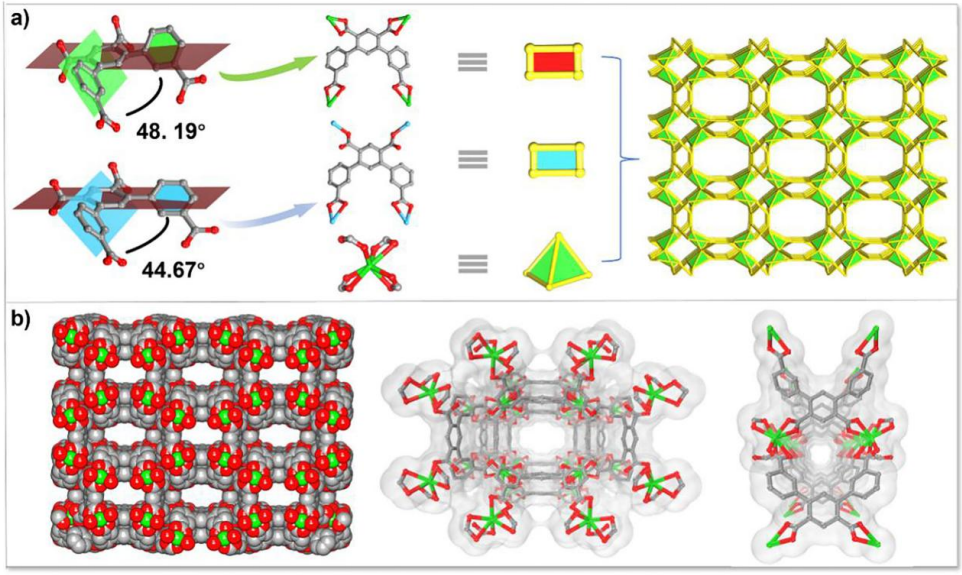

Fig. S1 Structural description of **ZJNU-401** (a) Simpliffcation of 4-connected SBUs and polyhedron view; (b) CPK view and their pore environment.

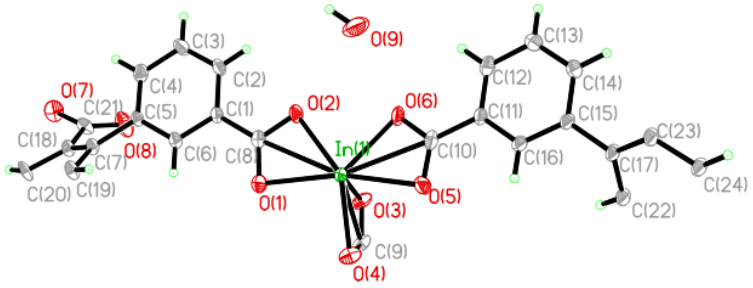

Fig. S2 The thermal ellipsoid diagrams of the crystal structure to illustrate the asymmetric unit.

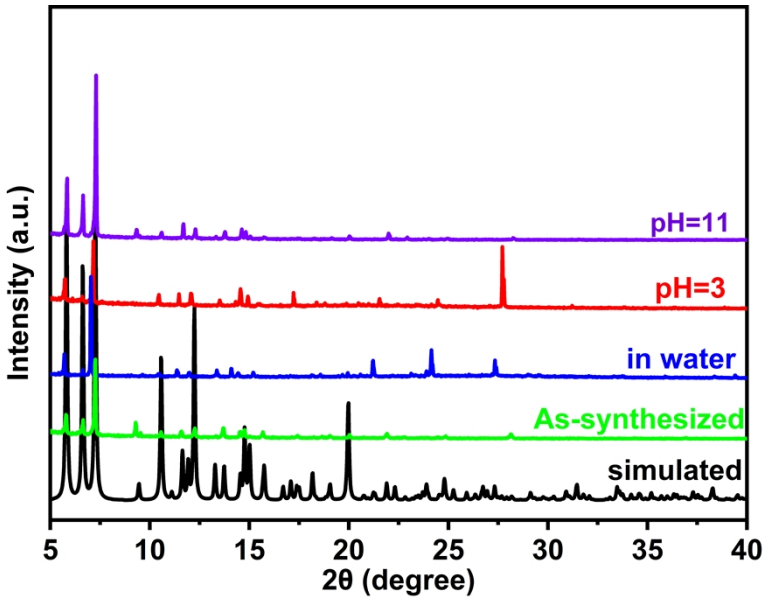

Fig. S3 PXRD patterns of **ZJNU-401** immersed in different acid-base aqueous solution for three days.

