Electronic Support Information

Investigation on Zr-based metal-organic framework (MOF-801) for high-performance separation of light alkanes

Hao Liu [a, b, †], Boran Li [a, c, †], Yayun Zhao [a,b*], Chunlong Kong [a], Chen Zhou [a], Yichao Lin [a,b], Ziqi Tian [a, b*] and Liang Chen [a, b*]

[a] Institute of New Energy Technology, Ningbo Institute of Materials Technology and Engineering, CAS, 1219 Zhongguan Road, 315201, Ningbo, P. R. China

[b] University of Chinese Academy of Sciences, 100049, Beijing, P. R. China

[c] Beijing University of Chemical Technology, 100010, Beijing, P. R. China

[†] Both authors contributed equally to this work.

*zhaoyayun@nimte.ac.cn; tianziqi@nimte.ac.cn; chengliang@nimte.ac.cn

Materials

All chemicals were obtained commercially and used without further purification: zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, Aladdin, ≥98.0 %), fumaric acid (H_2fum, Aladdin, ≥99.0 %), *N*, *N*-dimethylformamide (DMF, Aladdin, ≥99.5 %), formic acid (FA, Aladdin, ≥99.0 %).

Characterization

SEM was conducted on a Hitachi S-4800 instrument with a cold field emission gun operating at 4 kV and 7 μA. The data of XRD on Bruker D8 Advance was collected at room temperature under ambient pressure using Cu Kα (λ=1.5406 Å) radiation at 5-40°. TGA was carried out on Perkin-Elmer heating from 40 °C to 800 °C at a rate of 5 °C/min in nitrogen atmosphere.

Gas sorption

The N_2 adsorption-desorption isotherms of the samples at -196 °C were measured on the Micrometrics ASPS 2020. Upon calculation based on the N_2 adsorption isotherm, the BET surface area and the pore size distribution can be obtained using the BET equation and the Horvath-Kawazoe method, respectively. The CH_4, C_2H_6 and C_3H_8 single-component adsorption isotherms were collected on Micrometrics ASAP 2020 as well at 0 °C and 25 °C. Prior to each measurement, the sample was activated at 150 °C under vacuum for 6 h.

Breakthrough experiment

The breakthrough experiment was completed employing a fixed bed. Before test, MOF-801 sample was heated in a dynamic inoculation drier at 150 °C for 2 h

accompanied by He flow (50 mL/min) for activation. Then, 1.4 g of activated crystal MOF-801 was loaded onto a stainless steel column with an inner diameter of 1 cm and a packing length of 9 cm. $CH_4/C_2H_6/C_3H_8$ mixture (85/10/5, v/v/v) was introduced into the adsorption column at a rate of 10 mL/min. The mass spectrometer (BSD-MAD) was used to determine the composition of the cuvette exit gas stream. The temperature of the cuvette was controlled by an incubator and the breakthrough curves were obtained at 25 ^oC and 1 bar.

Synthesis of MOF-801

MOF-801 was obtained following the same procedure as reported elsewhere.[1] Typically, $ZrOCl_2 \cdot 8H_2O$ (2.8 mmol, 0.92 g), H_2fum (2.8 mmol, 0.32g) and FA (280 mmol, 10.6 mL) were dissolved in 72 mL DMF in a 200 mL breaker, and the mixture was stirred for 30 min before transferring to the Teflon-lined autoclave. Then, the Teflon-lined autoclave was kept in an oven at 100 ^oC for 24 h under static conditions. After cooling down to room temperature, the obtained crystals were collected by centrifugation with 8000 rpm/min. The as-synthesized sample was washed with DMF several times. Finally, the product was dried in an oven at 120 ^oC for 24 h. Calculated on the basis of H_2fum, the white nano-crystals of MOF-801 were obtained in 93 % yield (0.60 g).

Simulation Details

The GCMC simulations were performed to simulate gas isotherms and adsorption heat by using RASPA code.[2] MOF-801 model and force fields parameters are from Iacomi et al.,[3] as shown in Table S1. Lorentz-Berthelot mixing-rule was

applied to calculate the crossing interaction parameters with cutoff of 15 Å. The long-range electrostatic interaction was solved by Ewald summation with a precision of 1×10^{-6}. The simulations consist of 3×10^{5} Monte Carlo (MC) cycles, where first 1×10^{5} MC cycles was used for equilibration. The Peng-Robinson equation of state was applied to transform pressure to fugacity. The MC trial moves considering translation, rotation, and reinsertion were used in all adsorption simulations.

