Electronic Supplementary Material (ESI) for Energy and Environmental Science

High and Selective CO_2 Uptake, H_2 Storage and Methanol Sensing on the Amine-Decorated 12-Connected MOF CAU-1

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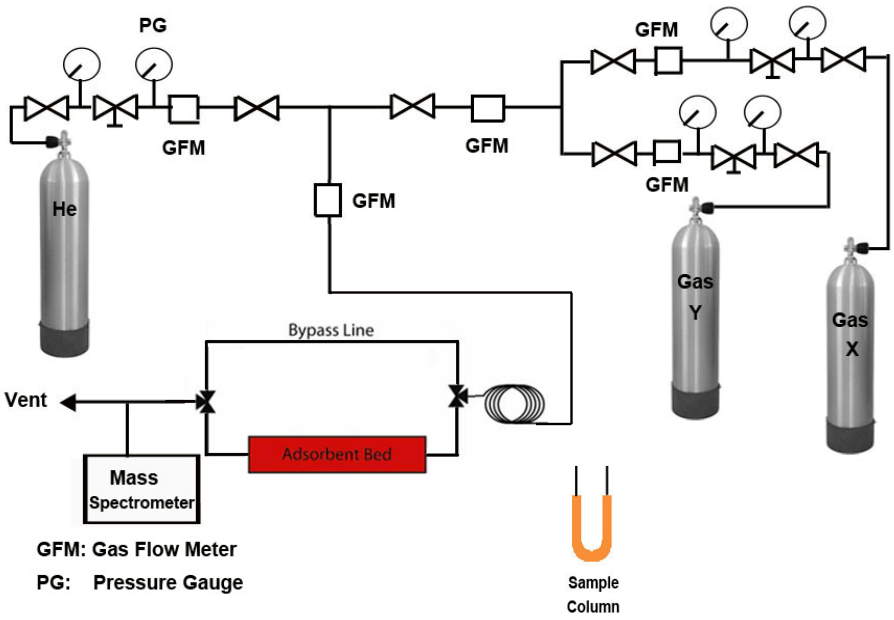
Fig. S1. Apparatus used in collecting breakthrough data for gas separation



Schematic representation of gas separation apparatus.

Heat of Sorption Calculation for CO_2 and H_2 Uptakes

The enthalpy of CO_2 or H_2 adsorption into the activated MOF framework was calculated using a modified version of the Clausius-Clapeyron equation:

$$\ln(\frac{P_1}{P_2}) = \triangle H_{ads} \times \frac{T_2 - T_1}{R \times T_1 \times T_2} \qquad \textbf{(A)}$$

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

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

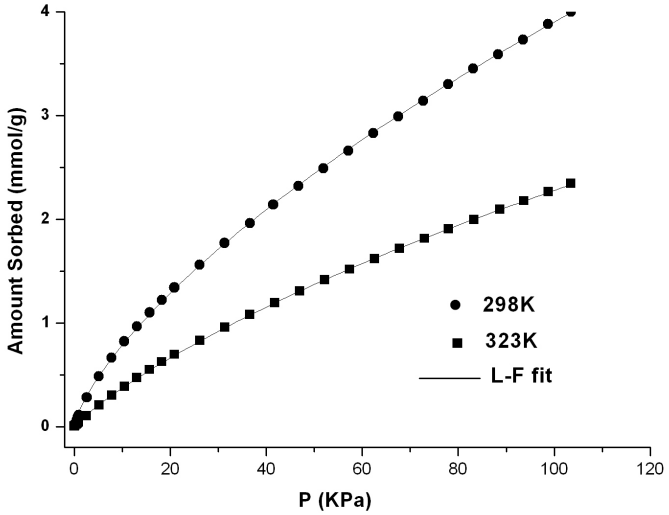
$$\frac{Q}{Q_m} = \frac{B \times P^{(1/t)}}{1 + B \times P^{(1/t)}} \qquad \textbf{(B)}$$