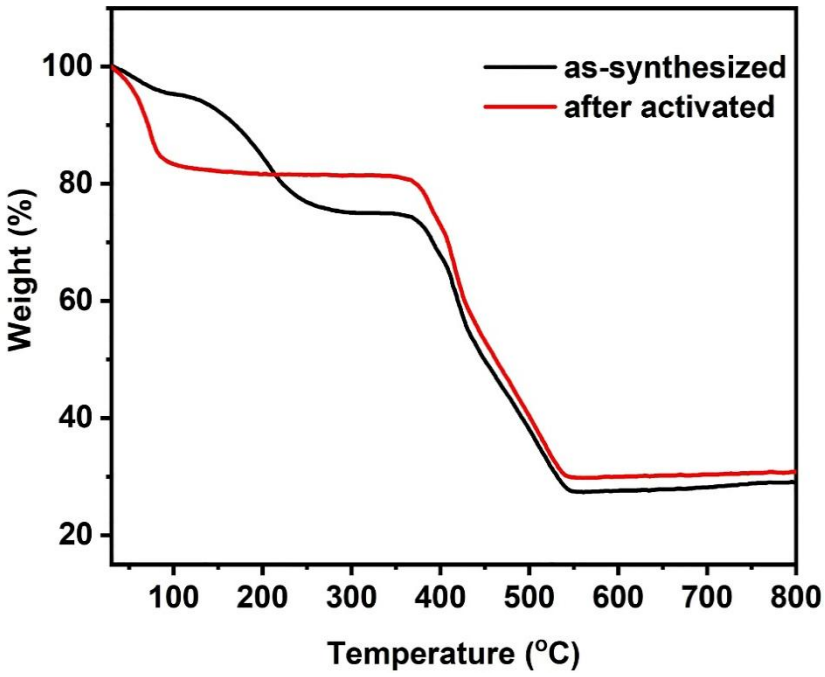

Fig. S4 TG curves of as-synthesized and after activated samples of **ZJNU-401**.

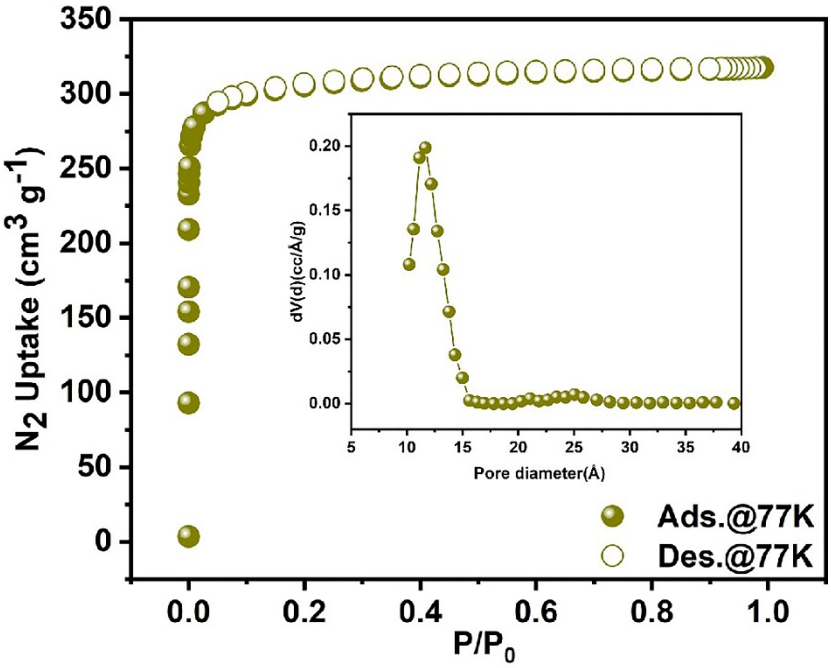

Fig. S5 N_2 sorption isotherms for **ZJNU-401** at 77 K and the pore size distribution.

