Electronic supplementary information (ESI) for

A chemically stable hydrogen-bonded organic framework for SO₂/CO₂

separation

Jun Liang,^{a,b} Shang–Hua Xing,^{a,b} Philipp Brandt,^b Alexander Nuhnen,^b Carsten Schlüsener,^b Yang–Yang Sun,^b

and Christoph Janiak*a,b

^a Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic, 7098 Liuxian Blvd, Nanshan District, Shenzhen, China

^b Institut für Anorganische Chemie und Strukturchemie, Heinrich–Heine–Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany

Additional Emails: liangj@uni-duesseldorf.de; xingshanghua@126.com; p.brandt@hhu.de; Alexander.Nuhnen@uniduesseldorf.de; carsten.schluesener@hhu.de; Yangyang.Sun@uni-duesseldorf.de

Table of Contents

S1. Experimental Details

- 1. Materials
- 2. Characterization methods
- 3. Preparation of nanoCB6-H and CB6-H
- 4. Gas sorption measurements

S2. Computational details

- 1. Virial analysis for SO₂
- 2. IAST calculations
- 3. Molecular simulation
- 4. Breakthrough simulations

S3. Fig. S1-S31

Fig. S1 TEM images and SEM images of nanoCB6-H crystals.

- Fig. S2 PXRD patterns of nanoCB6-H at different temperature under air.
- Fig. S3 TGA curve of nanoCB6-H at different temperature under air.
- Fig. S4 The pore size distributions of nanoCB6-H before and after SO_2 sorption.
- Fig. S5 SO_2 uptake isotherms of recycled nanoCB6-H measured up to 1 bar at 273 K and 293 K.
- **Fig. S6** Comparison of SO₂ uptakes of nanoCB6-H and representative MOFs at 0.1 bar.
- Fig. S7 Comparison of SO_2 uptakes of nanoCB6-H and representative MOFs at 1.0 bar.
- Fig. S8 CO_2 uptake isotherms of recycled nanoCB6-H measured up to 1 bar at 273 K and 293 K.
- Fig. S9 CH₄ uptake isotherms of nanoCB6-H measured up to 1 bar at 273 K and 293 K.
- Fig. S10 N_2 uptake isotherms of nanoCB6-H measured up to 1 bar at 273 K and 293 K.
- Fig. S11 Virial analysis of the SO_2 sorption data for nanoCB6-H
- Fig. S12 Virial analysis of the CO₂ sorption data for nanoCB6-H.
- Fig. S13 Virial analysis of the CH₄ sorption data for nanoCB6-H.
- Fig. S14 Virial analysis of the N_2 sorption data for nanoCB6-H.
- Fig. S15 The automatic isotherm parameters of SO₂ (blue curve) and CO₂ (green curve) fitted by the Dual Site Langmuir (DSLAI) model (top).
- Fig. S16 The revised isotherm parameters of SO₂ and CO₂ re-fitted by Dual Site Langmuir model (top).
- **Fig. S17** The IAST prediction calculation result for SO₂/CO₂ mixture based on the revised fitted isotherm parameters from the fit presented in Fig. SY (top). The IAST SO₂/CO₂ selectivity result (bottom).
- Fig. S18 IAST selectivities of recycled nanoCB6-H for SO₂/CO₂ mixtures with varying volume ratio from 10:90 to 50:50 (v/v) at 293 K and 1 bar.
- Fig. S19 SO₂/CO₂ selectivity of recycled nanoCB6-H and representative MOFs for gas mixtures.

- Fig. S20 IAST selectivities of recycled nanoCB6-H for SO₂/CH₄ mixtures with varying SO₂ molar fractions in gas phase at 293 K and 1 bar.
- Fig. S21 IAST selectivities of recycled nanoCB6-H for SO₂/N₂ mixtures with varying SO₂ molar fractions in gas phase at 293 K and 1 bar.
- Fig. S22 SO₂ adsorption isotherms of newly activated nanoCB6-H for only the first run measured up to 1 bar at 273 K and 293 K.
- Fig. S23 Isosteric heat of adsorption of SO₂ for newly activated nanoCB6-H materials based on the first runs data (grey), and recycled nanoCB6-H materials based on the recycled runs data (brown).
- Fig. S24 Virial analysis of the SO₂ sorption data from the first runs with newly prepared and activated nanoCB6-H samples.
- Fig. S25 a) PXRD patterns, b) N₂ sorption isotherms (77 K) of nanoCB6-H before and after SO₂ sorption for the first run at 293 K. c) The SO₂ sorption isotherms of nanoCB6-H for the first and second runs. Note: nanoCB6 was activated at 150 °C under a dynamic vacuum for 2 days.
- Fig. S26 SO₂ and CO₂ uptake isotherms of recycled nanoCB6-H samples measured up to 0.97 bar at 353 K.
- Fig. S27 Simulated breakthrough curves for nanoCB6-H with SO₂/CO₂/N₂; 0.1/15.0/84.9; v:v:v at 293 K.
- Fig. S28 Chemical view of the void volume based on the accessible surface in a unit cell of CB6 H.
- Fig. S29 Chemical view of a pair of SO₂ molecules encapsulated in the intrinsic pore of a CB6 cage.
- Fig. S30 FTIR spectra of nanoCB6-H and nanoCB6-H after uptake of SO₂ under atmosphere condition.
- Fig. S31 FTIR spectra of nanoCB6-H, nanoCB6-H after uptake of SO₂, and the recycled nanoCB6-H materials.
- **Fig. S32** a) PXRD patterns of CB6-H before and after SO₂ uptake at 293 K up to 0.97 bar. b) The N₂ adsorption isotherms (77 K) of CB6-H. The SEM images of CB6-H c) before and d) after SO₂ uptake at 293 K up to 0.97 bar.
- **Fig. S33** Comparison of SO₂ sorption isotherms of nanoCB6-H and CB6-H up to 0.97 bar at 293 K for the first runs.
- Fig. S34 a) PXRD patterns and b) N_2 adsorption isotherms (77 K) of nanoCB6-H before and after exposure to humid HCI.

S4. Table S1–S7

Table S1. Textural properties of nanoCB6-H before and after dry SO₂ adsorption.

 Table S2. Experimental results of gas adsorption in recycled nanoCB6-H.

Table S3. Parameters for DSLAI modelling on different gas adsorption isotherm of nanoCB6-H.

Table S4. IAST selectivity results of different gas mixtures at 293 K and 1 bar.

- Table S5. SO₂ sorption and separation properties of nanoCB6-H and other representative adsorbents.
- Table S6. SO2 sorption and separation properties of representative MOF adsorbents.
- Table S7. Representative non-covalent bonds between CB6 cage and SO2 molecules, and bonding energies based on DFT calculations.

S5. References

S1. Experimental Details

1. Materials

All starting materials and solvents were obtained from commercial sources. Hydrochloric acid (37 wt%), methanol (99.99%), urea (> 99.5%) were obtained from Sigma–Aldrich. Paraformaldehyde (95–100.5%) was bought from Carl roth. Glyoxal (40 wt% solution in H_2O) was obtained from J&K company.

2. Characterization methods

Powder X–ray diffraction patterns (PXRD). All samples were measured over the 2θ range of $5 - 50^{\circ}$ with a scan speed of 1.5° min⁻¹ on a Bruker D2 Phaser powder diffractometer equipped with a flat silicon, low background sample holder using Cu–K α radiation (λ = 1.5418 Å, 30 kV, 10 Ma, ambient temperature). Simulated patterns of CB6 H were calculated with CCDC Mercury 3.7 program using the single crystal data (CCDC no. 676880, Refcode KOBNEV).

SEM and TEM. High resolution scanning electron microscopy (SEM) image was recorded with a Jeol JSM– 6510LV QSEM Advanced electron microscope with a LAB–6 cathode at 20 keV.

Transmission electron microscope (TEM) images were taken on a FEI TECNAI G2 F20 microscope at an accelerating voltage of 200 kV.

FT–IR. Fourier transform infrared (FT–IR) spectra of samples were recorded on a Bruker FT–IR Tensor 37 as attenuated total reflection in the range of 550–4000 cm⁻¹. For IR measurement on nanoCB6-H with SO₂ adsorbate, nanoCB6-H powder was first degassed at 423 K for 24 hours before the dose of SO₂ by manual up to 350 Torr and held by 10 minutes, then the sample was backfilled with helium. The sample tube with SO₂@nanoCB6-H powder was immediately put in a Dewar bottle with very limited amount of liquid N₂ for a short time (within two minutes) and the sample was poured out to measure IR spectra. For comparison, activated nanoCB6-H without SO₂ adsorption was also treated with the same procedure. SO₂@nanoCB6-H powder was activated under vacuum at 423 K for two hours before the collection of IR spectra of recycled nanoCB6-H again.

NMR. The ¹H NMR was performed at AVANCE III Bruker Biospin spectrometer, operating at 300 MHz. **EA**. Elemental analyses of C, H, and N were carried out on an Elementar Vario EL III analyzer. **TGA**. Thermogravimetric analysis (TGA) were carried out with a Netzsch TG 209 F3 Tarsus in the range of 30 °C to 650 °C with a heating rate of 10 K min⁻¹ under oxygen atmosphere.

3. Preparation of nanoCB6-H and CB6-H

For gas sorption by porous adsorbents, it is recognized that the uptake amount can be affected by various factors including the pore size (the critical pore diameter) and overall particle size of the adsorbent material, as each uptake point is related to the equilibrium time at certain partial pressure. If the critical pore diameter of the adsorbent is close to the kinetic diameter of the adsorbate molecule, or the particle size of the adsorbent is relatively large, then this will lower the permeance, and longer equilibrium times are usually needed. Therefore, an uptake by an adsorbent with larger particle size could be under-determined under the same equilibrium time parameters. Taking this into consideration, we have chosen nanoscale particle sizes of CB6-H, termed nanoCB6-H in this work for investigation in order to facilitate the exposure of CB6 cages to SO₂ molecules, and to minimize the diffusion time effect as the portal size of CB6 (3.9 Å) is very close to the kinetic diameter of SO₂ (4.1 Å). micro-size crystallites of CB6-H were also prepared and investigated for comparison.

nanoCB6-H was prepared according to a reported method with modification.^{1a} 250 mg CB6 was dissolved in 5 mL 6 M HCl after sonication for two minutes. Then the solution was filtered through membrane (20 um). The obtained CB6 solution was rapidly poured into 25 mL methanol under string at 300 rpm, and kept stirring for two minutes. Transfer the white mixture into a 50 mL centrifugation tube, 5000 rpm for 5 minutes, and the upper solution was removed. 25 mL fresh methanol was added to disperse the solid under sonication, then being centrifugated at 5000 rpm for 5 minutes. This process was repeated one more time. Put the solid product in vacuum oven at 60 °C for 12 hours before cooling down to R.T, and grind slightly the product into powder, then put the powder under dynamic vacuum oven at 100 °C for 48 hours. Elemental analysis data for nanoCB6-H. Calcd (%) for $C_{36}H_{36}N_{24}O_{12}$ ·1.8H₂O: C, 42.01; H, 3.88; N, 32.66. Found: C, 41.94; H, 4.34; N, 31.18. ¹H NMR, (300 MHz, D₂O/KCI, 25 °C): δ (ppm) = 5.83–5.78 (d, 12H, N–CH₂–N), 5.72 (s, 12H, –CH–), 4.48–4.43 (d, 12H, N–CH₂–N). FT–IR characteristics (KBr, u_{max} , cm⁻¹): 3471 (w, H₂O), 2999, 2927 (w, C–H), 1734 (w, C=O), 1476 (s, CH₂), 1329 (s), 1236 (s), 1190 (s), 966 (s), 800 (s).