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

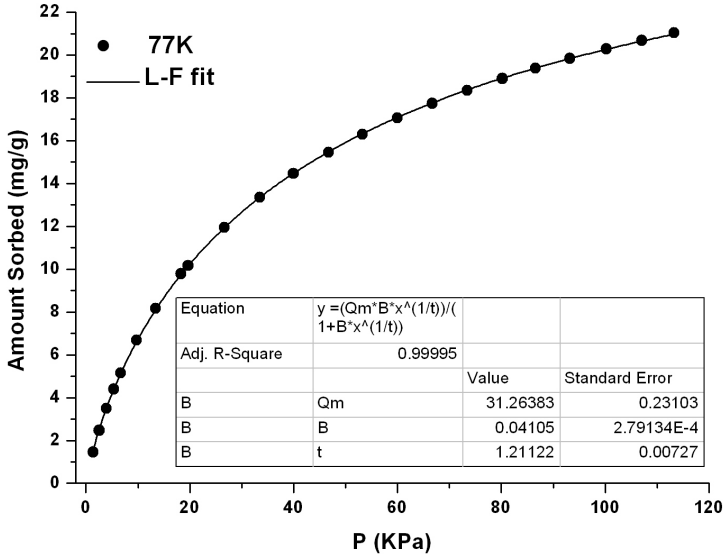
Equation B can be rearranged to $P = (\frac{Q/Q_m}{B - B \times Q/Q_m})^t$

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.

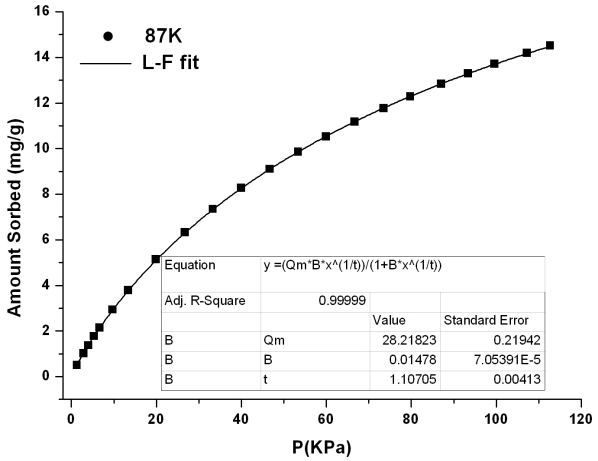


(b) H_2 adsorption isotherms for CAU-1 at 77 k (black circles). Solid line corresponds to Langmuir-Freundlich fits to the experimental data.

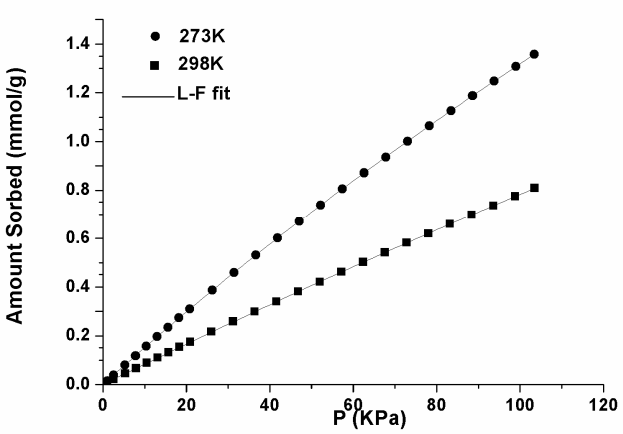


Equation	y =(Qm*B*x^(1/t))/(1+B*x^(1/t))		
Adj. R-Square	0.99995		
		Value	Standard Error
B	Qm	31.26383	0.23103
B	B	0.04105	2.79134E-4
B	t	1.21122	0.00727

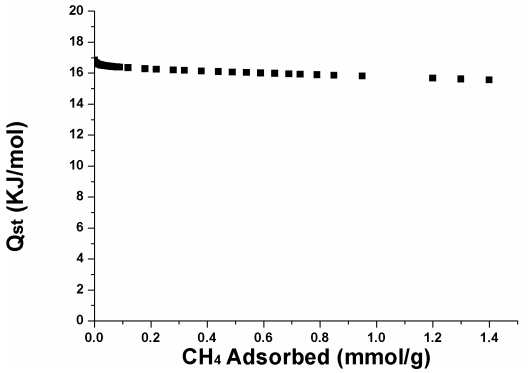
(c) H_2 adsorption isotherms for CAU-1 at 87 k (black circles). Solid line corresponds to Langmuir-Freundlich fits to the experimental data.