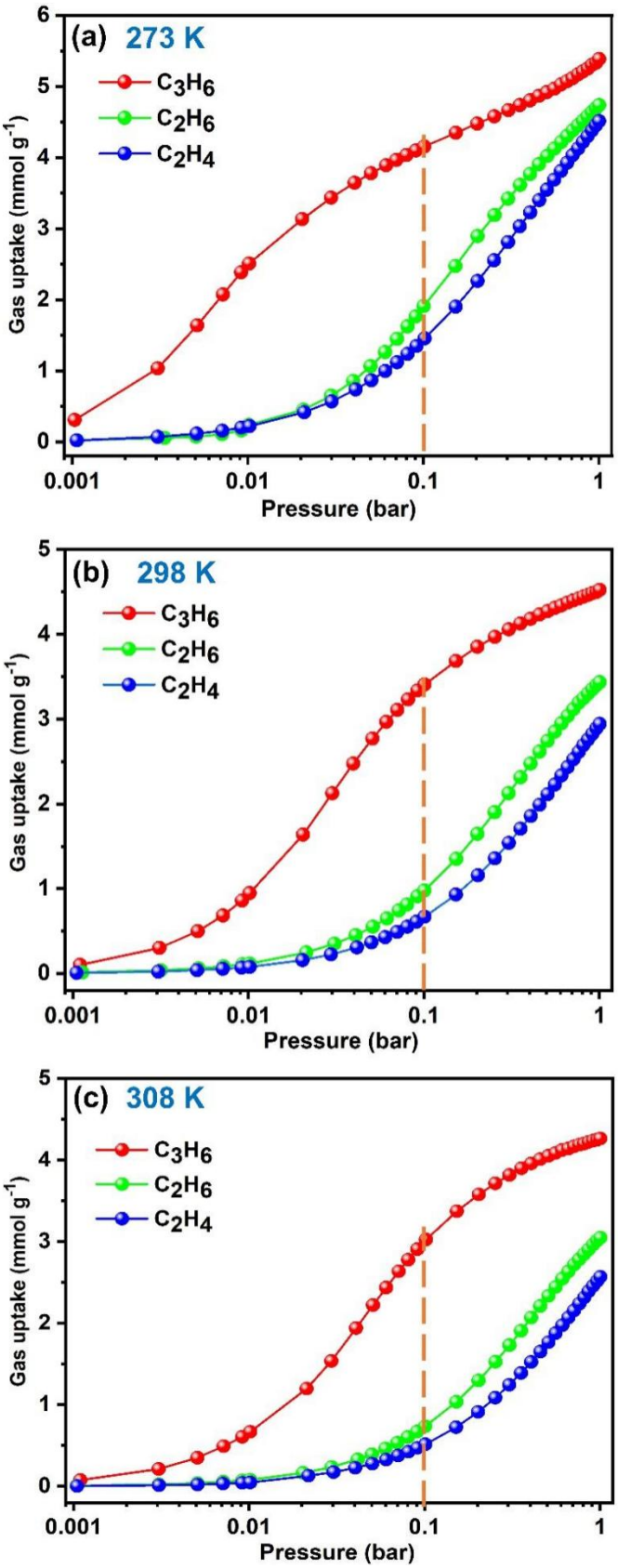

Fig. S6 The adsorption isotherms of C_3H_6, C_2H_4 and C_2H_6 at 273/298/308 K under 1bar.

