Supplementary Information for

Mechano-assisted synthesis of an ultramicroporous metal-organic framework for trace CO_2 capture

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Experimental section

Materials: All chemicals were commercially available and used as supplied without further purification.

Synthesis of ZU-36-Ni (GeFSIX-3-Ni)

$(NH_4)_2GeF_6$ (4 mmol), $Ni(NO_3)_2$ (4 mmol) and pyrazine (12 mmol) were put into 50 mL ball-milling jar with several steel core grinding balls. The mixture was then ground for 10 min in a Retstch PM 100 laboratory ball mill with a speed of 220 rpm to form the precursor. The precursor was then heated at 413 K for 12 h under vacuum condition, leading to ZU-36-Ni. ZU-36-Co was synthesized *via* the same method except replacing $Ni(NO_3)_2$ by $Co(NO_3)_2$.

Furthermore, ZU-36-Ni was also synthesized by wet chemical method. Briefly, $Ni(BF_4)_2$ (1 mmol), $(NH_4)_2GeF_6$ (1 mmol) and pyrazine (1.0 g) were dissolved in 2 ml water and 2 ml methanol, and stirred for 2 days at room temperature to blue powders. The blue powders were heated at 413 K under vacuum conditions for 12 h, leading to ZU-36-Ni material.

Despite extensive attempts, we were not able to obtain single crystals of sufficient size suitable for single crystal diffraction studies and therefore structural determination by powder diffractometry was explored.

Powder X-ray diffraction and structure refinement

Powder X-ray diffraction (PXRD) was carried out at room temperature on a Bruker D8 Advance diffractometer using Cu-Kα radiation (λ=1.5418 Å). Data treatment and structure solution were initially performed using FullProf software.[2] Then the JANA program was used for Rietveld refinements.[3] CCDC-1887519 and 1967852 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html.

Low-pressure gas adsorption

The measurements for CO_2, CH_4, and N_2 isotherms were performed on a fully automated ASAP 2020 adsorption analyzer (Micromeritics Instruments, USA) at relative pressures up to 1 atm. The bath temperature was controlled using an H_2O re-circulating bath.

Breakthrough tests

The breakthrough experiments were accomplished by a dynamic gas breakthrough set-up (Figure S4). The experiment was conducted using a stainless-steel column (4.6 mm inner diameter × 50 mm). The column packed with ZU-36-Ni (0.63 g) was firstly activated with He flow (5 ml min^{-1}) for 10 h at 373 K. After activation, the mixed gas (CO_2/N_2 or CO_2/CH_4) was introduced. Outlet gas from the column was monitored using the mass spectrometer After the breakthrough experiment, the column was regenerated with He flow (5 mL min^{-1}) at 373 K for 2 h.

Density-functional theory calculations

First-principles density functional theory (DFT) calculations were performed in Castep software (Materials Studio, Accelrys Software Inc.).[4] A semi-empirical addition of dispersive forces to conventional DFT was included in the calculation to account for van der Waals interactions.[4] Vanderbilt-type ultrasoft pseudopotentials and generalized gradient approximation with Perdew–Burke–Ernzerhof exchange correlation were used. A cutoff energy of 590 eV and a 1 × 1 × 2 *k*-point mesh (generated using the Monkhorst-Pack scheme) were found to be enough for the total energy to converge within 0.01 meV $atom^{-1}$. The structures of the synthesized materials were firstly optimized. Then various guest gas molecules were introduced to various locations of the channel pore, followed by a full structural relaxation. To obtain the gas binding energy, an isolated gas molecule placed in a supercell (with the same cell dimensions as the material crystal) was also relaxed as a reference. The static binding energy (at $T = 0$ K) was then calculated using: $E_B = E_{(MOF)} + E_{(gas)} - E_{(MOF + gas)}$.

Calculation of IAST separation selectivities

The isotherm data for CO_2, N_2, CH_4 on different materials were fitted with either the Langmuir-Freundlich isotherm model: [5]

$$q = q_{sat}\frac{bp^v}{1 + bp^v} \quad (2)$$

With T-dependent parameters b:

$$b = b_0 exp^{[7]}(\frac{E}{RT}) \quad (3)$$

Ideal Adsorbed Solution Theory Model (IAST) Calculations of Adsorption Selectivities: The adsorption selectivity for CO_2/CH_4 separation is defined by: [6-8]

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (4)$$

Where q_1 and q_2 are the molar loadings in the adsorbed phase in equilibrium with the bulk gas phase with partial pressures p_1 and p_2.

