Supplementary Information

Inverse CO₂/C₂H₂ Separation Assisted by Coordinated Water in a Dysprosium (III) Metal–Organic Frameworks

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Materials and Methods

1.1 Generals

All chemicals and solvents used were commercially available and used without further purifications. Powder X-ray diffraction (PXRD) data were collected with a Rigaku-Miniflex-600 X-ray powder diffractometer or a Rigaku SmartLab using Cu Kα radiation (λ = 1.5406 Å nm). Field emission scanning electron microscope (FE-SEM) experiments were characterized by FEI Verios G4 SEM. Thermogravimetric analysis (TGA) was carried out in a flow of nitrogen using a TGA-2 (METTLER TOLEDO) with a heating rate of 10 °C/min.

1.2 Preparation of Dy-F-oxa

The powder sample of Dy-F-oxa were prepared according to the literature report with some modifications. To a 100 mL Teflon vial, 20 mL Dy(NO$_3$)$_3$·6H$_2$O (0.02 M), 20 mL NaF (0.02 M) and 20 mL Na$_2$C$_2$O$_4$ (0.02 M) aqueous solutions were added and heated to ca. 60 °C under stirring. The precipitate was collected by filtration and washed with distilled water. Yield (based on Dy): 90.5%.

1.3 Gas adsorption

A Micromeritics 3Flex instrument was used for recording all gas sorption isotherms, CO$_2$ (195, 273 and 298 K) and C$_2$H$_2$ (273 and 298 K). For N$_2$ adsorption isotherms, the temperature was controlled at 77 K using a Dewar containing 4 L liquid N$_2$. Precise control of 273 K and 298 K temperatures was implemented by a dc-2006 from Ningbo Scientz Biotechnology, which contained a cyclic control system of ethylene glycol and water mixture ($v/v = 1:1$). Helium was used for the estimation of dead space for gas and water adsorption measurements. The activation of the Dy-F-oxa sample was achieved by degassing for 4 h at 80 °C under a dynamical vacuum using a degassing station.

1.4 Isosteric heat of adsorption

A virial-type expression of the below form was used to fit the combined isotherm data of CO$_2$ and C$_2$H$_2$ at 273 and 298 K, where $P$ is the pressure described in Pa, $N$ is the adsorbed amount in mmol/g, $T$ is the temperature in K, $a_i$ and $b_i$ are virial coefficients, and $m$ and $n$ are the number of coefficients used to describe the isotherms. $Q_{st}$ is the coverage-dependent enthalpy of adsorption and $R$ is the universal gas constant.
\[
\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j
\]

\[
Q_{st} = -R \sum_{i=0}^{5} a_i N^i
\]

1.5 **Langmuir-Freundlich fitting**

The isothermal for different gases at 298 K were fitted using the Langmuir-Freundlich model as following:

\[
q = q_{sat} \frac{b_A p^n}{1 + b_A p^n}
\]

where \(q\) and \(q_{sat}\) are gas loading at a specific pressure and saturation respectively, \(b_A\) is Langmuir-Freundlich constant at A site, \(n\) is Freundlich exponent and \(p\) is pressure.

1.6 **IAST calculations of adsorption selectivity**

The selectivity of equimolar CO\(_2\)/C\(_2\)H\(_2\) binary mixtures at 298 K was calculated using ideal adsorption solution theory (IAST) method\(^3\), and the selectivity is defined as following:

\[
S = \frac{x_A/x_B}{y_A/y_B}
\]

where \(S\) is the selectivity of A towards B, \(x_A\) and \(x_B\) are the molar fractions of A and B in the adsorbent respectively, \(y_A\) and \(y_B\) are the molar fractions of A and B in the gas mixture respectively.