CB6-H was prepared according to previous report,^{1c} and characterized by PXRD and N_2 sorption at 77 K (Fig. S32).

4. Gas sorption measurements

SO₂, CO₂, CH₄ and N₂ sorption isotherms for both newly activated and recycled nanoCB6-H materials were recorded at 293 K (water bath with temperature control system) and 273 K (ice/water bath) on a Quantachrome Autosorb IQ MP. Before the measurement, the nanoCB6-H samples were activated at 373 K in vacuum for 48 hours. In control experiments, nanoCB6-H or CB6-H was activated continuously at 423 K in vacuum for 48 hours. All gases were of ultrapure grades (99.999%) supplied by Air Liquide Germany and used as–received.

SO₂ sorption experiments were performed on an Autosorb iQ MP instrument within a pressure range of 1·10⁻³–1 bar. For safety precautions of toxic SO₂, a Dräger Pac 6000 SO₂–detector (0–100 ppm in 0.1 ppm steps) was used in close range to the sorption-device. SO2-sorption experiments with our setup involve some limitations emerging from the corrosive nature of the SO₂ adsorptive. Each SO₂ sorption run had to be completed within a maximal time of 10 h. This time limit was specified by the Quantachrome company to prevent damage to the gaskets. Irreversible swilling of the SO₂ adsorbing gaskets in the measurement device could cause leaks in the system. Thus, the measurement time (10 hours at maximum) should be set to protect the device. After each measurement, the system had to be regenerated by flushing with nitrogen for at least five times, and remained under N₂ atmosphere for at least 12 hours to regenerate the gaskets. In the case of long equilibration times upon adsorption and desorption, we decided to collect the adsorption data points as complete as possible with long-enough equilibration times at the expense that fewer data points could be measured for desorption. This compromise then led to incomplete, i.e. not-closed desorption branches, which however are solely due to the experimental boundary conditions and cannot be interpreted in terms of decomposition or chemisorption. In SO₂ adsorption recycle experiments, recycled sample was degassed at 373 K under vacuum for at least two hours. For SO₂ adsorption at 353 K conditions, recycled sample after conducting SO₂ adsorption at 293 K for ten runs was used, and an oil batch with temperature control system was set up.

Nitrogen sorption measurements at 77 K were carried out on a Micrometrics ASAP 2020 or Autosorb 6 gas sorption analyzer. Before the measurement, the samples were activated at 373 K in vacuum for 48 hours. The Brunauer–Emmett–Teller (BET) surface areas were calculated based on a few points in the p/p_o range of 0.005–0.08 using the ASAP 2020 v3.05 software. Total pore volumes were calculated from nitrogen

adsorptions isotherms at $p/p_o = 0.9$. Micropore volumes were calculated based on t–plot method in the p/p_o range of 0.1–0.2. The pore size distributions were obtained using nonlocal density functional theory (NLDFT) calculations with an "N₂–Tarazona, cylinder" model.

S2. Computational details

1. Virial analysis for SO₂

To calculate the isosteric enthalpy of adsorption (ΔH_{ads}) for SO₂ isotherm data, virial method was used. Equation (eq. 1) was used to fit the adsorption data simultaneously at 273 K and 293 K in Origin.

$$\ln(P) = \ln(n) + \frac{1}{T} \sum_{i=0}^{n} a_{i} n^{i} + \sum_{j=0}^{m} b_{j} m^{j}$$
(1)

In equation (1), *P* is the pressure in kPa, *n* is the total amount adsorbed in mmol g^{-1} , *T* is the temperature in K (here 273K, 293K), *a_i* and *b_i* are virial coefficients, and *n*, *m* represent the number of coefficients required to adequately fit the isotherms.

Then ΔH_{ads} can be calculated from equation (eq. 2), where R is the universal gas constant.

$$\Delta H_{ads} = -Q_{st} = R \sum_{i=0}^{n} a_i n^i$$
(2)

2. IAST calculations²

Selectivities of SO₂ over CO₂ of nanoCB6-H were calculated from the dual–site Langmuir (DSL) (eq. 3) fitted isotherm data.

$$q_{eq} = q_{m,1} \cdot \frac{K_1 \cdot p}{1 + K_1 \cdot p} + q_{m,2} \frac{K_2 \cdot p}{1 + K_2 \cdot p}$$
(3)

The 3P sim software (3P Instruments, Germany, version 1.1.0.7) calculates the maximal loadings of each gas depending on the given mole fraction.

IAST selectivities *S* of binary gas mixtures were calculated using equation 4, where x_i represents the absorbed gas amount and y_i the mole fraction of each adsorptive.

$$S = \frac{x_1/x_2}{y_1/y_2}$$
(4)

Selectivities of SO₂ over CH₄, and SO₂ over N₂ of nanoCB6-H were calculated from the dual–site Langmuir (DSL) (eq. 3) fitted isotherm data. IAST with DSLangmuir isotherm mode was chosen, and the total pressure was fixed at 1 bar to give the IAST selectivity versus the SO₂ molar fractions between 0.01 and 0.5 bar in gas mixtures. Alternatively, SO₂ to CH₄ (or SO₂ to N₂) volume ratio was fixed to give the IAST selectivity vs pressure between 0.1 to 1.0 bar based on eq.4.

3. Molecular simulation

All density functional theory (DFT) calculations were performed with Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional by using Gaussian 16 software.³ The initial configuration of CB6 was obtained from the single-crystal structure (CCDC no. 676880, Refcode KOBNEV). The geometric optimization of CB6 was carried out at the level of B3LYP/6-311G^{**} method. The same level of method for CB6 geometric optimization was also used on other literatures.⁴ The SO₂ molecule was manually placed on the optimized CB6 configuration with different site, and then the fully relax optimizations of complex models SO₂_CB6 were

performed. The binding energy of SO₂ molecule with CB6 was calculated by the dispersion corrected B3LYP-D3 functional⁵ along with 6-311G^{**}. The basis set superposition error (BSSE) was corrected by the counterpoise method.⁶ The binding energy was thus obtained from the equation 5:

 $E(binding energy) = E(SO_2_CB6) - E(CB6) - E(SO_2) + E(BSSE)$ (5)

where $E(SO_2_CB6)$ corresponds to the total energy of CB6 model with one SO_2 molecule, and E(CB6) and $E(SO_2)$ are the total energies of CB6 model without SO_2 and only one SO_2 molecule, respectively.

4. Breakthrough simulations

Breakthrough simulations were calculated using 3P sim software. The calculations were based on a 30 cm high column with an inner diameter of 3 cm, axial dispersion of 50 cm² min⁻¹ and a continuous gas flow of 20 mL min⁻¹. Generally mass transfer coefficients in our dispersion model were set to 10 min⁻¹ for all gases.



Fig. S1 a) TEM images of nanoCB6-H with different magnification. SEM images of nanoCB6-H b) before and c) after SO₂ uptake at 293 K up to 0.97 bar.



Fig. S2 PXRD patterns of nanoCB6-H at different temperature under air.



Fig. S3 TGA curve of nanoCB6-H at different temperature under oxygen atmosphere.



Fig. S4 The pore size distributions of nanoCB6-H before SO₂ sorption (green) and after ten runs of SO₂ sorption (blue).



Fig. S5 SO₂ uptake isotherms (the 7th and 8th runs) of recycled nanoCB6-H measured up to 1 bar at 293 K and 273 K, respectively. Filled and empty symbols represent adsorption and desorption, respectively.



Fig. S6 Comparison of SO₂ uptakes of nanoCB6-H and representative MOFs at 0.1 bar. Plot of SO₂ adsorption (at 0.1 bar and 298 K) against BET surface area. Temperature for nanoCB6-H and MIL–160 is at 293 K. Cage involved materials are underlined.



Fig. S7 Comparison of SO₂ uptakes of nanoCB6-H and representative MOFs at 1.0 bar. Plot of SO₂ adsorption (at 1.0 bar and 298 K) against BET surface area. Temperature for nanoCB6-H and MIL–160 is at 293 K. Cage involved materials are underlined.



Fig. S8 CO₂ uptake isotherms of recycled nanoCB6-H measured up to 1 bar at 273 K and 293 K, respectively. Filled and empty symbols represent adsorption and desorption, respectively.



Fig. S9 CH₄ uptake isotherms of nanoCB6-H measured up to 1 bar at 273 K and 293 K, respectively. Filled and empty symbols represent adsorption and desorption, respectively.



Fig. S10 N_2 uptake isotherms of nanoCB6-H measured up to 1 bar at 273 K and 293 K, respectively. Filled and empty symbols represent adsorption and desorption, respectively.



Fig. S11 Virial analysis of the SO₂ sorption data for recycled nanoCB6-H.



Fig. S12 Virial analysis of the CO₂ sorption data for recycled nanoCB6-H.



Fig. S13 Virial analysis of the CH₄ sorption data for nanoCB6-H.



Fig. S14 Virial analysis of the N₂ sorption data for nanoCB6-H.



Fig. S15 The automatic isotherm parameters of SO_2 (blue curve) and CO_2 (green curve) fitted by the Dual Site Langmuir (DSLAI) model (top). The corresponding fitting results of chart with log(x) and log(y) for better visualization (bottom).



