

Supporting Information for

Highly selective sorption of CO₂ and N₂O and strong gas-framework interactions in a nickel(II)-organic material

Xiaoping Zhang, Wenjie Chen, Wei Shi,* and Peng Cheng*

Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (MOE), State Key Laboratory of Elemento-Organic Chemistry, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, P. R. China, Fax: (+86) 22-23502458, E-mail: shiwei@nankai.edu.cn; pcheng@nankai.edu.cn.

Table of Contents

Section S1	Materials and crystal structure	S2-S3
Section S2	Thermogravimetric analysis	S4
Section S3	Powder X-ray diffraction analysis	S5
Section S4	Low-pressure gas sorption measurements	S6-S10

Section S1. Materials and X-ray Crystal Structure

Table S1. Crystal data and structure refinements for Ni-MOF.

	Ni-MOF
formula	C ₁₁ H ₁₆ NO ₈ Ni
FW	348.94
T (K)	129.60(10)
crystal system	Tetragonal
space group	I4 ₁ 22
a (Å)	15.1780(5)
b (Å)	15.1780(5)
c (Å)	12.0813(5)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
V (Å ³)	2783.19(18)
Z	8
ρ _{calc} (g/cm ³)	1.211
μ (mm ⁻¹)	1.397
index ranges	-18 ≤ h ≤ 8 -12 ≤ k ≤ 15 -14 ≤ l ≤ 13
reflins collected	2606
Independent(<i>R</i> _{int})	1219 (0.0808)
data/restraints/parameters	1219, 75, 36
GOF on <i>F</i> ²	1.066
<i>R</i> ₁ , ω <i>R</i> ₂ [>2σ (<i>I</i>)]	0.0691, 0.1735
<i>R</i> ₁ , ω <i>R</i> ₂ (all data)	0.0732, 0.1792
largest diff. peak/hole (e/Å ³)	1.997, -0.788

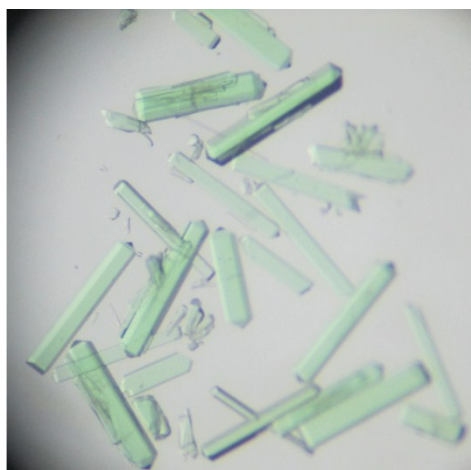


Fig. S1 View of the strip crystal Ni-MOF.

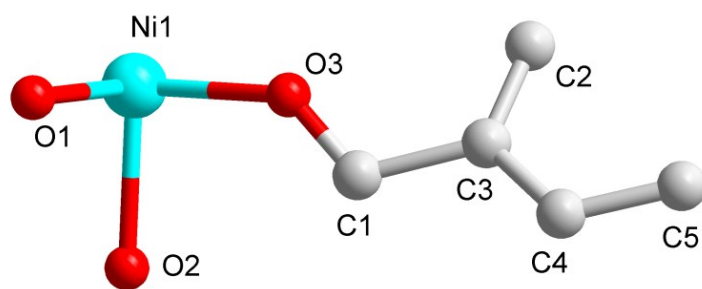


Fig. S2 Asymmetric unit of Ni-MOF (hydrogen atoms have been omitted for clarity).