Isosteric heat of adsorption calculations

The isosteric heat of adsorption, Q_{st}, defined as

$$Q_{st} = RT^2\left(\frac{\partial lnp}{\partial T}\right)_q$$

were determined using the pure component isotherm fits. The Langmuir-Freundlich isotherm fits were differentiated with the Clausius-Clapeyron equation.

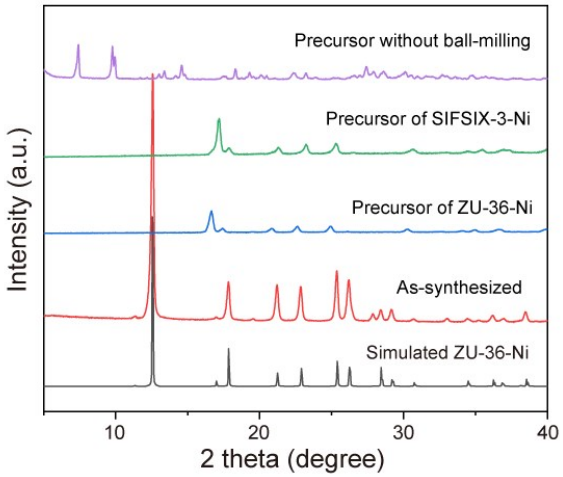

Figure S1. XRD patterns of ZU-36-Ni, the precursor of ZU-36-Ni and precursor of SIFSIX-3-Ni.

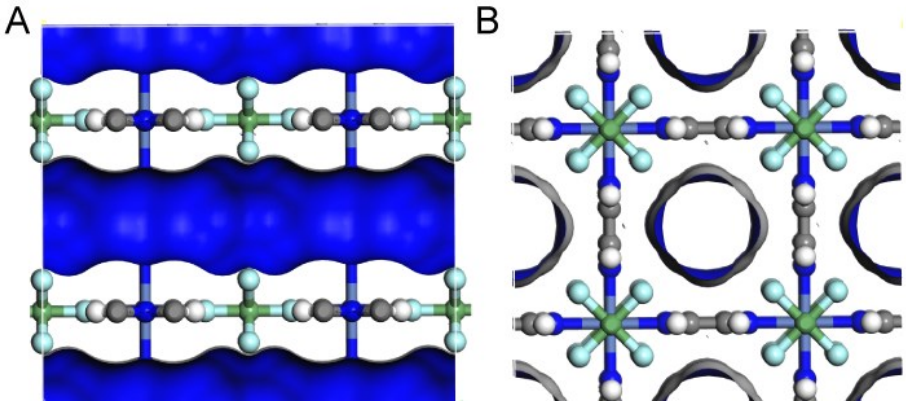

Figure S2. The pore structure of ZU-36-Ni.

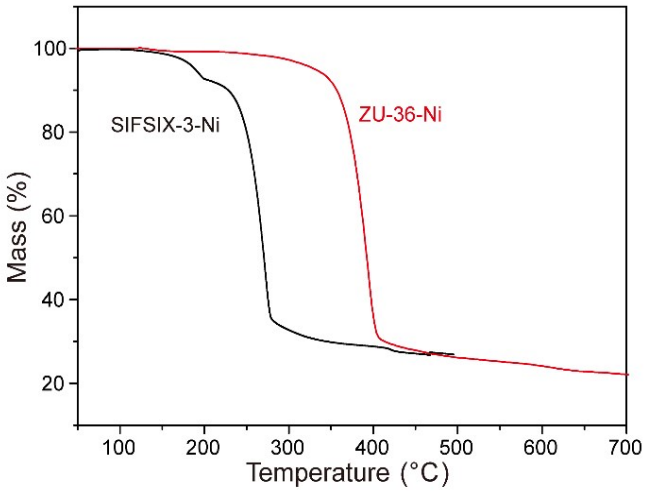

Figure S3. TGA curves of ZU-36-Ni and SIFSIX-3-Ni. TGA tests were conducted from room temperature to 700 ºC under N_2 atmosphere with flow rate of 20 mL min^{-1}.