Calculation of isosteric enthalpy of adsorption [4]

The isosteric enthalpies of these light hydrocarbons were calculated by the Clausius-Clapeyron equation:

$$Q_d = \frac{RT^2}{p}\left(\frac{\partial p}{\partial T}\right)_q$$

Where Q_d is the isosteric enthalpy of adsorption (kJ/mol), R is the gas constant [kJ/(mol·K)], T is the adsorption temperature (K), and p is the adsorption pressure (kPa).

IAST calculation of C_3H_8/CH_4 and C_2H_6/CH_4 on MOF-801[5]

The adsorption selectivity factor S can be estimated by using following equation:

$$S = x_1 y_2 / (x_2 y_1)$$

Where S is the adsorption selectivity factor, x_i and y_i represent the mole fraction of component *i* (*i* = 1 or 2) in the adsorbed and gas phase. Here, component 1 represents C_3H_8 or C_2H_6, and component 2 represents CH_4.

The adsorption isotherm of pure gas is fitted by the single-site Langmuir model:

$$q = a\frac{bp^c}{1 + bp^c}$$

Where q is the gas amount adsorbed per gram of adsorbent (mmol/g), p is the equilibrium pressure of pure gas with the adsorbed phase (kPa), a is the saturation capacities of site 1, b is the affinity coefficients of site 1 (1/kPa), $\frac{1}{c}$ represents the corresponding deviations from an ideal homogeneous surface.

Table S1 Force field parameters for MOF-801 and adsorbates.

Atom type	ε/k_b (K)	σ (Å)
Zr	52.9	3.85
O	27.0	2.80
C	79.0	3.05
H	34.7	3.66
$CH_4\_sp^3$	148.0	3.73
$CH_3\_sp^3$	108.0	3.76
$CH_2\_sp^3$	56.0	3.96

Table S2 Comparison of adsorption and separation performance of some reported materials at 1 bar.

materials	C_2H_6 (mmol/g)	C_3H_8 (mmol/g)	C_2H_6/CH_4	C_3H_8/CH_4	Temperature (°C)	Ref.
MOF-801	2.26	3.02	28	255	25	This work
MFM-202a	4.21	6.76	10	87	20	[6]
Ni(TMBDC)$(DABCO)_{0.5}$	5.51	5.73	29	247	25	[7]
NKM-101a	2.92	3.43	20	223	23	[8]
USTA-35a	2.43	3.29	8	80	25	[9]
PAF-40	1.95	2.39	15	48		
PAF-40-Fe	1.85	2.58	16	56	25	[10]
PAF-40-Mn	2.05	2.51	31	246		
JUC-100	4.11	6.07	8	65	25	[11]
UPC-98	2.03	4.34	15	118	25	[5b]

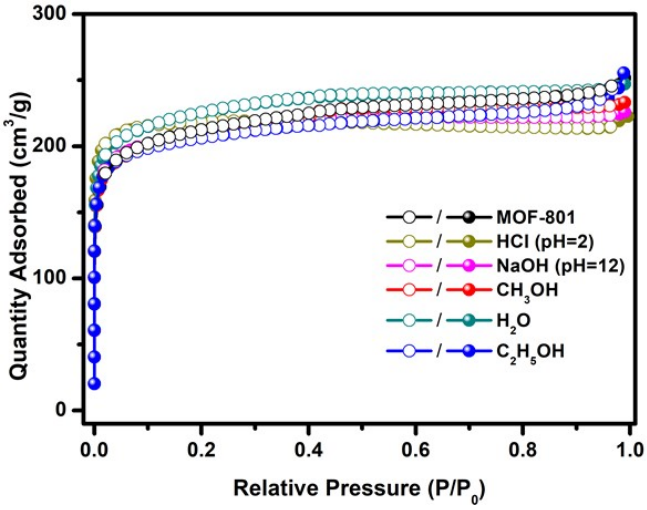

Fig. S1 N_2 adsorption-desorption isotherms of MOF-801 at -196 °C before and after different treatments.