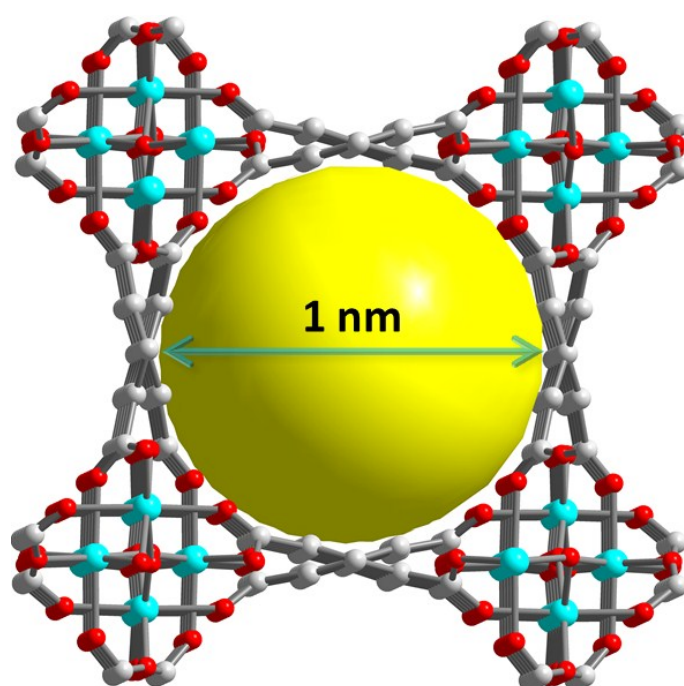


Fig. S3 View of 1D nanosized channel in Ni-MOF along the crystallographic *c* axis.

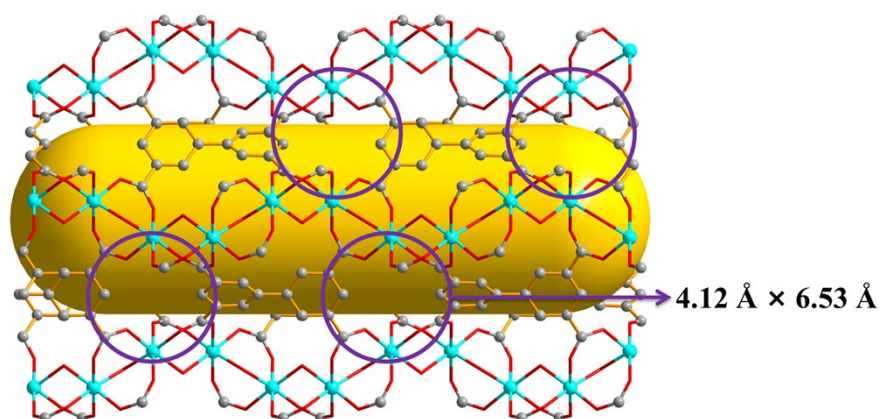


Fig. S4 View of 1D nanosized channel in Ni-MOF along the crystallographic *a* axis (*b* direction exhibits the same window as *a* axis).

Section S2 Thermogravimetric analysis

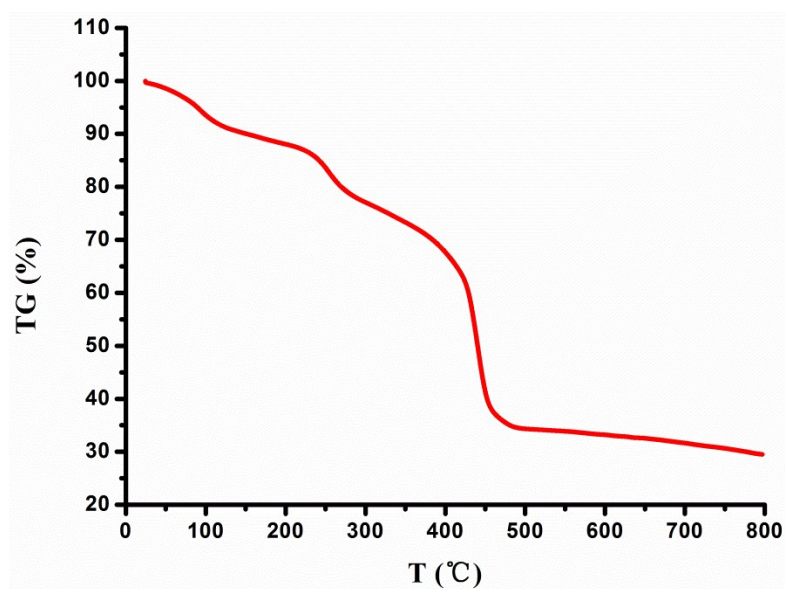


Fig. S5 Thermogravimetric analysis of as-synthesized material of Ni-MOF.