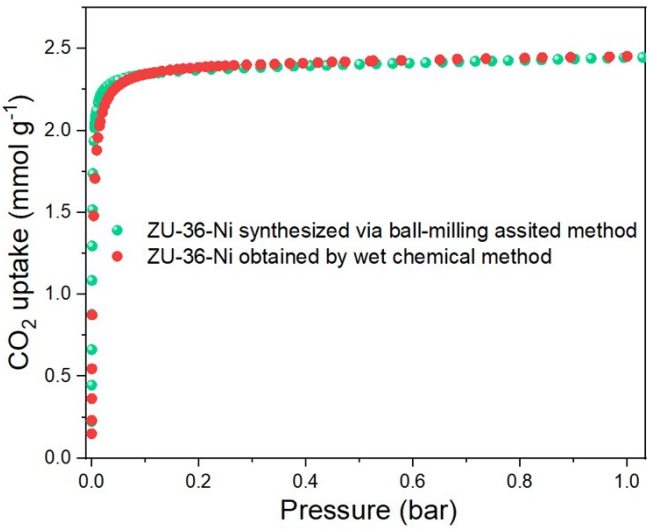

Figure S4. CO_2 adsorption isotherm on ZU-36-Ni synthesized by different methods at 298 K.

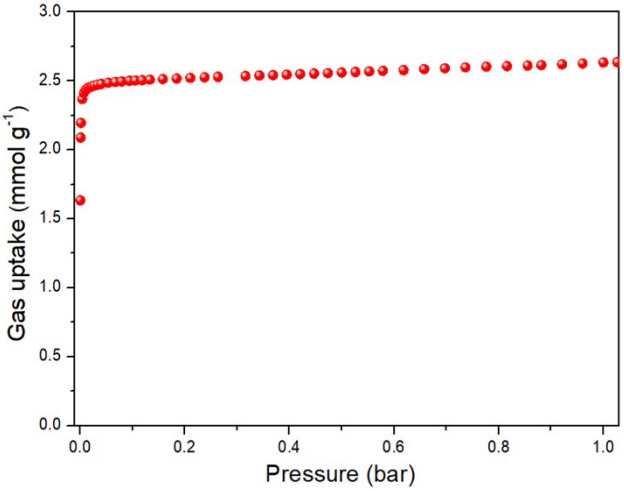

Figure S5. CO_2 adsorption isotherm on ZU-36-Ni at 273 K.

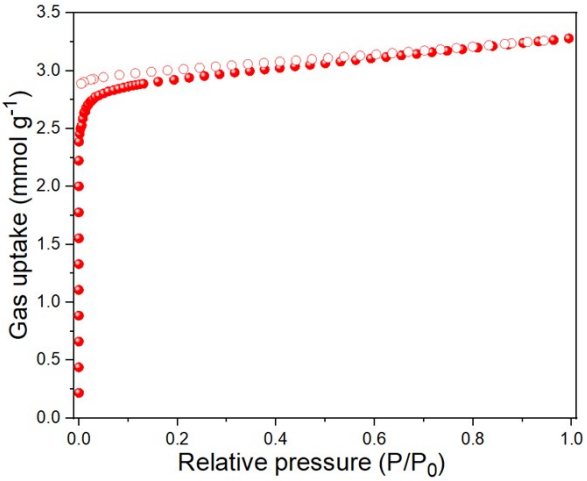

Figure S6. CO_2 adsorption isotherm on ZU-36-Ni at 196 K.