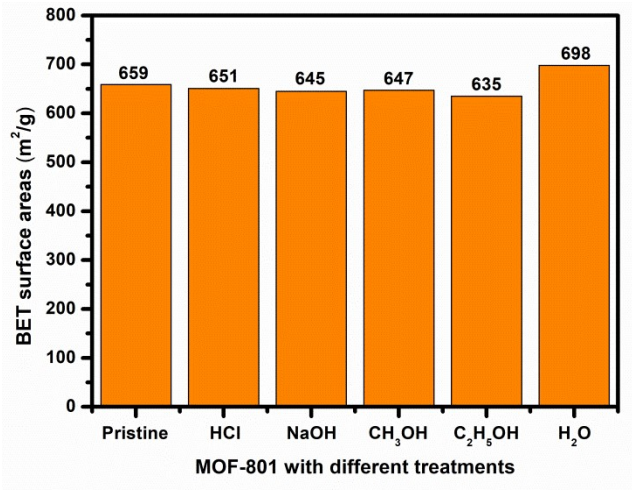

Fig. S2 BET surface areas of MOF-801 samples before and after different treatments (CH_3OH, C_2H_5OH, H_2O, HCl aqueous solution (pH = 2), and NaOH aqueous solution (pH = 12)).

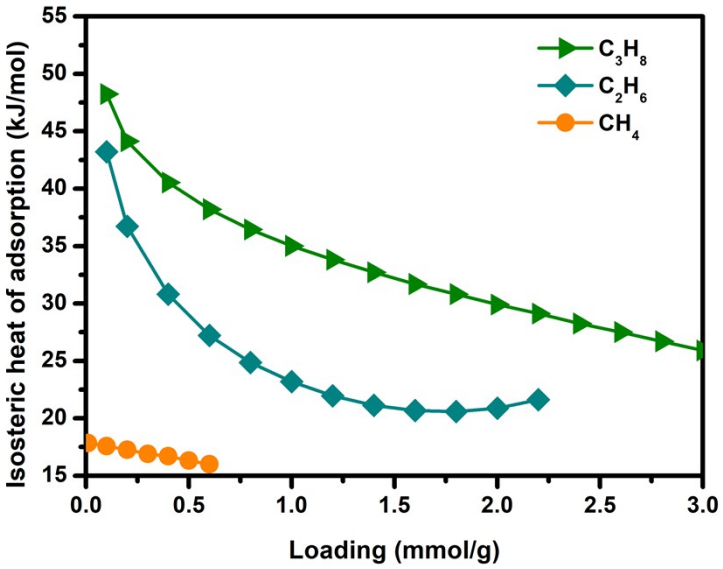

Fig. S3 Isosteric enthalpies of CH_4, C_2H_6 and C_3H_8 adsorption on MOF-801. "These data points are calculated according to the Clausius-Clapeyron equation and linked by lines to guide the reader."