Section S3 powder X-ray diffraction analysis

The crystal structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material, CH₃OH-exchange sample and sample after gas sorption was verified by powder X-ray diffraction

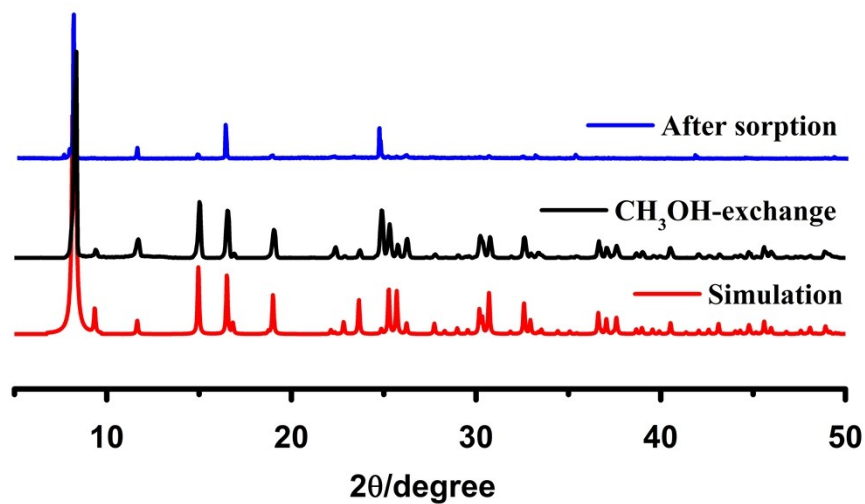


Fig. S6 Simulated PXRD patterns, CH₃OH-exchanged, and sample after gas sorption of Ni-MOF.

Section S4 Low-pressure gas sorption measurements

Estimation of the isosteric heats of gas adsorption.

A virial-type expression comprising the temperature-independent parameters a_i and b_j is employed to calculate the enthalpies of adsorption for CH₄, N₂O and CO₂ (at 273 and 298 K/313 K) on **Ni-MOF**. The zero-coverage isosteric heat of adsorption is evaluated by first fitting the temperature-dependent isotherm data to a virial-type expression,¹ which can be written as follows:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j \quad (\text{S1})$$

In eq (S1), P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_j are virial coefficients, and m , n represent the number of coefficients required to adequately describe the isotherms (m and n are gradually increased until the contribution of extra added a and b coefficients is deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values is minimized). The values of the virial coefficients a_0 through a_m are then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (\text{S2})$$

and it follows that the zero-coverage isosteric heat of adsorption is given by:

$$Q_{st} = -R a_0 \quad (\text{S3})$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of CO₂, N₂O and CH₄ sorption for **Ni-MOF** in the paper is determined by using the low pressure gas sorption data measured in the pressure range from 0 to 1 bar (273 and 298 K/313 K).

Selectivity Prediction for Binary Mixture Adsorption: Ideal adsorbed solution theory (IAST).

Ideal adsorbed solution theory (IAST)² is used to predict binary mixture adsorption from the experimental pure-gas isotherms. To perform the integrations required by IAST, the single component isotherms should be fitted by a proper model. There is no restriction on the choice of the model to fit the adsorption isotherm, however, data over the pressure range under study should be fitted very precise.³ To determine the amount adsorbed in the mixture, as opposed to the mole fraction, the following equation can be used:

$$\frac{1}{n_{total}} = \frac{x_i}{n_i^0} + \frac{x_j}{n_j^0} \quad (\text{S4})$$

where, at a given pressure, n_{total} is the total number of moles adsorbed in the mixture and n_i^0 is

the amount of pure component i adsorbed per gram of adsorbent.

Several isotherm models are tested to fit the experimental pure isotherms for CO_2 , N_2O , N_2 , O_2 and CH_4 at 273 and 298 K/313 K.