Fig. S16 The revised isotherm parameters of SO₂ and CO₂ re-fitted by Dual Site Langmuir model (top) by omitting the data below 0.01 bar which gave an 'Affinity constant 1' for SO₂ of 660 bar⁻¹. The corresponding fitting results of chart with log(x) and log(y) for better visualization (bottom).

| Openant Openant <t< th=""><th>culation of Equilib</th><th>brium Data for N</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></t<> | culation of Equilib | brium Data for N | | | | | | | | | | |
|---|------------------------|---|---|---------------------|-------------|-------------------|---------------------------------------|---|---|--|--|--|
| Image: Mark | Clipboard Hel | lp | | | | | | | | | | |
| Name Description Description <thdescription< th=""> <thde< th=""><th>tion Chart</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></thde<></thdescription<> | tion Chart | | | | | | | | | | | |
| Performant 1 Compare 1 </td <td>ameter of Isotherms</td> <td>and mole fraction</td> <td></td> <td>parameter of compor</td> <td>ients</td> <td></td> <td></td> <td></td> <td>calcul</td> <td>ation conditions</td> <td></td> <td></td> | ameter of Isotherms | and mole fraction | | parameter of compor | ients | | | | calcul | ation conditions | | |
| Bits Bits <th< td=""><td></td><td></td><td></td><td>Component 1</td><td>Component 2</td><td>Compone</td><td>ent 3</td><td>Component</td><td>4</td><td></td><td></td><td></td></th<> | | | | Component 1 | Component 2 | Compone | ent 3 | Component | 4 | | | |
| unter capady pendig DES D <thd< th=""> <thd< th=""> D D</thd<></thd<> | nity constant 1 [1/ba | ar] 59.15 | 4 | 660.36 | 59.154 | 0 | | 0 | 0 | constant gas comp | osition, pressure va | nabel |
| mit order 2 (1-bd) 1183 1 181 0 </td <td>uration capacity 1 fm</td> <td>nmol/g] 0.605</td> <td>1÷1</td> <td>3.154</td> <td>0.605</td> <td>0</td> <td></td> <td>0</td> <td>۲</td> <td>constant pressure,</td> <td>gas composition va</td> <td>nabel</td> | uration capacity 1 fm | nmol/g] 0.605 | 1÷1 | 3.154 | 0.605 | 0 | | 0 | ۲ | constant pressure, | gas composition va | nabel |
| Image: Second | - A 11 C tretteneo ute | 1 881 | <u></u> | 1.142 | 1 001 | 0 | | | calcu | lation range | , | variabel component |
| Second system Second s | iny constant 2 (1/ba | 2 075 | | 1.143 | 1.001 | 0 | | 0 | minin | mum 0 | 0.01 | Component 1 |
| Interfactor Interfactor <thinterfactor< th=""> <thinterfactor< th=""></thinterfactor<></thinterfactor<> | uration capacity 2 [m | nmol/g] 3.075 | | 3.989 | 3.075 | 0 | | 0 | | | | |
| d researe Bay text of any output in the second of the se | e fraction in gas pha | ase 0.500 | ÷ | 0.5 | 0.5 | 0 | | 0 | max | mum | .99 🗧 | Component 2 |
| See of components Nathem model Note value Note value <t< td=""><td>al pressure [bar]</td><td>1.00</td><td>-</td><td></td><td></td><td></td><td></td><td></td><td>num</td><td>ber of calc.</td><td>60 🜲</td><td>Component 3</td></t<> | al pressure [bar] | 1.00 | - | | | | | | num | ber of calc. | 60 🜲 | Component 3 |
| Name Nam Name Name | aber of components | leatha | mmodel | set value | 🖌 set valu | e 🖌 : | et value | √ set | value | | | Component 4 |
| Image: Second | noor of components | | | A | A | | - 12 | A | | aslaulata | | |
| Image Y1 Y2 Y3 Y4 X1 X2 X3 Y4 N1 X2 X4 In termslage In termsla | | | o congritari | Cut | 0 | | Cuit | / | cur | Calculate | | |
| Mode Y1 Y2 Y3 Y4 X1 X2 X3 X4 n1 bmody1 n2 bmody1 1000 0000 0.590 0.055 0.455 0.772 0.266 0.772 0.266 0.772 0.2875 0.657 0.365 0.772 0.266 0.272 0.266 0.272 0.266 0.377 0.277 0.365 0.377 0.277 0.365 0.377 0.278 0.277 0.335 0.277 0.336 0.377 0.278 0.277 0.337 0.206 0.337 0.206 0.337 0.206 0.337 0.206 0.337 0.206 0.337 0.206 0.337 0.206 0.337 0.206 0.366 0.347 0.206 0.365 0.064 0.355 0.170 1000 0.147 0.653 0.664 0.345 0.170 1006 0.147 0.853 0.666 0.345 0.207 0.266 0.187 0.237 0.266 0.137 1 1 1 1 | | | | | | | | | | | | |
| 1000 0.000 0.990 0.955 0.455 0.455 0.714 1.317 1000 0.049 0.951 0.022 0.020 2.255 0.673 1000 0.649 0.951 0.059 0.117 2.259 0.020 0.335 1000 0.668 0.952 0.321 0.059 0.010 3.397 0.700 1000 0.686 0.952 0.956 0.0564 2.326 0.77 1000 0.177 0.833 0.956 0.0564 2.334 0.156 1000 0.167 0.833 0.956 0.064 2.355 0.116 1000 0.167 0.833 0.956 0.046 2.255 0.73 1.228 Err = (\$NB/\$\SOB)/\$(\$L8/\$MB) | total pressure | Y1 | Y2 | ¥3 | Y4 | X1 | X2 | | X3 | X4 | n1 (mmol/g) | n2 (mmol/g) |
| 1000 0.009 0.570 0.732 0.268 0.177 0.255 0.573 1000 0.689 0.511 0.683 0.117 0.273 0.486 1000 0.689 0.511 0.693 0.117 0.273 0.486 1000 0.689 0.512 0.693 0.117 0.273 0.283 1000 0.689 0.512 0.695 0.664 0.317 0.223 1000 0.188 0.692 0.595 0.664 0.355 0.170 1000 0.187 0.623 0.664 0.555 0.170 1000 0.187 0.623 0.646 0.555 0.170 1000 0.187 0.623 0.646 0.555 0.170 1000 0.187 0.623 0.646 0.555 0.170 1000 0.187 0.623 0.649 0.512 0.171 1.55 1000 0.187 0.626 0.249 1.111 Y1 | 1.000 | 0.010 | 0.990 | | | 0.565 | 0.435 | | | | 1.714 | 1.317 |
| 1000 0.049 0.951 0.053 0.137 0.250 0.456 1000 0.068 0.831 0.059 0.101 0.070 0.325 0.077 1000 0.068 0.822 0.0256 0.064 0.317 0.250 0.161 1000 0.168 0.892 0.055 0.064 0.317 0.235 0.161 1000 0.188 0.892 0.054 0.954 0.964 0.162 0.165 0.161 0.255 0.161 0.255 0.161 0.255 0.161 0.255 0.161 0.255 0.161 0.255 0.143 0.267 0.256 0.149 | 1.000 | 0.030 | 0.970 | | | 0.792 | 0.208 | | | | 2.555 | 0.673 |
| 1000 0.669 0.831 0.089 0.101 0.033 0.223 0.234 1000 0.188 0.822 0.955 0.664 1.327 0.230 1000 0.188 0.822 0.955 0.664 1.327 0.230 1000 0.147 0.853 0.954 0.064 1.955 0.147 1000 0.147 0.853 0.954 0.046 1.955 0.149 1000 0.147 0.853 0.954 0.046 1.955 0.149 1000 0.147 0.833 0.956 0.046 1.955 0.149 1000 0.147 0.833 0.956 0.046 1.955 0.149 1000 0.147 0.833 0.956 0.046 1.955 0.149 1000 0.147 0.837 1.957 1.957 1.957 1.957 1000 0.147 0.949 9.951 2.879 0.456 122.535 1001 0.017 </td <td>1.000</td> <td>0.049</td> <td>0.951</td> <td></td> <td></td> <td>0.863</td> <td>0.137</td> <td></td> <td></td> <td></td> <td>2.879</td> <td>0.456</td> | 1.000 | 0.049 | 0.951 | | | 0.863 | 0.137 | | | | 2.879 | 0.456 |
| I 000 0.88 0.912 0.221 0.079 1228 0.271 1000 0.188 0.692 0.936 0.064 1.312 0.220 1000 0.188 0.692 0.946 0.064 1.342 0.186 1000 0.147 0.653 0.955 0.046 3.453 0.18 1000 0.147 0.633 0.956 0.046 3.453 0.19 ion model for mixture data : IAST with DSLangmuit Ione Ione <td>1.000</td> <td>0.069</td> <td>0.931</td> <td></td> <td></td> <td>0.899</td> <td>0.101</td> <td></td> <td></td> <td></td> <td>3.078</td> <td>0.345</td> | 1.000 | 0.069 | 0.931 | | | 0.899 | 0.101 | | | | 3.078 | 0.345 |
| 1000 0.188 0.892 0.995 0.054 1.347 0.230 1000 0.128 0.672 0.955 0.054 0.466 0.365 0.186 1000 0.147 0.653 0.956 0.646 0.365 0.186 1000 0.147 0.653 0.956 0.646 0.365 0.189 1000 0.147 0.653 0.956 0.646 0.365 0.199 1000 0.147 0.653 0.646 0.640 3.50 0.199 1000 0.147 0.653 0.640 0.640 0.57 0.56 1.19 1000 0.147 0.653 0.640 0.640 0.51 2.57 0.673 122.751 1000 0.999 1.714 1.317 128.842 0.038 0.923 3.247 0.237 122.551 0.673 122.751 120.697 122.551 0.57 122.512 120.579 120.520 120.77 120.697 122.525 | 1.000 | 0.088 | 0.912 | | | 0.921 | 0.079 | | | | 3.226 | 0.277 |
| 100 0.128 0.972 0.946 0.094 100 147 0.853 0.116 1000 0.147 0.853 0.954 0.046 3.515 0.110 1000 0.147 0.853 0.956 0.440 3.503 0.149 inn model for miture data : IAST with DSLangmuir 0.019 fr G H J K L M N O P inn model for miture data : IAST with DSLangmuir 1.011 1.837 1.2884 inn model for miture data : IAST with DSLangmuir 0.013 0.97 2.555 0.673 1.22.751 inn data fraction 0.014 0.97 2.555 0.673 1.22.751 1.22.751 1.22.751 1.22.751 1.22.751 1.22.751 1.22.101 1.22.101 1.22.101 1.22.101 1.22.102 1.22.101 1.22.101 1.22.101 1.22.101 1.22.101 1.22.101 1.22 | 1.000 | 0.108 | 0.892 | | | 0.936 | 0.064 | | | | 3.347 | 0.230 |
| IDDO 0.147 0.83 0.954 0.066 9.545 0.100 IDDO 0.167 0.833 0.950 0.040 36.00 0.143 Isom model for mixture dats: IAST with DSLangmuin F G H J K L M N O P Isom model for mixture dats: IAST with DSLangmuin F G H J K L M N O P Isom model for mixture dats: IAST with DSLangmuin V1 V2 x1 (mmol/g) x2(mmol/g) IAST selectiving X1 (mmol/g) x2(mmol/g) X2(mmol/g) IAST selectiving X2 (mmol/g) X2 (mm | 1.000 | 0.128 | 0.872 | | | 0.946 | 0.054 | | | | 3.452 | 0.196 |
| 1000 0.167 0.833 0.960 0.00 1000 | 1.000 | 0.147 | 0.853 | | | 0.954 | 0.046 | | | | 3.545 | 0.170 |
| Free Loss Loss <thlos< th=""> <thloss< th=""> Loss Lo</thloss<></thlos<> | | | | | | | 10000000000 | | | | 2 020 | 0 149 |
| I O II I J K L II C I I I I I I I I III IIII IIII IIII IIIII IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII | ion model for mix | 0.167 xture data : IAST | 0.833 with DSLangmuir 18/\$O8)/(\$L8 | /\$M8) | | 0.960 | 0.040 | | | | 3.630 | 0.190 |
| y1 y2 x1 (mmol/g) x2(mmol/g) IAST selectivit 0.01 0.09 1.714 1.317 128.842 0.03 0.97 2.555 0.673 122.751 0.049 0.951 2.879 0.456 122.535 0.059 0.931 3.078 0.345 120.37 0.069 0.931 3.078 0.345 120.37 0.0108 0.912 3.226 0.277 120.697 0.108 0.892 3.347 0.23 120.190 0.128 0.872 3.452 0.196 119.983 0.107 0.833 3.545 0.171 121.003 0.167 0.833 3.63 0.149 112.520 0.167 0.833 3.63 0.149 122.530 0.167 0.833 3.63 0.149 122.530 0.226 0.774 3.852 0.107 123.292 0.265 0.755 3.918 0.097 124.472 | ion model for mix | 0.167 xture data : IAST \$x ={\$N F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 | /\$M8) | | 0.960 | 0.040 | | M | N | 3.630 | P |
| 0.01 0.99 1.714 1.317 128.842 0.03 0.97 2.555 0.673 122.751 0.049 0.951 2.879 0.456 122.535 0.069 0.931 3.078 0.345 120.37 0.088 0.912 3.226 0.277 120.697 0.108 0.892 3.347 0.23 120.190 0.128 0.872 3.452 0.196 119.983 0.128 0.872 3.452 0.196 119.983 0.167 0.833 3.63 0.149 121.520 0.206 0.774 3.852 0.107 123.292 0.206 0.774 3.852 0.107 123.292 0.206 0.774 3.852 0.107 123.292 0.206 0.774 3.852 0.107 123.292 0.225 0.735 3.918 0.097 124.472 0.265 0.735 3.918 0.097 124.472 | ion model for mix | 0.167 xture data : IAST 5x =(\$N F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | 0.960 K | 0.040 | L | M | N | 0 | P |