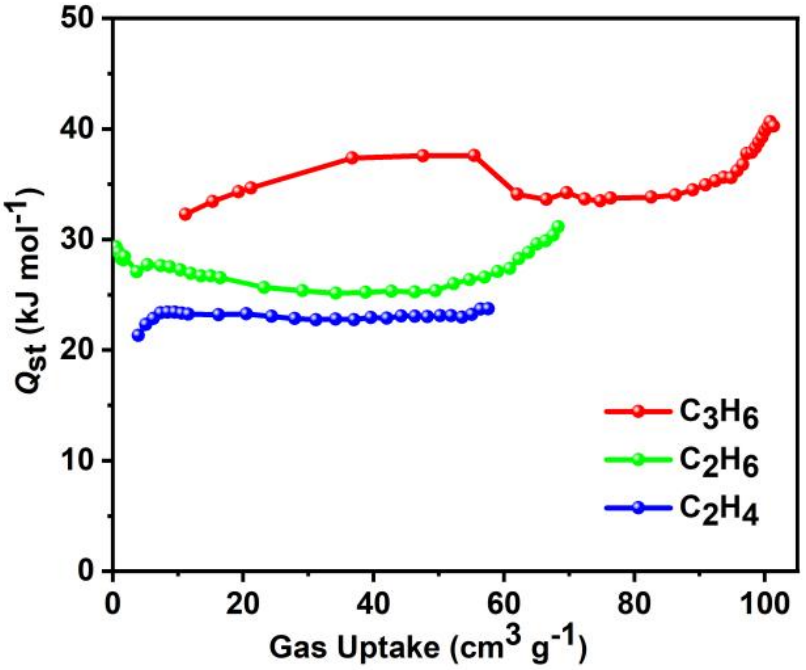

Fig. S7 The Q_{st} of **ZJNU-401** for C_3H_6, C_2H_6 and C_2H_4.

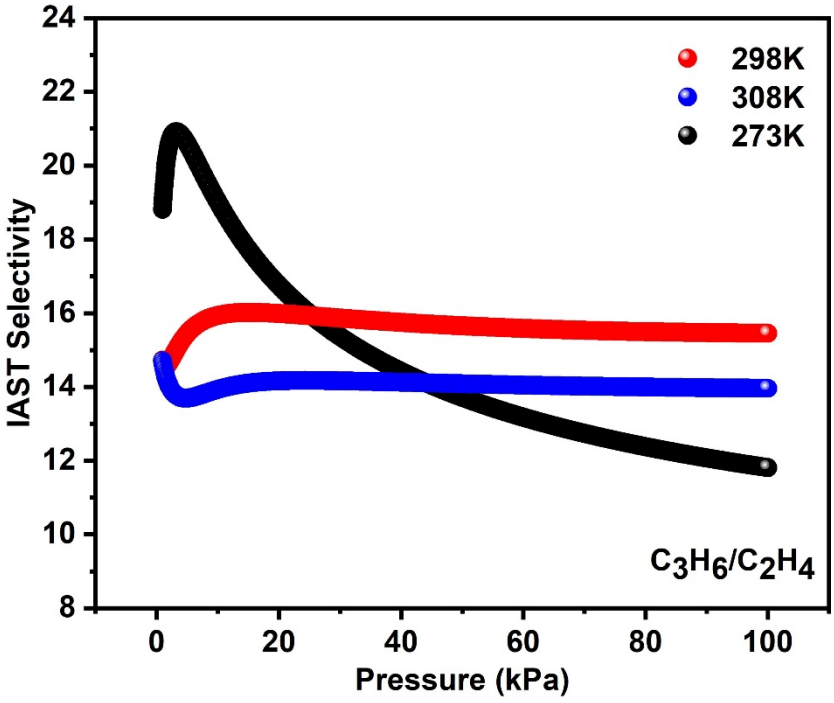

Fig. S8 Selectivity of equimolar mixtures of C_3H_6/C_2H_4 for **ZJNU-401** at 273/298/308 K.