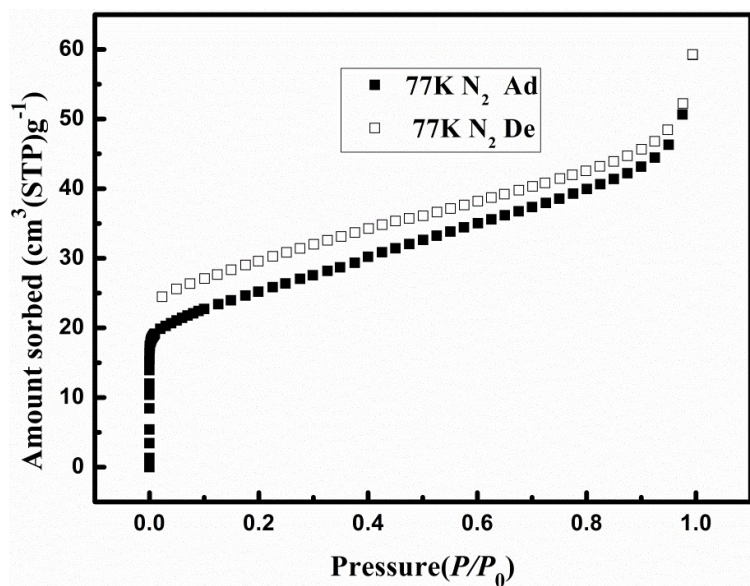


Fig. S7 N_2 gas sorption at 77K. Adsorption and desorption branches are shown with filled and empty symbols, respectively.

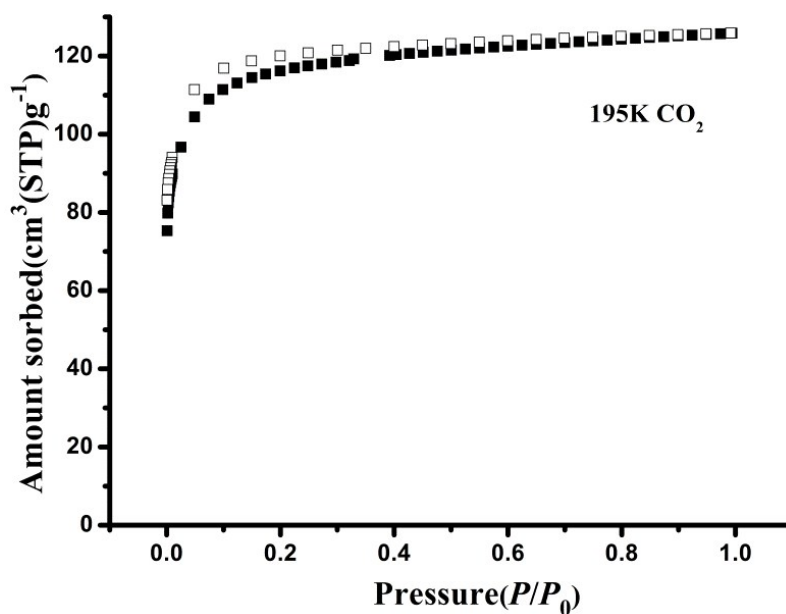


Fig. S8 CO_2 capture at 195 K. Adsorption and desorption branches are shown with filled and empty symbols, respectively.

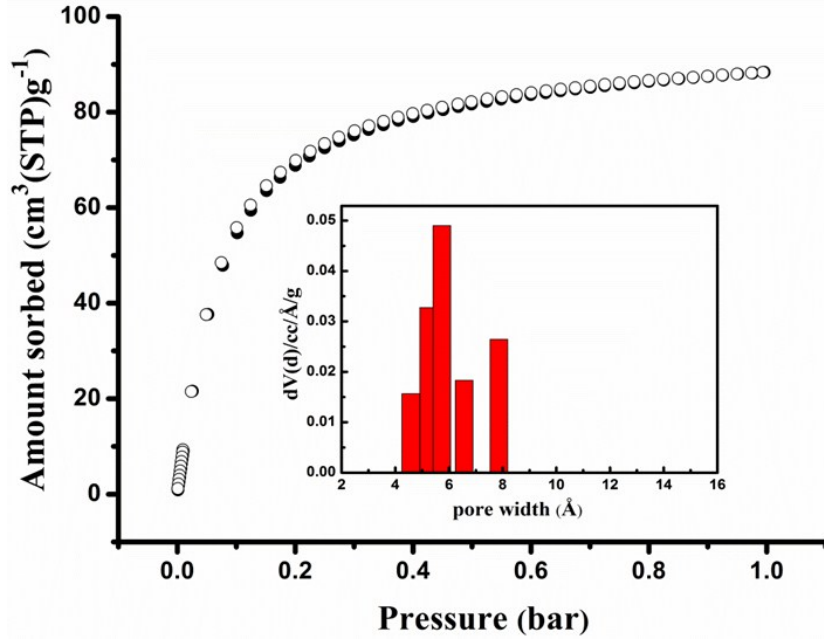


Fig. S9 CO₂ capture at 273 K and the pore size distribution. Adsorption and desorption branches are shown with filled and empty symbols, respectively.