| 0.03 0.97 2.555 0.673 122.751 0.049 0.951 2.879 0.456 122.535 0.069 0.931 3.078 0.345 120.37 0.088 0.912 3.226 0.277 120.697 0.108 0.892 3.345 0.123 120.190 0.128 0.872 3.452 0.196 119.983 0.147 0.853 3.545 0.17 121.003 0.167 0.833 3.63 0.149 121.520 0.167 0.833 3.63 0.149 121.520 0.206 0.794 3.783 0.119 122.530 0.206 0.794 3.852 0.107 123.292 0.006 0.794 3.852 0.007 123.292 0.026 0.794 3.852 0.007 123.292 0.0265 0.735 3.98 0.088 125.44 0.2045 0.755 3.918 0.097 124.472 | ion model for mix | 0.167 xture data : IAST xture data : IAST F F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | <u>0.960</u> К | 0.040 | L molar f | M fraction v2 | N x1 (mmol/g) | 0 x2(mmol/e) | P IAST selectivit |
| 0.049 0.951 2.879 0.456 122.535 0.069 0.931 3.078 0.345 120.37 0.088 0.912 3.226 0.277 120.697 0.108 0.892 3.452 0.123 120.190 0.128 0.872 3.452 0.171 121.033 0.147 0.853 3.545 0.17 121.033 0.147 0.833 3.63 0.149 121.520 0.167 0.833 3.63 0.149 121.520 0.186 0.814 3.709 0.133 122.044 0.206 0.794 3.852 0.107 123.529 0.226 0.774 3.852 0.107 123.529 0.226 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 125.44 0.304 0.696 4.097 0.073 128.492 | ion model for mix | 0.167 xture data : IAST \$\$\$ =(\$N F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | <u>0.960</u> К | 0.040 | L molar f | M fraction y2 0.99 | N x1 (mmol/g) 1.714 | 0 x2(mmol/g) | P IAST selectivit 128.842 |
| 0.069 0.931 3.078 0.345 120.37 0.088 0.912 3.226 0.277 120.697 0.108 0.892 3.347 0.23 120.190 0.128 0.872 3.545 0.117 121.093 0.147 0.853 3.545 0.117 121.003 0.147 0.853 3.63 0.149 121.520 0.167 0.833 3.63 0.149 122.530 0.206 0.794 3.783 0.119 122.530 0.226 0.775 3.918 0.007 124.472 0.226 0.775 3.918 0.007 124.472 0.226 0.775 3.918 0.008 125.44 0.226 0.755 3.918 0.007 124.472 0.226 0.755 3.918 0.007 124.472 0.226 0.755 3.918 0.007 124.492 0.324 0.676 4.151 0.067 122.924 | ion model for mix | 0.167 xture data : IAST \$\$\$ =(\$N F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | K | 0.040 | L molar f 0.01 0.03 | M fraction y2 0.99 0.97 | N x1 (mmol/g) 1.714 2.555 | 0 x2(mmol/g) 1.317 0.673 | P IAST selectivit 128.842 122.751 |
| 0.088 0.912 3.226 0.277 120.697 0.108 0.892 3.347 0.23 120.190 0.128 0.872 3.452 0.196 119.983 0.147 0.853 3.545 0.17 121.003 0.167 0.833 3.63 0.149 121.520 0.167 0.833 3.63 0.149 122.544 0.186 0.814 3.709 0.133 122.644 0.206 0.794 3.783 0.119 122.520 0.226 0.774 3.852 0.107 123.292 0.226 0.774 3.852 0.107 123.292 0.245 0.755 3.918 0.097 124.472 0.245 0.755 3.918 0.097 124.472 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.244 0.716 4.04 0.081 127.316 | ion model for mix | 0.167 xture data : IAST \$x =(\$N F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | K | 0.040 | L molar f 0.01 0.03 0.049 | M fraction y2 0.99 0.97 0.951 | N x1 (mmol/g) 1.714 2.555 2.879 | 0 x2(mmol/g) 1.317 0.673 0.456 | P IAST selectivit 128.842 122.751 122.535 |
| 0.108 0.892 3.347 0.13 120.190 0.128 0.872 3.452 0.196 119.983 0.147 0.853 3.545 0.17 121.003 0.167 0.833 3.63 0.149 121.520 0.166 0.814 3.709 0.133 122.044 0.206 0.774 3.852 0.107 123.292 0.206 0.774 3.852 0.107 123.292 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.245 0.755 3.918 0.097 124.472 0.304 0.696 4.097 0.073 128.492 0.304 0.696 4.097 10.73 129.264 0.304 0.696 4.097 130.965 132.099 | 1.000 | 0.167 xture data : IAST $f_{x} = ($N$ F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | K | v1 | L molar f 0.01 0.03 0.049 0.069 | M fraction y2 0.99 0.97 0.951 0.931 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 | O x2(mmol/g) 1.317 0.673 0.456 0.345 | P IAST selectivit 128.842 122.751 122.535 120.37 |
| 0.128 0.872 3.452 0.195 119.983 0.147 0.853 3.545 0.17 121.003 0.167 0.833 3.63 0.149 121.520 0.186 0.814 3.709 0.133 122.044 0.206 0.774 3.852 0.107 123.293 0.206 0.774 3.852 0.107 123.293 0.206 0.774 3.852 0.007 123.292 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 127.316 0.304 0.696 4.097 0.073 128.492 0.324 0.676 4.151 0.067 129.264 0.324 0.676 4.151 0.067 129.264 0.324 0.676 4.151 0.067 139.065 0.324 0.676 4.254 0.057 130.965 | 1.000 | 0.167 xture data : IAST xture data : IAST F F | 0.833 with DSLangmuir 8/\$O8)/(\$L8 G | /\$M8) H I | J | K | v | L molar f 0.01 0.03 0.049 0.069 0.088 | M fraction y2 0.99 0.97 0.951 0.931 0.931 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 | P IAST selectivit 128.842 122.751 122.535 120.37 120.697 |
| 0.147 0.853 0.17 121.003 0.147 0.853 3.545 0.17 121.003 0.167 0.833 3.63 0.149 121.520 0.186 0.814 3.709 0.133 122.044 0.206 0.794 3.783 0.119 122.530 0.226 0.774 3.852 0.107 123.292 0.226 0.774 3.852 0.107 123.292 0.265 0.735 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.284 0.716 4.04 0.08 127.316 0.304 0.696 4.097 0.073 128.492 0.324 0.676 4.151 0.061 132.009 0.363 0.657 4.224 0.051 133.095 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.044 134.810 0.424 | 1 000 | ture data : IAST | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | K | v1 | L molar f 0.01 0.03 0.049 0.069 0.088 0.108 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 | P IAST selectivit 128.842 122.751 122.535 120.37 120.697 120.190 |
| 0.167 0.833 3.63 0.14 121.520 0.167 0.833 3.63 0.14 121.520 0.186 0.814 3.709 0.133 122.044 0.206 0.794 3.783 0.119 122.530 0.226 0.774 3.852 0.107 123.292 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.918 0.097 124.472 0.265 0.735 3.918 0.097 124.472 0.265 0.735 3.918 0.097 124.472 0.265 0.735 3.988 0.088 125.44 0.284 0.716 4.04 0.08 127.316 0.304 0.696 4.097 0.073 128.492 0.324 0.676 4.151 0.061 132.009 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 | ion model for mix | 0.167 xture data : IAST \$x = (\$N F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | K | v1 | L molar f 0.01 0.03 0.049 0.069 0.088 0.108 0.128 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.872 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 | 0 x2(mmol/g) 1.317 0.673 0.456 0.345 0.345 0.345 0.277 0.23 | P IAST selectivit 128.842 122.751 122.535 120.67 120.190 119.983 |
| 0.186 0.186 0.187 0.183 122.044 0.206 0.794 3.783 0.119 122.530 0.226 0.774 3.852 0.107 123.292 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 127.316 0.304 0.666 4.097 0.073 128.492 0.324 0.676 4.151 0.067 129.264 0.324 0.676 4.151 0.067 129.264 0.343 0.657 4.204 0.061 132.009 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.044 134.810 0.421 0.578 4.395 0.044 137.207 | 1 000 | 0.167 xture data : IAST x =(\$N F | 0.833 with DSLangmuir (\$/\$O8)/(\$L8 | /\$M8) H I | | K | v1 | L 0.01 0.03 0.049 0.069 0.088 0.108 0.128 0.147 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.873 0.853 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 0.196 0.17 | P IAST selectivit 128.842 122.751 122.535 120.37 120.697 120.190 119.983 121.003 |
| 0.205 0.794 3.783 0.105 122.530 0.206 0.794 3.783 0.119 122.530 0.226 0.774 3.852 0.107 123.292 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 127.316 0.304 0.696 4.097 0.073 128.492 0.324 0.676 4.151 0.067 129.264 0.343 0.657 4.204 0.061 132.099 0.363 0.637 4.254 0.057 130.965 0.363 0.637 4.254 0.057 130.965 0.402 0.578 4.303 0.052 133.873 0.402 0.578 4.395 0.044 134.810 0.421 0.578 4.395 0.044 137.207 | 1.000 | 0.167 xture data : IAST \$ [=(\$N] F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | v1 | L molar f 0.01 0.03 0.049 0.069 0.088 0.108 0.108 0.128 0.147 0.167 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.872 0.853 0.833 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.545 3.545 | O x2(mmol/g) 1.317 0.673 0.455 0.345 0.277 0.23 0.196 0.17 0.19 | P IAST selectivit 128.842 122.751 120.37 120.697 120.190 119.983 121.003 121.520 |
| 0.226 0.774 3.852 0.107 123.292 0.245 0.755 3.918 0.097 124.472 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 127.316 0.304 0.696 4.097 0.073 128.492 0.304 0.696 4.097 0.073 128.492 0.304 0.696 4.097 0.073 128.492 0.304 0.696 4.097 0.073 128.492 0.324 0.676 4.151 0.067 132.099 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.422 0.578 4.395 0.041 137.207 | 1.000 | 0.167 xture data : IAST \$\$ =(\$N F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | K | V.1 | L molar 1 0.01 0.049 0.069 0.088 0.108 0.128 0.128 0.147 0.186 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.872 0.853 0.833 0.834 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.645 3.545 3.645 3.709 | O x2(mmol/g) 1.317 0.673 0.456 0.277 0.23 0.196 0.17 0.149 0.133 | P IAST selectivit 128.842 122.751 120.535 120.37 120.697 120.190 119.983 121.003 121.520 122.044 |
| 0.245 0.755 3.918 0.007 124.472 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 125.44 0.265 0.735 3.98 0.088 125.44 0.284 0.716 4.04 0.08 127.316 0.304 0.696 4.097 0.073 128.492 0.324 0.676 4.151 0.067 129.264 0.324 0.676 4.151 0.067 132.095 0.343 0.657 4.224 0.057 130.965 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.441 0.559 4.438 0.041 137.207 | 1 000 | 0.167 xture data : IAST xture data : IAST F F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | V.1 | L molar f 0.01 0.03 0.049 0.069 0.088 0.128 0.128 0.147 0.167 0.186 0.206 | M fraction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.872 0.853 0.833 0.834 0.794 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.149 0.133 0.119 | P IAST selectivit 128.842 122.751 122.535 120.37 120.190 119.983 121.003 121.520 122.044 122.535 |
| 0.265 0.735 0.98 0.088 125.44 0.265 0.735 3.98 0.088 125.44 0.284 0.716 4.04 0.08 127.316 0.304 0.696 4.097 0.073 128.492 0.324 0.676 4.151 0.061 132.09 0.363 0.657 4.224 0.051 132.095 0.363 0.657 4.254 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.421 0.578 4.395 0.041 137.207 | 1.000 | 0.167 | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | y1 | L molar 1 0.01 0.03 0.049 0.069 0.088 0.108 0.128 0.147 0.167 0.186 0.206 0.206 | M fraction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.892 0.872 0.853 0.833 0.814 0.794 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 | O x2(mmol/g) 1.337 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.149 0.133 0.119 0.107 | P IAST selectivit 128.842 122.751 122.535 120.37 120.190 119.983 121.003 121.520 122.044 122.530 122.240 |