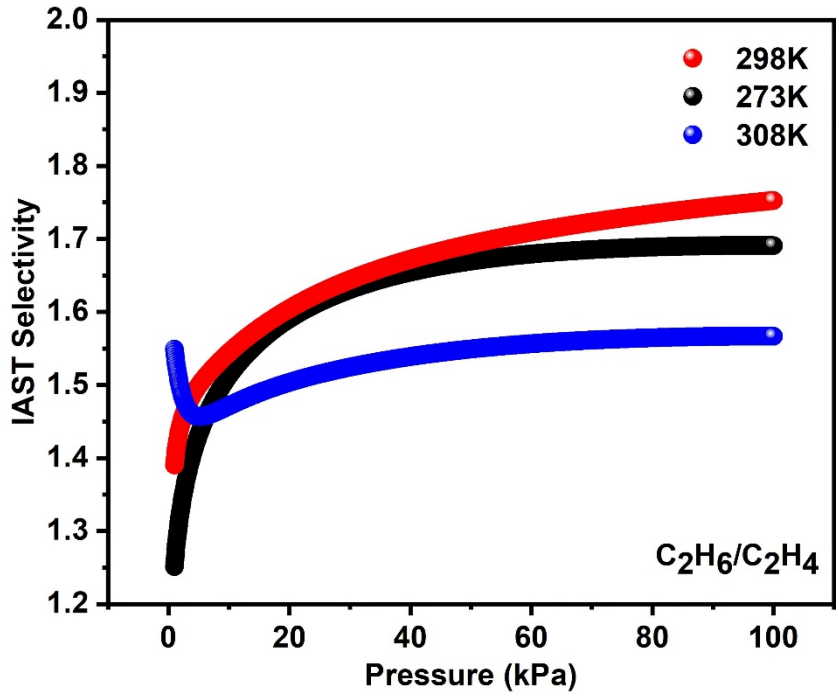

Fig. S9 Selectivity of equimolar mixtures of C_2H_6/C_2H_4 for **ZJNU-401** at 273/298/308 K.

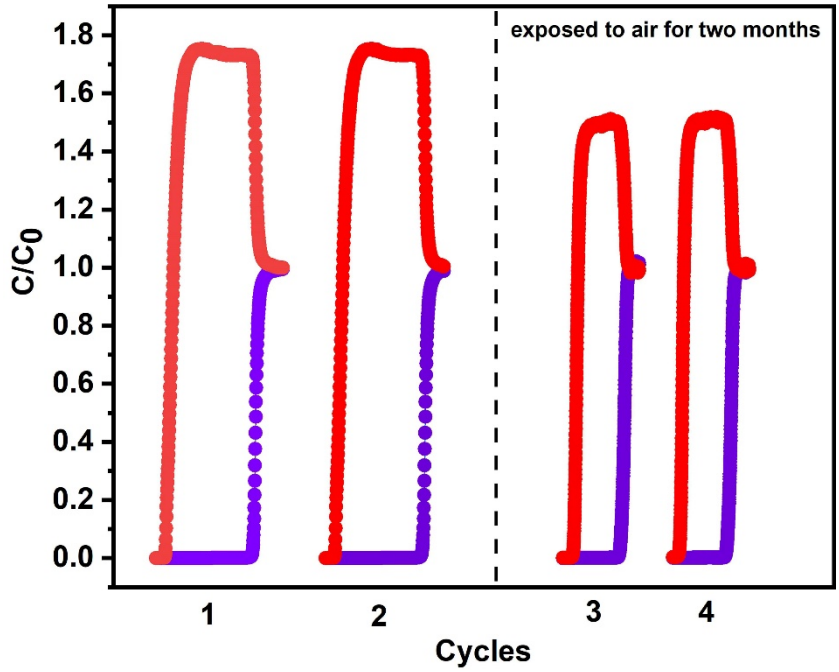

Fig. S10 The recycle of breakthrough curves and that after exposed to air for two months.

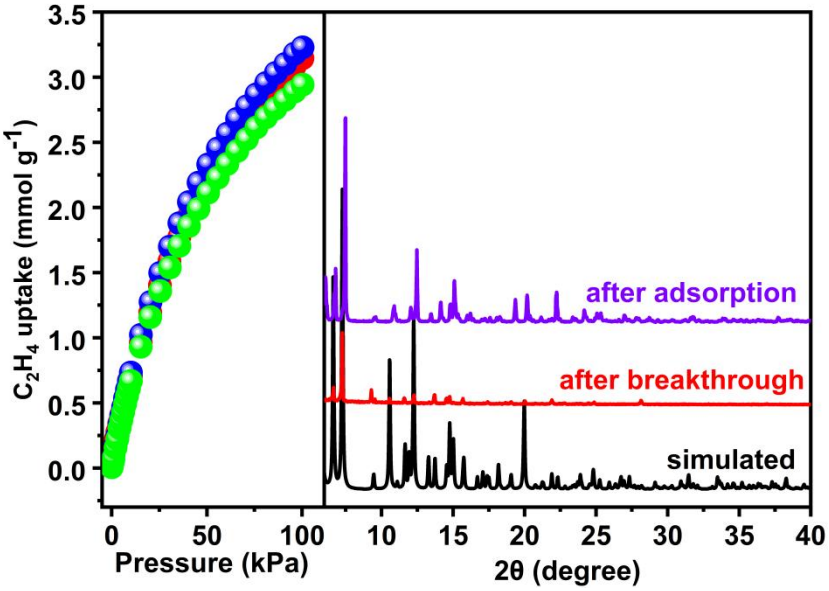

Fig. S11 The stability of sample proved by three times text of C_2H_4 adsorption and the PXRD.