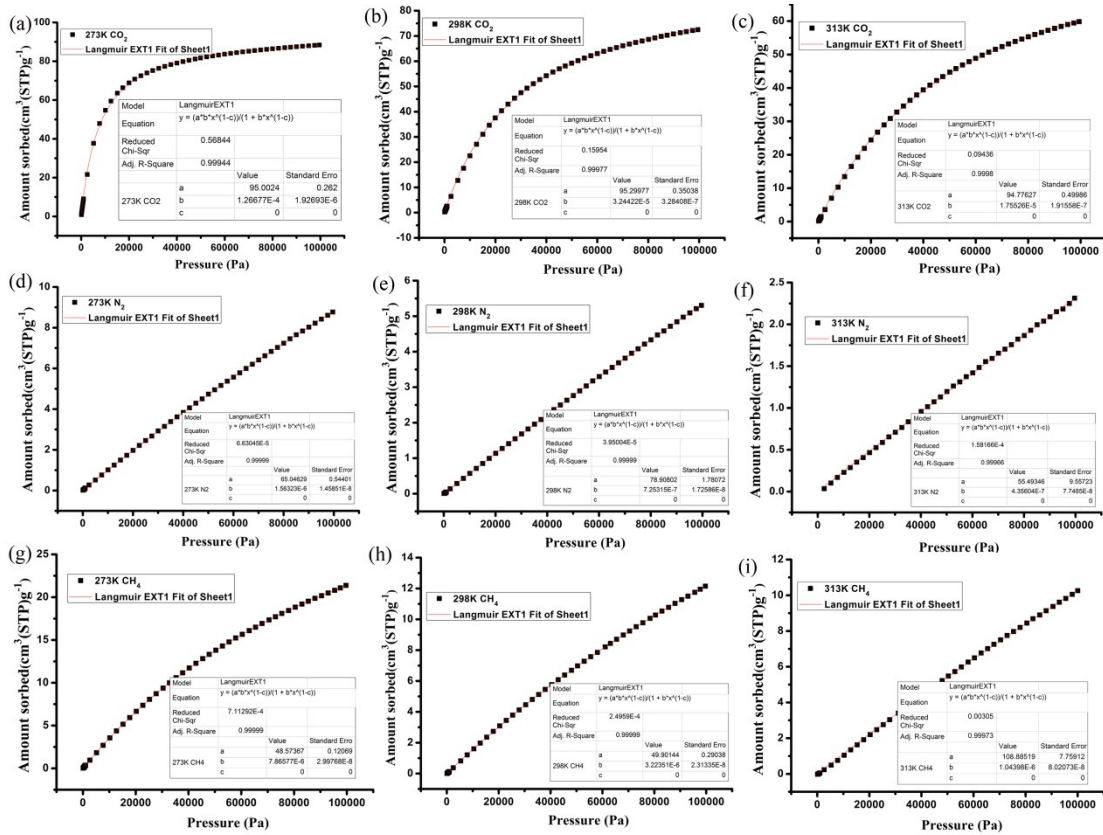


Fig. S10 IAST calculated selectivity abilities of CO₂, N₂ and CH₄ gases at 273, 298 K and 313 K, respectively.