| 0.284 0.716 4.04 0.080 127.316 0.304 0.695 4.097 0.073 128.492 0.324 0.676 4.151 0.067 129.264 0.343 0.657 4.204 0.061 132.009 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.422 0.578 4.395 0.044 137.207 | 1.000 | 0.167 | 0.833 with DSLangmuir (\$/\$O8)/(\$L8 | /\$M8) H I | | K | v1 | L molar f 0.01 0.03 0.049 0.069 0.088 0.128 0.128 0.147 0.167 0.186 0.206 0.206 0.226 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.872 0.853 0.833 0.814 0.794 0.755 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.709 3.783 3.852 3.854 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.345 0.345 0.345 0.345 0.17 0.23 0.19 0.17 0.133 0.119 0.107 | P IAST selectivit 128.842 122.751 122.535 120.97 120.190 119.983 121.003 121.520 122.044 122.530 123.292 124.472 |
| 0.304 0.695 4.097 0.073 128.492 0.324 0.676 4.151 0.067 129.264 0.343 0.657 4.204 0.061 132.009 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.421 0.578 4.395 0.044 137.207 | 1.000 | 0.167 | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | | L molar f 0.01 0.03 0.049 0.069 0.088 0.108 0.128 0.147 0.167 0.186 0.206 0.226 0.225 0.245 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.853 0.853 0.853 0.833 0.833 0.814 0.794 0.774 0.755 0.735 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.3452 3.545 3.63 3.709 3.783 3.852 3.852 3.918 3.98 3.98 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 0.196 0.177 0.149 0.133 0.119 0.107 0.097 0.088 | P IAST selectivit 128.842 122.751 122.535 120.37 120.697 120.190 119.983 121.003 121.520 122.044 122.530 123.292 123.292 124.472 125.44 |
| 0.324 0.675 4.151 0.675 129.264 0.343 0.657 4.204 0.061 132.009 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.422 0.578 4.395 0.044 135.811 | 1.000 | 0.167 xture data : IAST \$ xture data : IAST \$ F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | J | K | v 1 | L 0.01 0.03 0.049 0.088 0.108 0.128 0.147 0.186 0.206 0.226 0.245 0.265 0.265 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.853 0.833 0.834 0.794 0.774 0.755 0.735 0.735 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.545 3.545 3.545 3.545 3.545 3.709 3.783 3.852 3.918 3.988 4.94 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.133 0.119 0.107 0.097 0.088 0.088 | P IAST selectivit 128.842 122.751 120.37 120.697 120.190 119.983 121.003 121.520 122.044 122.530 123.292 124.472 125.44 127.316 |
| 0.343 0.657 4.204 0.061 132.09 0.343 0.657 4.204 0.061 132.09 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.422 0.578 4.395 0.041 137.207 | 1.000 | 0.167 xture data : IAST \$ xture data : IAST \$ F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | y1 | L molar f 0.01 0.03 0.049 0.069 0.088 0.128 0.128 0.147 0.167 0.167 0.266 0.226 0.225 0.265 0.284 0.304 | M fraction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.872 0.853 0.833 0.833 0.833 0.814 0.794 0.774 0.755 0.735 0.735 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 3.918 3.98 4.04 4.097 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.345 0.277 0.23 0.196 0.17 0.149 0.133 0.119 0.107 0.097 0.088 0.088 0.088 | P IAST selectivit 128.842 122.751 122.535 120.37 120.697 120.190 119.983 121.003 121.520 122.044 122.530 123.292 124.472 125.44 127.316 128.492 |
| 0.345 0.357 4.254 0.001 132.009 0.363 0.637 4.254 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.422 0.578 4.395 0.044 136.811 0.441 0.559 4.438 0.041 137.207 | 1.000 | 0.167 xture data : IAST xture data : IAST x F F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 | /\$M8) H I | | K | ¥1 | L molar 1 0.01 0.03 0.049 0.069 0.088 0.108 0.128 0.147 0.167 0.186 0.206 0.245 0.265 0.245 0.265 0.284 0.304 0.304 | M raction y2 0.99 0.97 0.951 0.931 0.892 0.872 0.853 0.833 0.814 0.774 0.775 0.775 0.735 0.716 0.696 0.676 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 3.918 3.98 4.04 4.097 4.151 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.345 0.177 0.23 0.196 0.177 0.097 0.0097 0.088 0.088 0.08 0.073 0.073 | P IAST selectivit 128.842 122.751 122.535 120.697 120.190 119.983 121.003 121.520 122.044 122.530 123.292 124.472 125.44 127.316 128.492 128.492 128.492 128.492 128.492 129.544 127.516 128.492 129.544 127.516 128.492 129.544 127.516 128.492 129.544 127.516 128.492 129.544 129.546 128.492 129.546 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 129.556 12 |
| 0.363 0.57 4.234 0.057 130.965 0.382 0.618 4.303 0.052 133.873 0.402 0.598 4.35 0.048 134.810 0.422 0.578 4.395 0.044 136.811 0.441 0.559 4.438 0.041 137.207 | 1.000 | 0.167 | 0.833 with DSLangmuir (\$/\$O8)/(\$L8 | /\$M8) H I | | K | v v v v v v v v v v v v v v v v v v v | L molar f 0.01 0.03 0.049 0.069 0.088 0.128 0.126 0.245 0.245 0.245 0.244 0.304 0.324 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.872 0.853 0.833 0.814 0.794 0.775 0.735 0.735 0.735 0.735 0.716 0.996 0.676 0.696 0.676 0.676 0.676 0.676 0.675 0.755 0.735 0.716 0.996 0.676 0.676 0.676 0.676 0.676 0.675 0.755 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.735 0.746 0.755 0.756 0.696 0.672 0.755 0.755 0.755 0.756 0.676 0.696 0.676 0.676 0.676 0.676 0.755 0.755 0.755 0.755 0.756 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.755 0.755 0.755 0.755 0.756 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.676 0.6776 0.775777 0.777777777777777777777777777777777 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 3.918 3.988 4.04 4.097 4.151 4.206 | O x2(mmol/g) 1.337 0.673 0.456 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.345 0.17 0.23 0.19 0.17 0.077 0.088 0.088 0.088 0.088 0.088 | P IAST selectivit 128.842 122.751 122.535 120.97 120.190 119.983 121.003 121.520 122.044 122.530 123.292 124.472 125.44 127.316 128.492 129.264 132.092 |
| 0.352 0.010 4.353 0.052 135.875 0.402 0.598 4.35 0.048 134.810 0.422 0.578 4.395 0.044 136.811 0.441 0.559 4.438 0.044 137.207 | 1.000 | 0.167 xture data : IAST x F F | 0833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | | L 0.01 0.03 0.049 0.089 0.088 0.108 0.128 0.147 0.186 0.206 0.226 0.226 0.225 0.265 0.265 0.265 0.245 0.265 0.245 0.265 0.244 0.304 0.304 0.324 0.324 0.324 0.324 0.324 0.324 0.324 0.324 0.324 0.325 0.265 0.285 0.285 0.285 0.285 0.285 0.285 0.285 0.285 0.285 0.285 0.285 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.265 0.285 0.265 0.265 0.285 0 | M raction y2 0.99 0.97 0.951 0.931 0.932 0.833 0.833 0.833 0.834 0.794 0.774 0.755 0.735 0.735 0.736 0.756 0.756 0.7570000000000 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.545 3.545 3.545 3.545 3.545 3.545 3.545 3.526 3.918 3.918 3.988 4.04 4.097 4.151 4.204 4.204 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.133 0.119 0.107 0.097 0.088 0.007 0.067 0.061 | P IAST selectivit 128.842 122.751 120.37 120.697 120.190 119.983 121.020 122.044 122.530 122.044 122.530 123.292 124.472 125.44 127.316 128.492 129.264 132.009 132.0095 132.00555 132.00555 132.00555 132.00555 132.005555 |
| 0.402 0.578 4.55 0.048 154.810 0.422 0.578 4.395 0.044 156.811 0.441 0.559 4.438 0.041 137.207 | 1.000 | 0.167 xture data : IAST xture data : IAST x F F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | Y1 | L molar f 0.01 0.03 0.049 0.088 0.128 0.147 0.186 0.206 0.226 0.245 0.265 0.265 0.284 0.324 0.324 0.324 0.324 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.822 0.833 0.814 0.794 0.774 0.755 0.735 0.716 0.696 0.676 0.657 0.637 0.642 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 3.918 3.988 4.04 4.097 4.151 4.204 4.254 4.255 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.133 0.199 0.133 0.199 0.133 0.199 0.037 0.088 0.097 0.088 0.089 0.087 0.067 0.067 0.057 0.0 | P IAST selectivit 128.842 122.751 122.535 120.697 120.697 120.190 119.983 121.520 122.544 122.530 123.292 124.472 125.444 127.316 128.492 129.264 132.009 130.955 192.92 |
| 0.441 0.550 0.044 1.058.11 | 1.000 | 0.167 xture data : IAST xture data : IAST x x F F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 G | /\$M8) H I | | K | y1 | L molar f 0.01 0.03 0.049 0.069 0.088 0.128 0.128 0.147 0.167 0.265 0.226 0.2265 0.2655 0.2655 0.2655 0.2655 0.2655 0.2655 0.2655 | M fraction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.872 0.853 0.833 0.833 0.814 0.794 0.774 0.755 0.735 0.716 0.656 0.657 0.637 0.618 0.576 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 3.918 3.98 4.04 4.097 4.151 4.204 4.254 4.303 4.254 | O x2(mmol/g) 1.317 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.196 0.17 0.196 0.17 0.097 0.088 0.088 0.097 0.088 0.097 0.088 0.097 0.057 0.052 0.052 | P IAST selectivit 128.842 122.751 122.535 120.697 120.190 119.983 121.003 121.520 122.044 122.530 123.292 124.472 125.44 127.316 128.492 129.264 132.009 130.965 133.873 134.920 |
| 0.441 0.559 4.458 0.041 13/20/ | 1.000 | 0.167 xture data : IAST xture data : IAST x F F | 0.833 with DSLangmuir 18/\$O8)/(\$L8 | /\$M8) H I | | K | y1 | L molar 1 0.01 0.03 0.049 0.069 0.088 0.108 0.108 0.108 0.128 0.147 0.167 0.167 0.265 0.245 0.265 0.245 0.265 0.284 0.304 0.304 0.304 0.304 0.304 0.304 0.304 0.304 0.265 0.265 0.284 0.304 0.304 0.265 0.265 0.284 0.304 0.265 0.26 | M raction y2 0.99 0.97 0.951 0.931 0.912 0.892 0.872 0.853 0.833 0.814 0.774 0.775 0.735 0.716 0.696 0.676 0.657 0.637 0.618 0.598 0.598 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 3.918 3.98 4.04 4.097 4.151 4.204 4.303 4.355 4.975 4.9 | O x2(mmol/g) 1.3.17 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.149 0.107 0.097 0.097 0.088 0.088 0.088 0.085 0.057 0.052 0.048 | P IAST selectivit 128.8421 122.7513 122.535 120.697 120.190 119.983 121.0031 121.520 122.540 122.540 122.540 123.2921 124.4722 125.447 125.4 |
| | 1.000 | 0.167 | 0833 with DSLangmuir (\$/\$O8)/(\$L8 | /\$M8) H I | | K | | L molar 1 0.01 0.03 0.049 0.069 0.088 0.128 0.147 0.167 0.186 0.226 0.245 0.265 0.284 0.304 0.324 0.304 0.324 0.304 0.363 0.382 0.402 0.422 | M raction y2 0.99 0.97 0.951 0.931 0.822 0.822 0.822 0.833 0.814 0.794 0.755 0.735 0.716 0.696 0.657 0.637 0.618 0.598 0.578 0.578 | N x1 (mmol/g) 1.714 2.555 2.879 3.078 3.226 3.347 3.452 3.545 3.63 3.709 3.783 3.852 3.918 3.988 4.04 4.097 4.151 4.204 4.303 4.355 4.305 4.305 4.305 4.000 | O x2(mmol/g) 1.337 0.673 0.456 0.345 0.277 0.23 0.196 0.17 0.149 0.133 0.196 0.177 0.088 0.088 0.088 0.088 0.088 0.067 0.052 0.048 0.052 0.048 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.044 0.055 0.0 | P IAST selectivit 128.8424 122.7511 122.5351 120.377 120.6970 129.9834 121.0033 121.520 122.0444 122.5300 122.9244 122.544 127.3166 128.4927 129.2644 132.00955 133.8730 134.8100 136.8111 127.2077 |