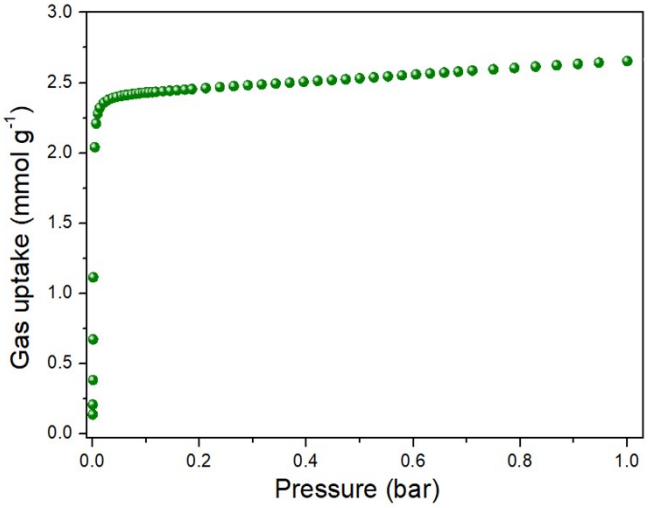

Figure S7. CO_2 adsorption isotherms on ZU-36-Co at 273 K.

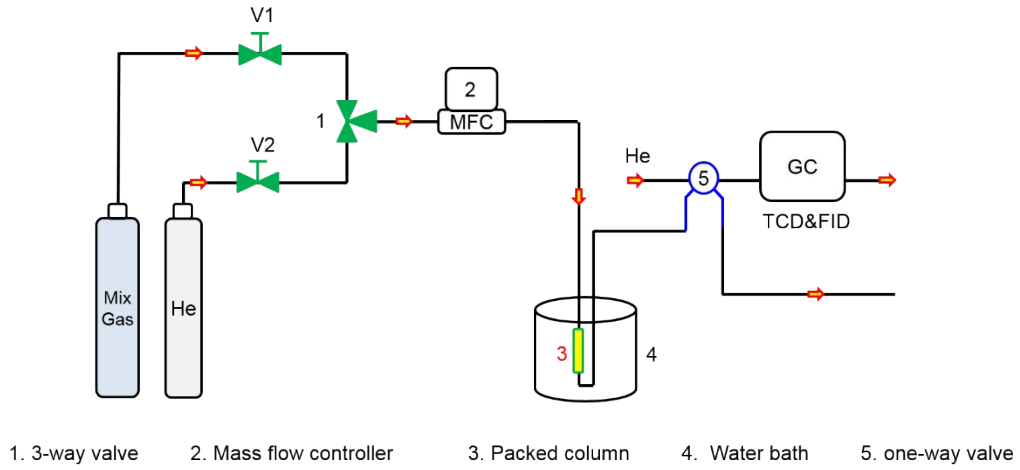

Figure S8. Schematic illustration of the apparatus for the breakthrough experiments.

Table S1. Crystallographic data of ZU-36-Co and ZU-36-Ni.

	ZU-36-Co	ZU-36-Ni
Formula	$C_8N_4H_8CoGeF_6$	$C_8N_4H_8NiGeF_6$
Formula weight (g mol^{-1})	405.5	405.46
Crystal system	Tetragonal	Tetragonal
Space group	*P4/mmm*	*P4/mmm*
a=b	7.094	6.9838
c	7.560	7.5872
V ($Å^3$)	390.35	380.28
Z	1	1
R_P, R_{WP}	0.0283, 0.0543	0.0304, 0.0444
GOF	3.50	2.28

Table S2. The distances between metal ions and pyrazine in porous materials.

Materials	M-N	Distance (Å)
SIFSIX-3-Ni	Ni-N	2.04
SIFSIX-3-Zn	Zn-N	2.17
ZU-36-Ni	Ni-N	2.08
ZU-36-Co	Co-N	2.09

Table S3 Single-site Langmuir-Freundlich parameter fits for CO_2, N_2, and CH_4 on ZU-36 materials.

		Site A			Site B		
		$q_{A,sat}$	b_{A0}	v_A	$q_{B,sat}$	b_{B0}	v_B
		mol kg^{-1}	Pa^{-vA}		mol kg^{-1}	Pa^{-vB}	
ZU-36-Co	CO_2	2.094	3.256	2.416	0.559	0.428	1.057
	N_2	137.1	8.31E-10	3.467			
	CH_4	2.781	0.0007	0.977			
ZU-36-Ni	CO_2	2.210	13.642	1.061	0.305	0.303	0.482
	N_2	0.354	0.004	1.043			
	CH_4	1.398	0.002	1.013			

References:

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