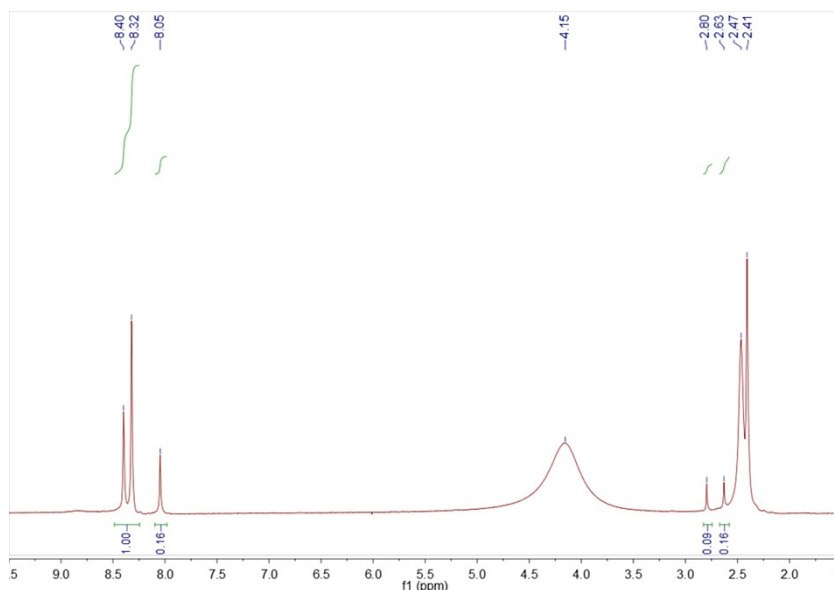


Fig. S11 ^1H NMR Spectrum of activated Ni-MOF (300 MHz, $\text{DMSO-}d_6$). Ni-MOF was digested in 750 μL $(\text{CD}_3)_2\text{SO}$ and 10 μL of 35% DCl with sonication for 10 min.

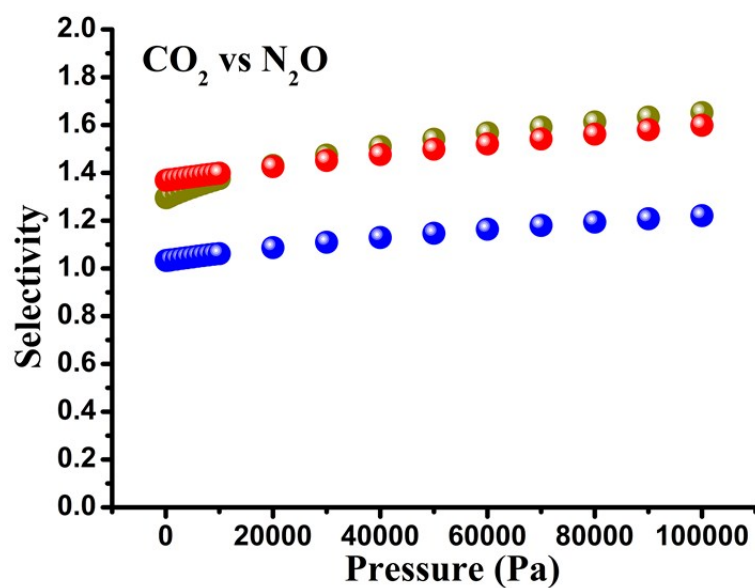


Fig. S12 IAST predicted selectivities for $\text{CO}_2/\text{N}_2\text{O}$ (273 K dark yellow, 298 K blue, and 313 K red).