Fig. S17 The IAST prediction calculation result for SO_2/CO_2 mixture based on the revised fitted isotherm parameters from the fit presented in Fig. S16 (top). The IAST SO_2/CO_2 selectivity result (bottom) with molar fraction as the x axis and IAST selectivity as y axis are plotted in Fig. 3a, main text.

0.48

0.5

0.52

0.5

4.522

4.561

0.035

0.032

139.9666667

142.53125

In the initial calculation, the parameters were automatically obtained as the isotherm data appeared well fitted with the Dual Site Langmuir, DSLAI model. **Fig. S15** shows the previous fitting results of SO₂ and CO₂ isotherm data at 293 K up to 0.97 bar. The x and y axis are in logarithmic mode to visualize the fitting results at low pressure more clearly, and even the low-pressure data below 0.01 bar were fitted reasonably well and were included in the fit. We noticed that uncertainties could exist at the low-pressure range, and the very high 'Affinity constant 1' for SO₂ of 1321 bar⁻¹ was caused by the very steep adsorption curve below 0.01 bar (58 cm³ g⁻¹ at 7.6 Torr).

In a modified fit, the isotherm data of each gas below 0.01 bar were omitted, with the remaining data fitted

with the DSLAI model to obtain parameters for the '3P sim' software by which we re-calculated the IAST selectivities for SO_2/CO_2 , SO_2/CH_4 and SO_2/N_2 . By omitting the data below 0.01 bar, the 'Affinity constant 1' for SO_2 changed to about 660 bar⁻¹ (see **Fig. S16**). In addition, as shown in **Fig. S17**, the IAST selectivity calculation process for SO_2/CO_2 is shown based on the equation (4) in the ESI⁺. As a result, a IAST selectivity of 120 at $SO_2:CO_2$ (10:90, v:v) could still be obtained, which highlighted the potential of nanoCB6-H for SO_2 separation. Accordingly, the IAST selectivities of SO_2/CH_4 and SO_2/N_2 , and breakthrough simulation have also been recalculated.



Fig. S18 IAST selectivities of recycled nanoCB6-H for SO_2/CO_2 mixtures with varying volume ratio from 10:90 to 50:50 (v/v) (light to dark colour) at 293 K. IAST calculations at low pressure (< 0.1 bar) carry large uncertainties due to the insufficient integration of spreading pressure and thus are not reported.



Fig. S19 SO_2/CO_2 selectivity of recycled nanoCB6-H and representative MOFs for gas mixtures with specific $SO_2:CO_2$ molar ratio (between 0.05:99.95 and 10:90) at 1.0 bar (details in Table S6). Plot of SO_2/CO_2 selectivity (at 1.0 bar and 298 K) against SO_2 adsorption. Temperature for nanoCB6-H and MIL–160 is at 293 K.



Fig. S20 IAST selectivities of recycled nanoCB6-H for SO_2/CH_4 mixtures with varying SO_2 molar fractions in the gas phase at 293 K and 1 bar.



Fig. S21 IAST selectivities of recycled nanoCB6-H for SO_2/N_2 mixtures with varying SO_2 molar fractions in the gas phase at 293 K and 1 bar.



Fig. S22 SO₂ adsorption isotherms (the first runs) of newly activated nanoCB6-H from the same batch measured up to 1 bar at 273 K and 293 K, respectively.



Fig. S23 Isosteric heat of adsorption of SO₂ for newly activated nanoCB6-H materials (grey) based on the first runs data, and recycled nanoCB6-H materials (brown) based on the recycled 7th and 8th runs data.



Fig. S24 Virial analysis of the SO₂ sorption data from the first runs with newly activated nanoCB6-H samples.



Fig. S25 a) PXRD patterns, b) N_2 sorption isotherms (77 K) of nanoCB6-H before and after SO₂ sorption for the first run at 293 K. c) The SO₂ sorption isotherms of nanoCB6-H for the first and second runs. Note: nanoCB6 was activated at 150 °C under a dynamic vacuum for 2 days.

There are factors, such as thermal treatment, interactions between SO_2 and the framework, and residual water molecules, which can affect the BET surface areas of HOFs. If there is residual water in the HOF, the possibility is high for the formation of "H₂SO₃", HSO₃⁻, SO₃²⁻, H₃O⁺ etc., which is detrimental to the hydrogen-bonded

supramolecular framework during SO_2 adsorption. Thus, we did control experiments to investigate the effect of residual water molecules on the surface areas and SO₂ uptake of nanoCB6-H. The control experiment indicated that residual water molecules in nanoCB6-H could have led to the decreased surface areas after SO₂ sorption. According to the literature, the water guest molecules in CB6-based solids could not be totally removed at 100 °C under a dynamic vacuum for two days,⁷ which was the same condition used for nanoCB6-H, $C_{36}H_{36}N_{24}O_{12} \cdot 1.8H_2O$, in our manuscript. However, guest-free porous CB6-H could be prepared by evacuation of the guest molecules inside the channels at 150 °C under a dynamic vacuum for two days reported by Kim.^{1b} Thus, we prepared water-free nanoCB6-H by activating at 150 °C under a dynamic vacuum for two days, and tested N₂ sorption at 77 K before and after SO₂ sorption up to 0.97 bar at 293 K (Fig. S25). The results showed that water-free nanoCB6-H retained the unchanged BET surface areas (434 m² g⁻¹) after one run of SO₂ sorption, and the SO₂ uptake values were still within experimental error of 145 cm³ g⁻¹ and 138 cm³ g⁻¹ for the first and the second run at 293 K and 0.97 bar. This enhanced behavior by water-free nanoCB6-H over that of nanoCB6-H with residual water (Fig. 3b), indicated that the removal of residual water molecules should avoid the possible formation of "sulfurous acid" etc. during SO₂ sorption, which is detrimental to the HOF, and led to decreased BET surface areas after SO₂ sorption. We tried to use FT-IR to detect the sulfurous acid species in nanoCB6-H with residual water after SO₂ sorption but failed due to the low amount.