(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

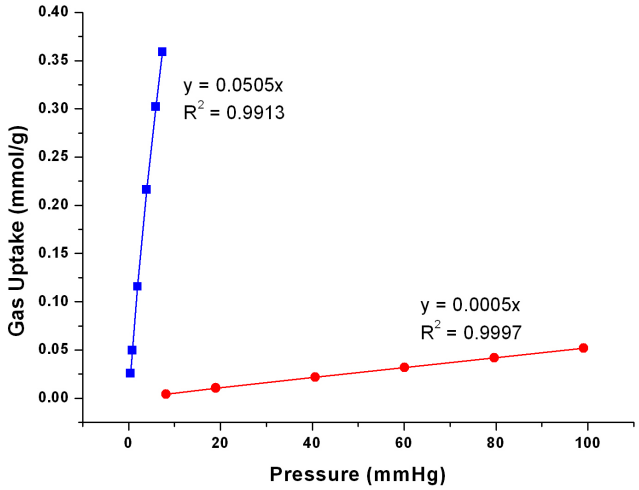


Fig. S3 (a). Initial slope calculation for CO_2 and N_2 isotherms collected at 273K (CO_2: blue squares; N_2: red circles).

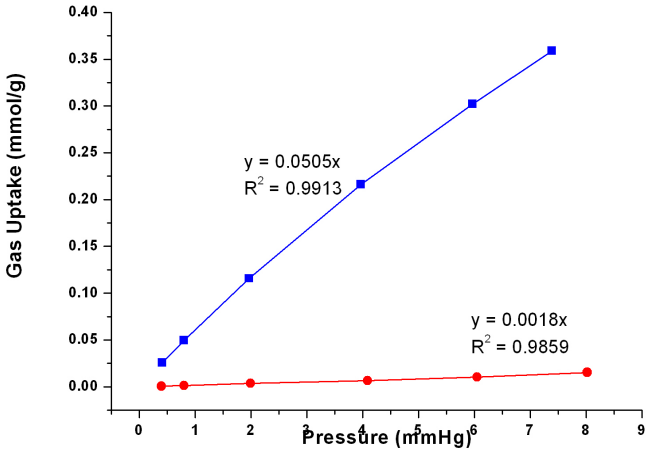
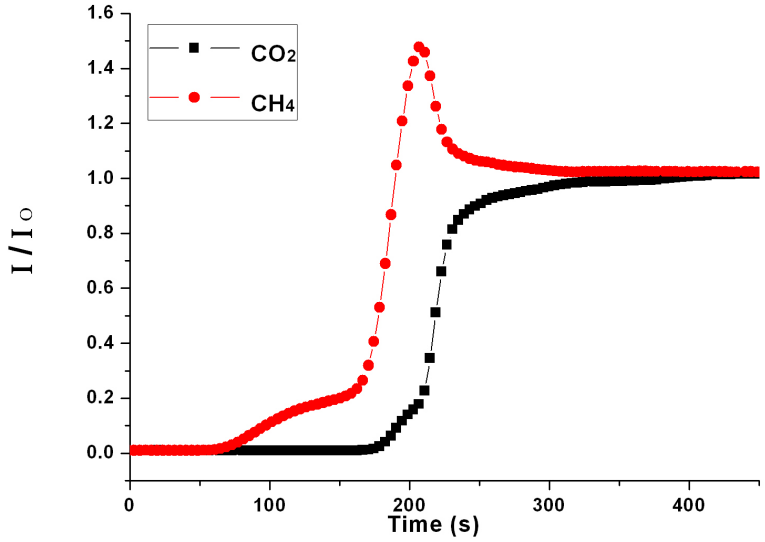


Fig. S3 (b). Initial slope calculation for CO_2 and CH_4 isotherms collected at 273K (CO_2: blue squares; CH_4: red circles).

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_3OH 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.