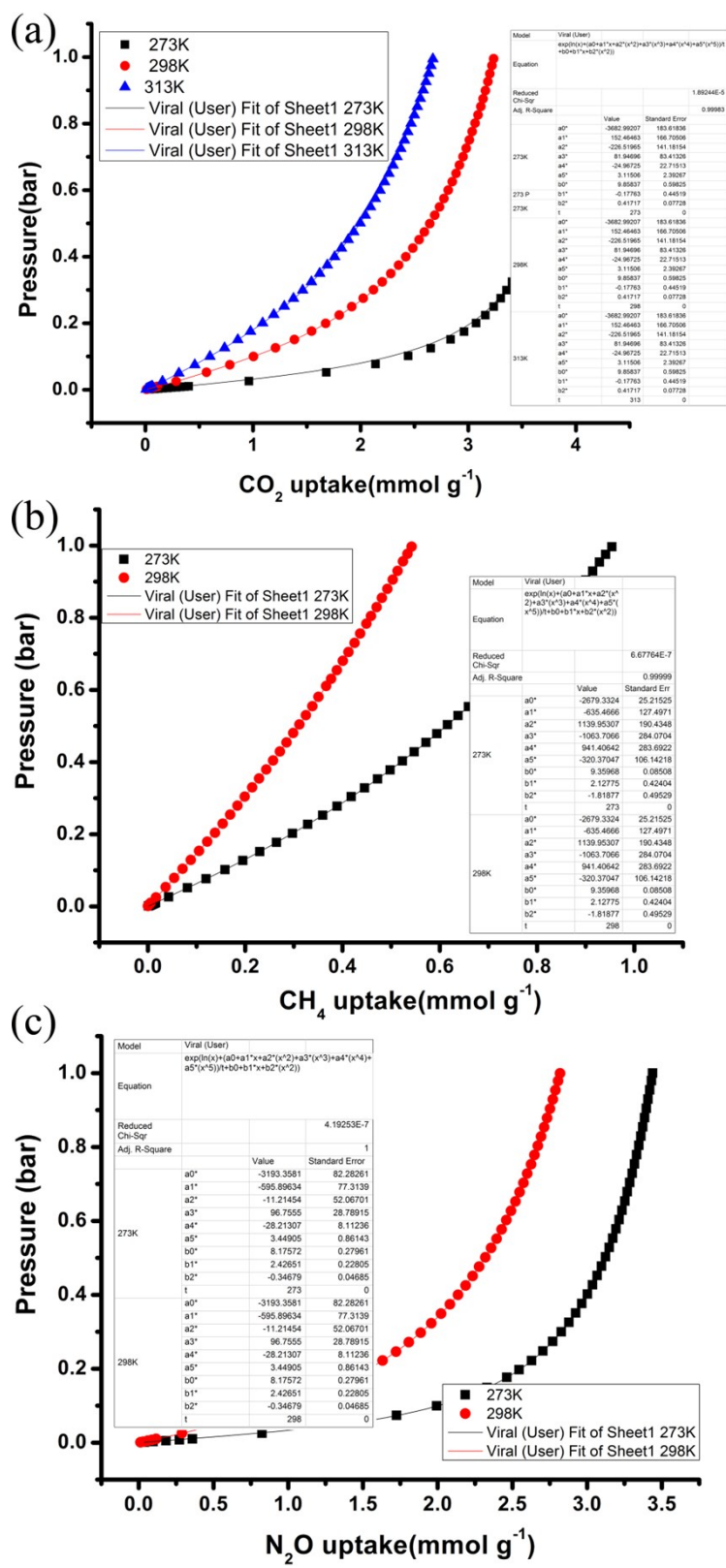


Fig. S13 The isosteric heat of adsorption (Q_{st}) of CO₂, CH₄ and N₂O calculated from the adsorption isotherms at 273, 298 K and 313K (for CO₂) by using virial-type fitting for Ni-MOF.

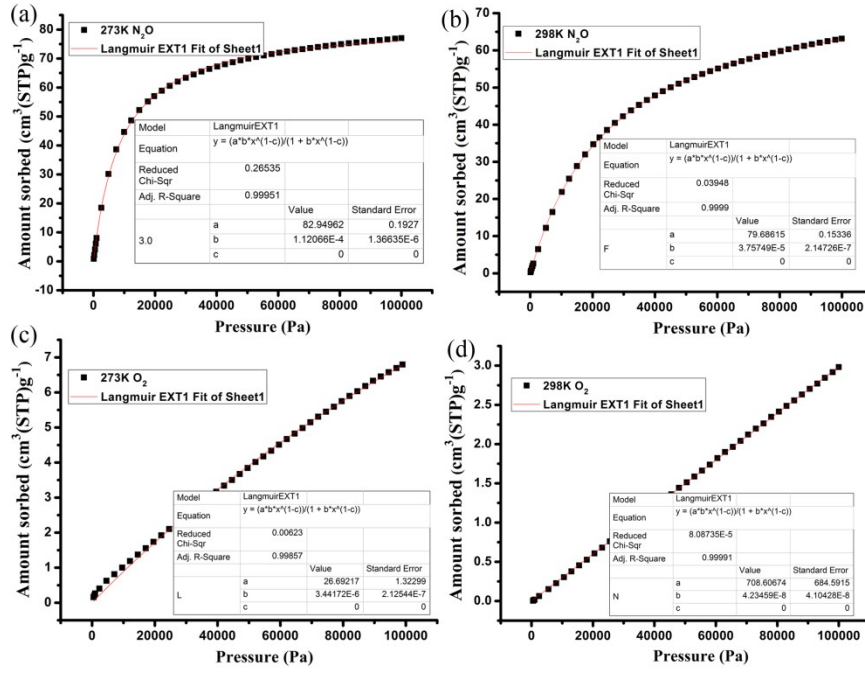


Fig. S14 IAST calculated selectivity abilities of N₂O and O₂ at 273 and 298 K.

References:

- 1 L. Czepirski and J. Jagiello, *Chem. Eng. Sci.*, 1989, **44**, 797.
- 2 A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
- 3 S. J. Keskin, *Phys. Chem. C*, 2011, **115**, 800.