High and Selective CO₂ Uptake, H₂ Storage and Methanol Sensing on the Amine-Decorated 12-Connected MOF CAU-1

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Fig. S1. Apparatus used in collecting breakthrough data for gas separation

Schematic representation of gas separation apparatus.
Heat of Sorption Calculation for CO₂ and H₂ Uptakes

The enthalpy of CO₂ or H₂ adsorption into the activated MOF framework was calculated using a modified version of the Clausius-Clapeyron equation:

\[
\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{\text{ads}} \times \frac{T_2 - T_1}{R \times T_1 \times T_2} \tag{A}
\]

\( T_i = \) temperature for isotherm \( i \); \( P_i = \) pressure for isotherm \( i \); \( R = 8.313 \text{ J K}^{-1} \text{ mol}^{-1} \)

The pressure as a function of the amount of hydrogen adsorbed was determined using the Langmuir-Freundlich fit for the isotherms:

\[
\frac{Q}{Q_m} = \frac{B \times P^{(1/t)}}{1 + B \times P^{(1/t)}} \tag{B}
\]

\( Q = \) moles adsorbed; \( Q_m = \) moles adsorbed at saturation; \( P = \) pressure; \( B \) and \( t = \) constants

Equation B can be rearranged to

\[
P = \left(\frac{Q / Q_m}{B - B \times (Q / Q_m)^t}\right)
\]

Heats of adsorption can be obtained by adding the P values derived from (B) into equation A.
**Fig. S2.** (a) CO$_2$ adsorption isotherms for CAU-1 at 298 K (black circles) and 323 K (black squares). Solid lines correspond to Langmuir-Freundlich fits to the experimental data.

(b) H$_2$ adsorption isotherms for CAU-1 at 77 K (black circles). Solid line corresponds to Langmuir-Freundlich fits to the experimental data.
(c) H$_2$ adsorption isotherms for CAU-1 at 87 k (black circles). Solid line corresponds to Langmuir-Freundlich fits to the experimental data.

(d) CH$_4$ adsorption isotherms for CAU-1 at 298 k (black circles) and 323 K (black squares). Solid lines correspond to Langmuir-Freundlich fits to the experimental data.

(e) The adsorption heat for CH$_4$ at different CH$_4$ loadings.
Calculation of CO$_2$/N$_2$ Selectivity

The initial slope was first calculated for CH$_4$, N$_2$ and CO$_2$ uptakes. The ratio of the slopes was used to calculate the selectivity at 273K.

**Fig. S3 (a).** Initial slope calculation for CO$_2$ and N$_2$ isotherms collected at 273K (CO$_2$: blue squares; N$_2$: red circles).

**Fig. S3 (b).** Initial slope calculation for CO$_2$ and CH$_4$ isotherms collected at 273K (CO$_2$: blue squares; CH$_4$: red circles).
Fig. S4. Separation of an equimolar CO$_2$/CH$_4$ mixture at 0.1 MPa and 303 K.
**Quartz crystal microbalance test**

1 mg dehydrated CAU-1 was fully dispersed in 1 ml CH$_3$OH solution after 60 min ultrasonic cleaning. 15 μl solutions were deposited on the 1.13 cm$^2$ chromium/platinum films on polished 9 MHz AT-cut crystals (Maxtek Inc.) and air dried. Before each experiment, the QCM disk was cleaned through immersion into a piranha solution for 10 min followed by a thorough rinsing with deionized water. The sensing measurements with the coated quartz crystals were carried out in a sealed chamber (0.5 L) at room temperature. The chamber was evacuated to below 0.01 MPa before each vapor sensing measurement to remove pre-adsorbed molecules and provoke a rapid solvent evaporation. After attaining a stable resonant frequency, different concentrations of solvents are in turn introduced into the chamber to detect the adsorption process with solvents. After each measurement, the chamber is evacuated again to guarantee the complete desorption until the frequency of coated QCM recovers its initial value. A decrease in QCM frequency corresponds to a proportional increase in film mass.