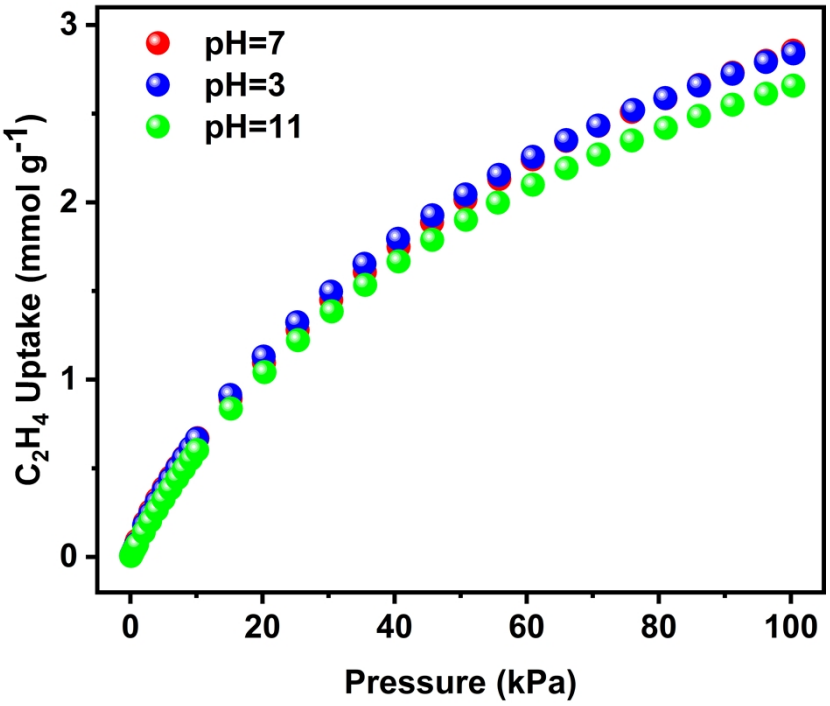

Fig. S12 The adsorption performance of **ZJNU-401** after soaking in acidic, basic, and aqueous solutions.

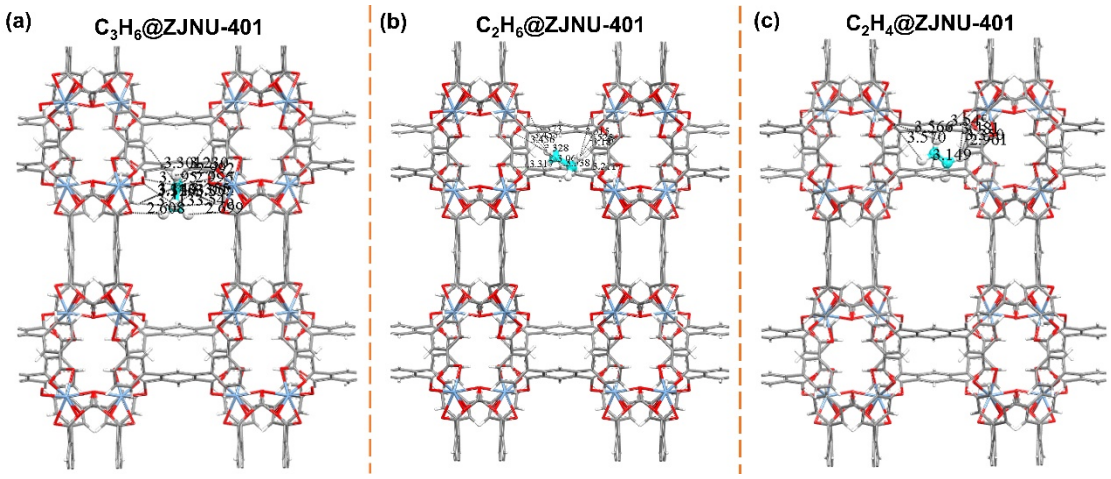

Fig. S13 Calculated optimized adsorption sites for (a) C_3H_6 and (b) C_2H_6 and (c) C_2H_4 in **ZJNU-401**.