Fig. S26 SO₂ and CO₂ uptake isotherms of recycled nanoCB6-H samples measured up to 0.97 bar at 353 K, respectively. Filled and empty symbols represent adsorption and desorption, respectively.



Fig. S27 Simulated breakthrough curves for recycled nanoCB6-H with SO₂/CO₂/N₂; 0.1/15.0/84.9; v:v:v at 293 K.



Fig. S28 Chemical view of the void volume of CB6-H based on the accessible surface in a unit cell with a probe 1.2 Å and 0.7 Å in mercury software.



Fig. S29 Chemical view of a pair of SO₂ molecules encapsulated in the intrinsic pore of a CB6 cage. CB6 is partially drawn for clarity.



Fig. S30 FTIR spectra of nanoCB6-H and nanoCB6-H after uptake of SO₂ under atmosphere condition.

In Fig. S30a, the intensity of water signals is increasing when SO₂@nanoCB6-H is exposed to air for a certain time. In Fig. S30b, a new band at 1144 cm⁻¹ is assigned to the V_1 symmetric stretch of adsorbed SO₂. IR signal peaks corresponding to carbonyl and methylene groups are redshifted and blue-shifted, respectively.



Fig. S31 FTIR spectra of nanoCB6-H, nanoCB6-H after uptake of SO₂, and the reactivated nanoCB6-H materials.

In Fig. S31 the reversible shifted peaks in nanoCB6-H and the disappearance of SO_2 signals in the reactivated nanoCB6-H indicate the release of SO_2 and the successful regeneration of materials.



Fig. S32 a) PXRD patterns of CB6-H before and after SO₂ uptake at 293 K up to 0.97 bar. b) N₂ adsorption isotherms (77 K) of CB6-H. SEM images of CB6-H c) before and d) after SO₂ uptake at 293 K up to 0.97 bar.



Fig. S33 Comparison of SO₂ sorption isotherms of nanoCB6-H and CB6-H up to 0.97 bar at 293 K for the first runs. Filled and empty symbols refer to adsorption and desorption, respectively.



Fig. S34 a) PXRD patterns and b) N₂ adsorption isotherms (77 K) of nanoCB6-H before and after exposure to humid HCI.

Activated nanoCB6-H powders (36 mg) in a small glass bottle were exposed to humid HCI atmosphere provided by 1 M HCI aqueous solution at room temperature for 24 hours. After that, the PXRD data of treated sample was collected, and the sample was further activated at 373 K for 48 hours before N₂ sorption at 77 K was measured. It is observed that the crystalline phase of nanoCB6-H has deteriorated and also changed to another unknown phase with very low BET surface areas (16 m² g⁻¹) (Fig. S34), which indicates the extrinsic pores between CB6 cages in the HOF are almost lost under the humid acidic atmosphere.

S4. Table S1–S7

| Table S1 | . Textural | properties | of nanoCB | 6-H before | and afte | r dry SC | 2 adsorption. |
|----------|------------|------------|-----------|------------|----------|----------|---------------|
| | | | | | | | |

| | Sample | S_{BET}^{a} | Langmuir | Total pore | Micropore | note |
|---|-----------|-----------------------------------|----------------|------------------------------------|------------------------------------|---------------------------------|
| | | (m ² g ⁻¹) | surface area | volume ^b | volume ^c | |
| | | | $(m^2 g^{-1})$ | (cm ³ g ⁻¹) | (cm ³ g ⁻¹) | |
| - | nanoCB6-H | 441 | 545 | 0.22 | 0.13 | before SO ₂ sorption |
| - | nanoCB6-H | 383 | 514 | 0.21 | 0.088 | after SO ₂ sorption |
| | | | | | | for ten runs at 293 K |
| | CB6-H | 228 | - | 0.10 | 0.070 | before SO ₂ sorption |

^a BET surface area was determined over 7 points in the relative pressure range $P/P_0 = 0.05 - 0.08$ from N₂ sorption isotherms at 77K.

^b Total pore volumes (V_{total}) were determined from N₂ sorption isotherms at 77 K (p/p₀ = 0.90) for pores \leq 20 nm diameter.

 $^{\circ}$ Micropore volumes were determined using the t-plot method from five adsorption points in the pressure range P/P₀ = 0.1 – 0.2 based on N₂ adsorption curves at 77 K.

Table S2. Experimental results of gas adsorption in recycled nanoCB6-H.

| SO ₂ | CO ₂ | CH ₄ | N ₂ | T (K) | Q _{st} ⁰ | Q _{st} ⁰ | Q _{st} ⁰ | Q _{st} ⁰ |
|----------------------|----------------------|----------------------|----------------------|-------|------------------------------|------------------------------|------------------------------|------------------------------|
| (cm ³ /g) | (cm ³ /g) | (cm ³ /g) | (cm ³ /g) | | (SO ₂) | (CO ₂) | (CH ₄) | (N ₂) |
| (mmol/g) | (mmol/g) | (mmol/g) | (mmol/g) | | kJ | kJ | kJ | kJ |
| mmol/mmol | mmol/mmol | mmol/mmol | mmol/mmol | | mol ⁻¹ | mol ⁻¹ | mol ⁻¹ | mol ⁻¹ |
| wt% | wt% | - | - | | | | | |
| 119.8 | 58 | 13.3 | 5.5 | 293 | 48 | 34.6 | 24.1 | 11.3 |
| 4.98 | 2.41 | 0.55 | 0.22 | | | | | |
| 4.96 | 2.40 | 0.55 | 0.22 | | | | | |
| 31.87 | 10.60 | | — | | | | | |
| 138.6 | 70.3 | 19.2 | 7.5 | 273 | | | | |
| 6.18 | 3.13 | 0.85 | 0.33 | | | | | |
| 6.16 | 3.12 | 0.85 | 0.33 | | | | | |
| 39.58 | 13.77 | | — | | | | | |

Table S3. Parameters for DSLAI modelling on different gas adsorption isotherm of recycled nanoCB6-H.

| Gas | Temp. | Model | R ² | affinity | max | affinity | max |
|-----------------|-------|-------|----------------|----------|-----------|----------|-----------|
| | (K) | | | const. 1 | loading 1 | const. 2 | loading 2 |
| | | | | (1/bar) | (mmol/g) | (1/bar) | (mmol/g) |
| SO ₂ | 293 | DSLAI | 0.992 | 660.360 | 3.154 | 1.143 | 3.989 |
| CO ₂ | 293 | DSLAI | 0.999 | 59.154 | 0.605 | 1.881 | 3.075 |
| CH4 | 293 | DSLAI | 0.999 | 3.698 | 0.245 | 0.056 | 7.835 |
| N_2 | 293 | DSLAI | 0.999 | 2.401 | 0.073 | 0.028 | 7.455 |

Table S4. IAST selectivity results of different gas mixtures for recycled nanoCB6-H at 293 K and 1 bar.

| Sample | IAST selectivity ^a | | | | | |
|-----------|--|--|---|--|--|--|
| | SO ₂ /CO ₂ (10:90) | SO _{2/} CH ₄ (10:90) | SO ₂ /N ₂ (10:90) | CO ₂ /CH ₄ (10:90) | | |
| nanoCB6-H | 120ª | 662ª | 1720ª | 25ª | | |
| | 120 ^b | 684 ^b | 1754 ^b | 25 ^b | | |

^a Constant pressure with varied molar ratios.

^b Constant molar ratio with varied pressure.

| Table S5. SO_2 sorption and separation properties of nanoCB6-H and other represe | entative adsorbents |
|---|---------------------|
|---|---------------------|

| sample | $S_{BET} (m^2 g^{-1})$ | SO ₂ uptake (cm ³ g ⁻¹) | | Temp. (K) | SO ₂ /CO ₂ (molar ratio, | Q _{st} ⁰ | ref. |
|--------------------------------|------------------------|--|--------------------|--------------|---|------------------------------|------|
| | | 0.1 bar | 1 bar | - | x : y) | | |
| POCs | | | | | | | |
| nanoCB6-H | 441 | 88 | 143.0ª | 293 | - | 64 ^a | this |
| | 383 | 81 | 121.2 ^b | 293 | 120 (10 : 90) ^c | 48 | work |
| CB6-H | 228 | 50 | 98 | 293 | - | - | this |
| | | | | | | | work |
| amorphous CB7 | 293 ^d | 54 | 105 | 297 | - | - | 8 |
| mPEI/ASPOC | nonporous | _ | 12.9 ^e | | - | - | 9 |
| composite | | | | | | | |
| COFs | | | | | | | |
| COF-6 | 750 | _ | 168.5 ^f | 303 | 40 | 31 | 10 |
| | | | | | (0.05 : 99.95) | | |
| PI-COF-m20 | 548 | _ | 137.0 | 298 | - | - | 11 |
| PI-COF-m40 | 279 | _ | 134.5 | 298 | - | - | 11 |
| PILs | | | | | | | |
| P([VBIm]Br) | nonporous | _ | 196.5 | 298 | - | - | 12 |
| [IRA-900][B(Im) ₄] | 13 | 255 | 268.9 | 293 | - | 50.6 ^h | 13 |
| Zeolites | | | | | | | |
| MFI zeolite | 713 | 61.1 ^f | 68.5 ^f | 298 | | 14 | 14 |
| | | | | | | | |

Note: ^a Data based on the first adsorption runs. ^b Data based on the 10th run of recycled nanoCB6-H. ^c Data based on IAST calculations. ^d Calculated from the isotherm of CO₂ at 196 K. ^e Determined gravimetrically with 200 ppm SO₂ in N₂ as the feed mixture. ^f SO₂ uptake capacity estimated from isotherm. ^h Interaction energy based on DFT calculations.