1.7 **Computational details**

To understand the host-guest interactions between the framework and CO\(_2\) and C\(_2\)H\(_2\) molecules, the Grand Canonical Monte Carlo (GCMC) simulations were performed using the Sorption module in Material Studio software package. The simulation box for **Dy-F-oxa** was built from the single-crystal
structure with $1 \times 1 \times 1$ supercell after making $P1$ and the CIF files were adapted from Cambridge Crystallographic Data Centre (CCDC) for free. All the frameworks and gas molecules were both treated as rigid bodies and the $Q_{eq}$ fitted charge and the ESP charge were assigned to the hosts and guests respectively. The loading steps, equilibration steps, and production steps were all set to $2.0 \times 10^7$. The Metropolis method was applied during the simulation$^4$. All the host-guest interaction behavior was described using Universal force field (UFF$^5$). The cut-off radius used for the Lennard–Jones interactions is 18.5 Å.

1.8 Breakthrough experiments

The breakthrough curves were recorded on a homemade apparatus. Activated Dy-F-oxa 3.2g particles were prepared and packed into a stainless-steel column. An equimolar mixture of CO$_2$ and C$_2$H$_2$ (total gas pressure and flow: 100 kPa and 1 cm$^3$/min) passes through the packing column at 298 K, and the outlet gas concentration was monitored by a gas chromatography analyzer (TCD-Thermal Conductivity Detector, detection limit 0.1 ppm). During gas breakthrough cycling tests, the sample in the column was regenerated under He flow of 20 cm$^3$/min at 80 °C for 8 hours, after each breakthrough experiment.

Productivity of C$_2$H$_2$ is derived from breakthrough experiments following this definition:

$$ p = \frac{F \times y_{C_2H_2} \times \int_{t_1}^{t_2} \frac{C(t)}{C_0} dt}{V_m} $$

where $P$ is the C$_2$H$_2$ productivity in mmol/g, $t_1$ is the C$_2$H$_2$ breakthrough time in min/g, $t_2$ is the breakthrough time of other gas, $F$ is the inlet gas volume flow rate, $y_{C_2H_2}$ is the volume fraction of C$_2$H$_2$ in mixed gas, $C(t)$ is the C$_2$H$_2$ concentration in the outlet gas, $C_0$ is the C$_2$H$_2$ concentration in the inlet gas, $V_m$ is molar volume of gas.
Fig. S1 As-synthesized (black) and simulated (red) PXRD patterns of Dy-F-oxa.
Fig. S2 TGA curve of Dy-F-oxa.
**Fig. S3.** The FESEM images of **Dy-F-oxa** samples. Scale bars on the image (A) and (B) are 10 and 2 μm, respectively.
**Fig. S4** TGA curve of activated **Dy-F-oxa**. With the heating rate of 10 °C/min, the sample was heated to 80 °C and keep this temperature for 4 hours. Then the activated sample was heated to 800 °C.
Fig. S5 CO$_2$ and C$_2$H$_2$ adsorption isotherms at 273 K of Dy-F-oxa.
Fig. S6 $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ adsorption isotherms at 298 K of Dy-F-oxa.
Fig. S7 The Langmuir-Freundlich fitting details of $\text{C}_2\text{H}_2$ adsorption isotherm at 298 K for **Dy-F-oxa** and the solid lines are the best fit for the data.
**Fig. S8** The Langmuir-Freundlich fitting details of CO$_2$ adsorption isotherm at 298 K for **Dy-F-oxa** and the solid lines are the best fit for the data.
**Fig. S9** Calculated IAST selectivity of **Dy-F-oxa** for CO$_2$/C$_2$H$_2$ with 1:1 ratio at 298 K.
Fig. S10 Virial equation (lines) fitting of the experimental CO$_2$ adsorption data (symbols) for Dy-F-oxa.
Fig. S11 Virial equation (lines) fitting of the experimental C$_2$H$_2$ adsorption data (symbols) for Dy-F-oxa.
Fig. S12 Interactions between electropositive C$^{5+}$ atom of CO$_2$ and nearby O atoms of two carboxyl groups in Dy-F-oxa. Distances are given in Å.
References.