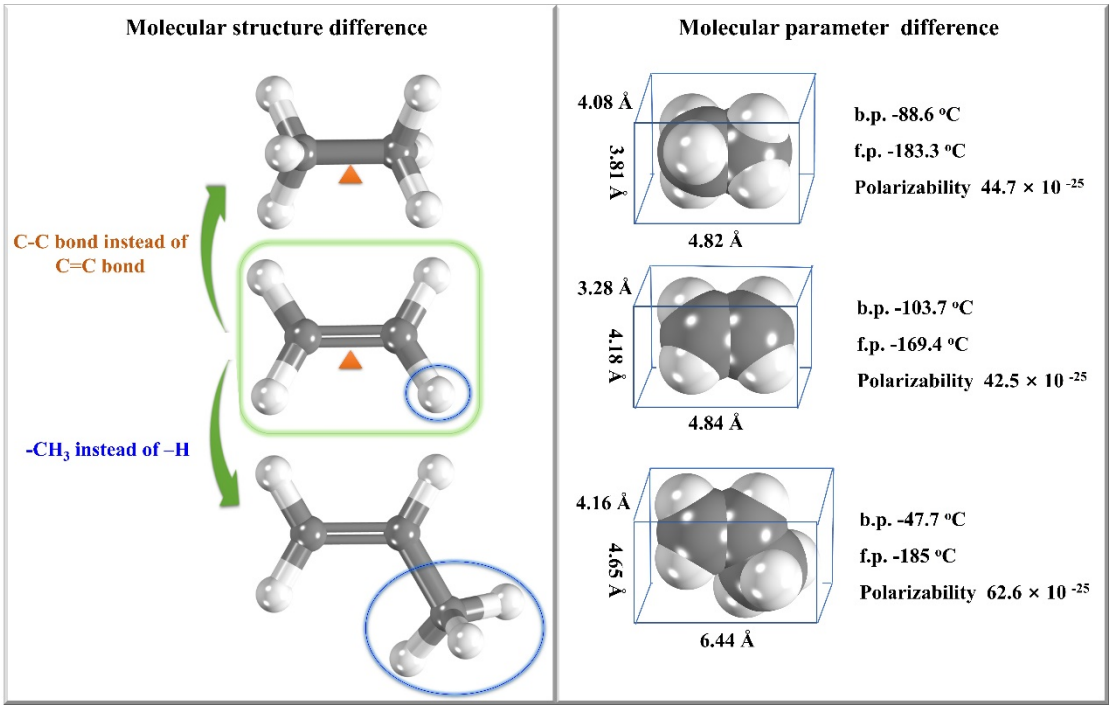

Fig. S14 Comparison of molecular structure and parameter of three gases.