| Table S6. SO; | 2 sorption and | separation | properties | of representative | MOF adsorbents |
|---------------|----------------|------------|------------|-------------------|----------------|
|---------------|----------------|------------|------------|-------------------|----------------|

| sample | S _{BET} | SO ₂ u | ptake | Temp. | SO ₂ /CO ₂ | Q _{st} ⁰ | ref. |
|----------------|------------------|------------------------------------|-------|-------|----------------------------------|------------------------------|------|
| | $(m^2 g^{-1})$ | (cm ³ g ⁻¹) | | (K) | (x : y) | | |
| | | 0.1 bar | 1 bar | _ | | | |
| MFM-170 | 2408 | 153ª | 428.1 | 298 | 28 (1 : 99) ^b | _ | 15 |
| ELM-12 | 706 | 43.7 | 61.2 | 298 | 30 (10 : 90) | 78 | 16 |
| MFM-601 | 3644 | 112 | 275.5 | 298 | 32 (10 : 90) | 38 | 17 |
| MFM-300(In) | 1071 | 171.2 | 202.5 | 298 | 50 (10 : 90) | 34.5 | 18 |
| KAUST–8 | 258 | 39.7 | 70.3ª | 298 | 66 | 73.9 ^d | 19 |
| | | | | | (0.05 : 99.95) ^c | | |
| SIFSIX-1-Cu | 1178 | 213.8 | 269.3 | 298 | 71 (10 : 90) | 36.1 | 20 |
| SIFSIX–2–Cu–i | 630 | 147.0 | 168.8 | 298 | 87.1 (10 : 90) | 38.1 | 20 |
| SIFSIX-3-Zn | 250 | 46.2 | 51.3 | 298 | _ | 45.2 | 20 |
| oxamato-based | 1460 | - | _ | 303 | 100 (2.5 : | _ | 21 |
| 3D MOF–2 | | | | | 97.5) | | |
| MIL-160 | 1070 | 123.2 | 161.0 | 293 | 128 (10 : 90) | 42 | 22 |
| MFM-305-CH3 | 256 | 107.6 | 126.2 | 298 | 125 (5 : 95) | 32 | 23 |
| MFM-305 | 779 | 122.3 | 171.0 | 298 | 135 (5 : 95) | 39 | 23 |
| HHU–2–Br | 620 | _ | 147.9 | 293 | - | | 24 |
| MFM-300(AI) | - | - | 129.6 | 298 | _ | _ | 25 |
| Prussian blue | 712 | - | 61.1 | 298 | _ | _ | 26 |
| analogues CoCo | | | | | | | |
| Prussian blue | 700 | 13.3 | 44.0 | 298 | - | _ | 26 |
| analogues ZnCo | | | | | | | |
| FMOF-2 | 378 | 10.8 | 43.7 | 298 | - | _ | 27 |

Note: ^a SO₂ uptake capacity estimated from isotherm. ^b Data based on IAST calculations. ^c Data based on breakthrough experiment result. ^d Interaction energy based on DFT calculations.

| Bond type | Bond length (Å) | Bonding energies (kJ mol ⁻¹) |
|--------------------------|-----------------|--|
| Site I | | -50.3 |
| S—0 | 2.69 | |
| S—0 | 3.01 | |
| (SO ₂) O—H | 2.19 | |
| Site II | | -59.5 |
| S—0 | 3.00 | |
| S—0 | 3.02 | |
| Site III | | -82.4 |
| S—0 | 3.03 | |
| S—0 | 3.04 | |
| (SO ₂) O—C=O | 3.13 | |
| (SO ₂) O—C=O | 3.15 | |
| S—O (SO ₂) | 3.40 | |
| S—O (SO ₂) | 3.40 | |
| Site IV | | -49.7 |
| (SO ₂) S—O | 2.63 | |
| (SO ₂) O—C=O | 2.97 | |
| (SO ₂) S—N | 3.52 | |
| (SO ₂) S—N | 3.65 | |
| (SO ₂) O—H | 2.64 | |
| Site V | | -18.8 |
| (SO ₂) O—H | 2.49 | |
| (SO ₂) O—H | 2.51 | |
| (SO ₂) O—H | 2.80 | |
| (SO ₂) O—H | 2.85 | |

Table S7. Representative non–covalent bonds between CB6 cage and SO₂ molecules, and bonding energies based on DFT calculations.

S5. References

- J. Tian, J. Liu, J. Liu and P. K. Thallapally, *CrystEngComm*, 2013, **15**, 1528–153; b) J. H. Park, K. Suh, M. R. Rohman,
 W. Hwang, M. Yoon and K. Kim, *Chem. Commun.*, 2015, **51**, 9313–9316; c) J. Liang, A. Nuhnen, S. Millan, H.
 Breitzke, V. Gvilava, G. Buntkowsky and C. Janiak, *Angew. Chem. Int. Ed.*, 2020, **59**, 6068-6073.
- 2 a) 3P INSTRUMENTS, 3P sim, Version 1.1.0.7, Simulation and Evaluation Tool for mixSorb, 3P INSTRUMENTS 2018;
 b) A. Möller, R. Eschrich, C. Reichenbach, J. Guderian, M. Lange and J. Möller, *Adsorption* 2017, 23: 197–209; c) C.
 A. Grande, R. Blom, A. Möller and J. Möller, *Chem. Eng. Sci.*, 2013, 89, 10–20.
- 3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. *Gaussian 16, Revision A.03*; Gaussian, Inc., Wallingford CT, 2016.
- 4 K. I. Assaf and W. M. Nau, Chem Soc Rev., 2015, 44, 394–418.
- 5 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. 2010,132, 154104–154122.
- 6 S. F. Boys and F. Bernardi, Mol. Phys. 1970, 19, 553-566.
- 7 S. Lim, H. Kim, N. Selvapalam, K.-J. Kim, S. J. Cho, G. Seo and K. Kim, Angew. Chem. Int. Ed., 2008, 120, 3400–3403.
- 8 J. Tian, S. Ma, P. K. Thallapally, D. Fowler, B. P. McGrail and J. L. Atwood, Chem. Commun., 2011, 47, 7626–7628.
- 9 G. Zhu, J.-M. Y. Carrillo, A. Sujan, C. N. Okonkwo, S. Park, B. G. Sumpter, C. W. Jones and R. P. Lively, J. Mater. Chem. A, 2018, 6, 22043–22052.
- 10 H. Wang, X. Zeng, W. Wang and D. Cao, Chem. Eng. Sci., 2015, 135, 373-380.
- 11 G. Y. Lee, J. Lee, H. T. Vo, S. Kim, H. Lee and T. Park, Sci. Rep., 2017, 7, 557.
- 12 L. Xia, Q. Cui, X. Suo, Y. Li, X. Cui, Q. Yang, J. Xu, Y. Yang and H. Xing, Adv. Funct. Mater., 2018, 28, 1704292.
- 13 X. He, X. Lv, X. Fan, W. Lin, H. Li and C. Wang, Acta Phys.-Chim. Sin., 2018, 34(8), 896-903.
- 14 I. Matito–Martos, A. Martin–Calvo, J. J. Gutierrez–Sevillano, M. Haranczyk, M. Doblare, J. B. Parra, C. O. Ania and S. Calero, *Phys. Chem. Chem. Phys.*, 2014, **16**, 19884–19893.
- 15 G. L. Smith, J. E. Eyley, X. Han, X. Zhang, J. Li, N. M. Jacques, H. G. W. Godfrey, S. P. Argent, L. J. McCormick McPherson, S. J. Teat, Y. Cheng, M. D. Frogley, G. Cinque, S. J. Day, C. C. Tang, T. L. Easun, S. Rudic, A. J. Ramirez–Cuesta, S. Yang and M. Schröder, *Nat. Mater.*, 2019, **18**, 1358–1365.
- 16 Y. Zhang, P. Zhang, W. Yu, J. Zhang, J. Huang, J. Wang, M. Xu, Q. Deng, Z. Zeng and S. Deng, ACS Appl. Mater. Interfaces, 2019, **11**, 10680–10688.
- 17 J. H. Carter, X. Han, F. Y. Moreau, I. da Silva, A. Nevin, H. G. W. Godfrey, C. C. Tang, S. Yang and M. Schröder, *J. Am. Chem. Soc.*, 2018, **140**, 15564–15567.
- 18 M. Savage, Y. Cheng, T. L. Easun, J. E. Eyley, S. P. Argent, M. R. Warren, W. Lewis, C. Murray, C. C. Tang, M. D. Frogley, G. Cinque, J. Sun, S. Rudic, R. T. Murden, M. J. Benham, A. N. Fitch, A. J. Blake, A. J. Ramirez–Cuesta, S. Yang and M. Schröder, *Adv. Mater.*, 2016, **28**, 8705–8711.
- 19 M. R. Tchalala, P. M. Bhatt, K. N. Chappanda, S. R. Tavares, K. Adil, Y. Belmabkhout, A. Shkurenko, A. Cadiau, N. Heymans, G. De Weireld, G. Maurin, K. N. Salama and M. Eddaoudi, *Nat. Commun.*, 2019, **10**, 1328.
- 20 X. Cui, Q. Yang, L. Yang, R. Krishna, Z. Zhang, Z. Bao, H. Wu, Q. Ren, W. Zhou, B. Chen and H. Xing, *Adv. Mater.*, 2017, **29**, 1606929.
- 21 M. Mon, E. Tiburcio, J. Ferrando-Soria, R. Gil San Millan, J. A. R. Navarro, D. Armentano and E. Pardo, Chem.

Commun., 2018, 54, 9063-9066.

- 22 P. Brandt, A. Nuhnen, M. Lange, J. Mollmer, O. Weingart, C. Janiak, ACS App. Mater. Interfaces 2019, **11**, 17350– 17358.
- 23 L. Li, I. da Silva, D. I. Kolokolov, X. Han, J. Li, G. Smith, Y. Cheng, L. L. Daemen, C. G. Morris, H. G. W. Godfrey, N. M. Jacques, X. Zhang, P. Manuel, M. D. Frogley, C. A. Murray, A. J. Ramirez–Cuesta, G. Cinque, C. C. Tang, A. G. Stepanov, S. Yang, M. Schroder, *Chem Sci* 2019, **10**, 1472–1482.
- 24 T. Matemb Ma Ntep, H. Breitzke, L. Schmolke, C. Schlüsener, B. Moll, S. Millan, N. Tannert, I. El Aita, G. Buntkowsky, C. Janiak, *Chem. Mater.*, 2019, **31**, 8629–8638.
- 25 X. Han, H. G. W. Godfrey, L. Briggs, A. J. Davies, Y. Cheng, L. L. Daemen, A. M. Sheveleva, F. Tuna, E. J. L. McInnes, J. Sun, C. Drathen, M. W. George, A. J. Ramirez–Cuesta, K. M. Thomas, S. Yang and M. Schröder, *Nat. Mater.*, 2018, **17**, 691–696.
- 26 P. K. Thallapally, R. K. Motkuri, C. A. Fernandez, B. P. McGrail and G. S. Behrooz, Inorg. Chem., 2010, 49, 4909–4915.
- 27 C. A. Fernandez, P. K. Thallapally, R. K. Motkuri, S. K. Nune, J. C. Sumrak, J. Tian and J. Liu, *Cryst. Growth Des.*, 2010, **10**, 1037–1039.