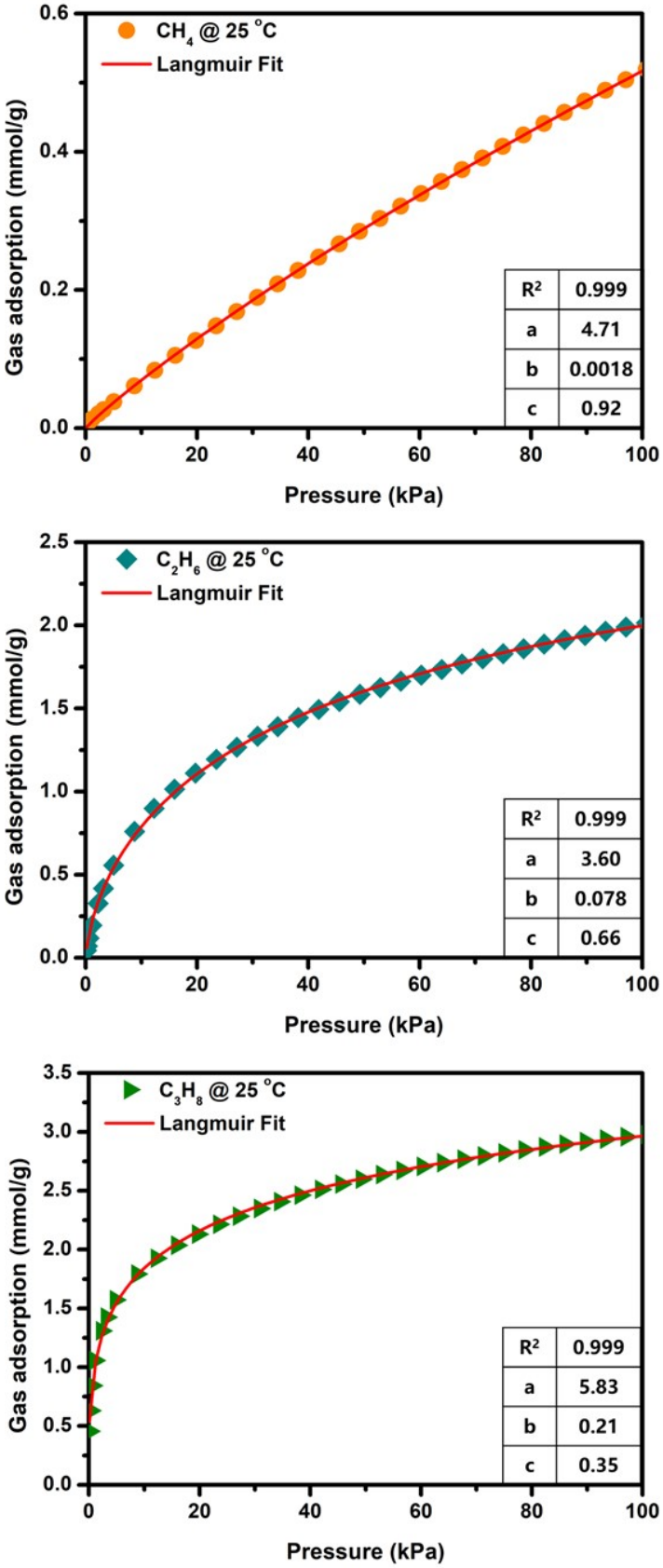

Fig. S4 CH_4, C_2H_6 and C_3H_8 adsorption isotherms of MOF-801 at 25 °C with fitting by Langmuir model.

References

1 H. Furukawa, F. Gandara, Y. B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, O. M. Yaghi, *J. Am. Chem. Soc.*, 2014, **136**, 4369-4381.

2 D. Dubbeldam, S. Calero, D. E. Ellis, R. Q. Snurr, *Mol. Simulat.*, 2016, **42**, 81-101.

3 P. Iacomi, F. Formalik, J. Marreiros, J. Shang, J. Rogacka, A. Mohmeyer, P. Behrens, R. Ameloot, B. Kuchta, P. L. Llewellyn, *Chem. Mater.*, 2019, **31**, 8413-8423.

4 (a) L. Czepirski, J. Jagiełło, *Chem. Eng. Sci.*, 1989, **44**, 797-801; (b) R. Krishna, *Chem. Eng. Sci.*, 2015, **123**, 191-196.

5 (a) A. L. Myers, J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121-127; (b) X. Wang, X. Wang, X. Zhang, W. Fan, Q. Li, W. Jiang, F. Dai, D. Sun, *Cryst. Growth Des.*, 2020, **20**, 5670-5675.

6 S. Gao, C. G. Morris, Z. Lu, Y. Yan, H. G. W. Godfrey, C. Murray, C. C. Tang, K. M. Thomas, S. Yang, M. Schröder, *Chem. Mater.*, 2016, **28**, 2331-2340.

7 Y. Wu, Z. Liu, J. Peng, X. Wang, X. Zhou, Z. Li, *ACS Appl. Mater. Inter.*, 2020, **12**, 51499-51505.

8 Y. Qiao, X. Chang, J. Zheng, M. Yi, Z. Chang, M. H. Yu, X. H. Bu, *Inorg. Chem.*, 2021, **60**, 2749-2755.

9 Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna, B. Chen, *Chem. Commun.*, 2012, **48**, 6493-6495.

10 S. Meng, H. Ma, L. Jiang, H. Ren, G. Zhu, *J. Mater. Chem. A,* 2014, **2**, 14536-14541.

11 J. Jia, L. Wang, F. Sun, X. Jing, Z. Bian, L. Gao, R. Krishna, G. Zhu, *Chem. Eur. J.,* 2014, **20**, 9073-9080.