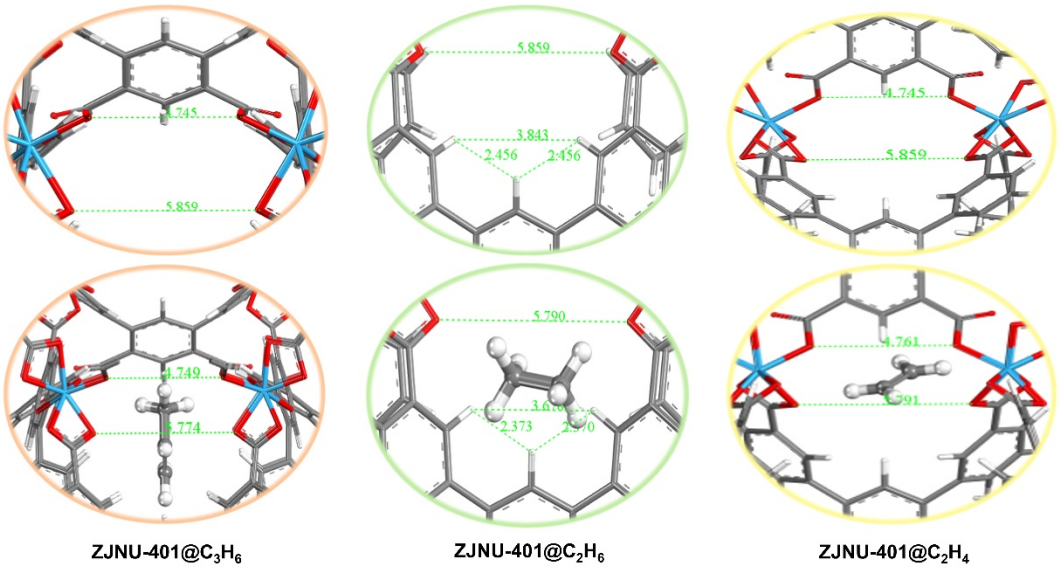

Fig. S15 Comparison of the bond lengths of the calculated structure and the host-crystal structure of **ZJNU-401**.

5. Supporting Tables

Table S1. Crystal data and structure refinement for **ZJNU-401**.

Compound	ZJNU-401
Empirical formula	$C_{176}In_8H_{80}O_{64}$
Formula weight	4136.96
λ (Å)	1.54178
Crystal system	orthorhombic
Space group	*Fmm*2
a (Å)	24.3316(19)
b (Å)	30.387(2)
c (Å)	18.6976(9)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å^3)	13824.2(16)
Z	2
D_c (g/cm^3)	1.011
μ (mm^{-1})	5.719
F (000)	4080.0
Reflections collected	65124
Unique (R_{int})	0.0430
Goodness-of-fit on F^2	1.113
R_1, wR_2 [$I > 2\sigma(I)$]	0.0543, 0.1701
R_1, wR_2 (all data)	0.0572, 0.1751

Table S2. The refined parameters for the Dual-site Langmuir-Freundlich equations fit for the pure isotherms of small gas molecule for **ZJNU-401** at 273 K.

Adsorbate	q_{m1} [mmol g^{-1}]	b_1 [kPa^{-1}]	n_1	q_{m2} [mmol g^{-1}]	b_2 [kPa^{-1}]	n_2	R^2
C_3H_6	4.46145	0.05954	0.55346	3.41758	1.84148	1.35768	0.99968
C_2H_6	4.28997	0.04022	1.0312	1.76072	0.07665	1	0.99981
C_2H_4	3.0233	0.01242	0.94534	3.8611	0.04899	0.9320	0.9999

Table S3. The refined parameters for the Dual-site Langmuir-Freundlich equations fit for the pure isotherms of small gas molecule for **ZJNU-401** at 298 K.

Adsorbate	q_{m1} [mmol g^{-1}]	b_1 [kPa^{-1}]	n_1	q_{m2} [mmol g^{-1}]	b_2 [kPa^{-1}]	n_2	R^2
C_3H_6	3.45961	0.27651	1.2859	2.44802	0.07781	0.50797	0.99997
C_2H_6	0.12353	0.3529	1.18812	4.73691	0.01757	1.1225	1
C_2H_4	3.85774	0.0066	1.17053	0.74039	0.0742	1.01203	0.99999

Table S4. The refined parameters for the Dual-site Langmuir-Freundlich equations fit for the pure isotherms of small gas molecule for **ZJNU-401** at 308 K.

Adsorbate	q_{m1} [mmol g^{-1}]	b_1 [kPa^{-1}]	n_1	q_{m2} [mmol g^{-1}]	b_2 [kPa^{-1}]	n_2	R^2
C_3H_6	0.66097	0.02869	2.55823	3.86659	0.19381	0.92339	0.99994
C_2H_6	3.15814	0.00575	1.35318	0.76388	0.08775	1.02498	1
C_2H_4	0.61103	0.06433	1	3.81109	0.00517	1.17311	0.99999

6. Reference

[1]. Rappé A K, Casewit C J, Colwell K S, et al. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations[J]. Journal of the American chemical society, 1992, 114(25): 10024-10035.

[2]. Rappé A K, Casewit C J, Colwell K S, et al. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations[J]. Journal of the American chemical society, 1992, 114(25): 10024-10035.

[3]. Wang Y, Sun S, Wu P. Adaptive ionogel paint from room-temperature autonomous polymerization of α-thioctic acid for stretchable and healable electronics[J]. Advanced Functional Materials, 2021, 31(24): 2101494.