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CO₂ Adsorption Sites in UTSA-16: a Multi Technique Approach

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1. Preparation of the sample

UTSA-16 was obtained by hydrothermal synthesis as follows: $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.249 g, 1 mmol), $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (0.21 g, 1 mmol), KOH (0.168 g, 3 mmol), H_2O (2.5 ml) and $\text{C}_2\text{H}_5\text{OH}$ (2.5 ml) in the molar ratio 1:1:3:139:43 were put in a Teflon-lined 23 ml Parr acid digestion bomb. The bomb was then placed in a furnace that was heated from room temperature to 393 K in half an hour, kept at 393 K for 2 days, and then slowly cooled to room temperature at a rate of $4\text{ }^\circ\text{C h}^{-1}$.

2. Microcalorimetry

Adsorbed amounts and integral heats have been plotted vs. pressure in the form of volumetric (quantitative) and calorimetric isotherms, respectively. The adsorption heats observed for each small dose of gas admitted over the sample (q_{diff}) have been reported in Fig. S1 as a function of coverage, in order to obtain the (differential) enthalpy changes associated with the proceeding adsorption process. The differential-heat plots presented here were obtained by the dose related adsorption heats ($\Delta Q_{\text{int}}/\Delta n_{\text{a}}$, kJ mol^{-1}) vs the middle point of the n_{ads} histogram relative to the individual adsorptive aliquot, prepared as small as possible. As for the volumetric experiments where the quantitative reversibility was stated, energetic reversibility of CO_2 adsorption on UTSA-16 was investigated through adsorption-desorption-adsorption cycles. After the adsorption run I (*primary isotherm*, Fig.S1 black line), samples were outgassed overnight (at 298 K), and then an adsorption run II (*secondary isotherm*, Fig.S1 light blue line) was performed, to check if secondary and primary adsorption runs coincided.

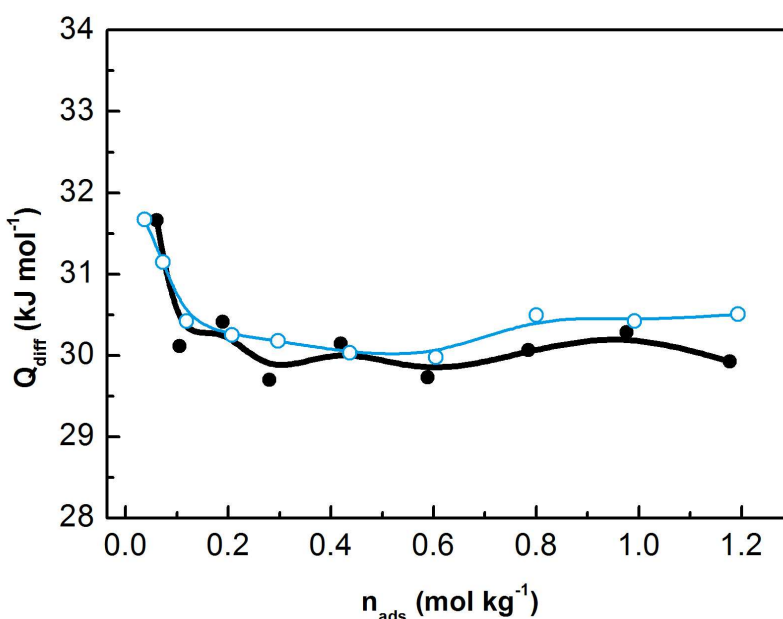


Fig. S1 Direct microcalorimetric measurement of CO_2 differential heat of adsorption on activated UTSA-16 collected at 303 K, in relation of CO_2 loading. On black full dots the primary adsorption isotherm is reported while on light blue empty dots the secondary isotherm.

Tab. S1 Zero-coverage differential heat of CO₂ adsorption (-ΔH) for some selected MOFs.

Adsorbent	-ΔH (kJ mol ⁻¹)	Technique	Reference
CPO-27(Mg)	53	Microcalorimetry	1
MIL-101(Cr)	44	Microcalorimetry	2
UTSA-16(K)	32	Microcalorimetry	Present work
H-KUST-1(Cu)	28.2	Microcalorimetry	3
UiO-66-NH ₂	27	Microcalorimetry	4
UiO-66(Zr)	22	Microcalorimetry	4

3. SSNMR

For what concern SSNMR measurements, both magic angle spinning (MAS) and static spectra were acquired depending on the required information. A single pulse experiment (SPE) was used with a ¹³C 90° pulse of 4.0 μs, recycle delays of 3 s (more than 5 times the longitudinal relaxation time T₁ as measured with the saturation recovery technique) and 800 transients. Because of the low natural abundance of ¹³C and the paramagnetic nature of the cobalt atoms, which leads to broad lines and unpredictable chemical shifts, the contribution to the signal from components other than the gas molecules (nearly pure ¹³CO₂) can be neglected. ¹³C chemical shifts were referenced to the resonance of hexamethylbenzene (¹³C methyl signal at 17.4 ppm), as external standard. Prior to gas adsorption, the UTSA-16 sample was packed in a SSNMR rotor placed in a home-built quartz vacuum cell and activated for 2h at room temperature directly connected to a vacuum manifold and then heated at 363 K over night. After activation, the UTSA-16 sample was contacted with increasing ¹³CO₂ dosages (5, 20, 50, 100, 200 and 600 mbar). Afterward, the rotor was sealed to prevent further modification of the sample. ¹³C-enriched (99%) CO₂ was supplied by SIAD S.p.A..

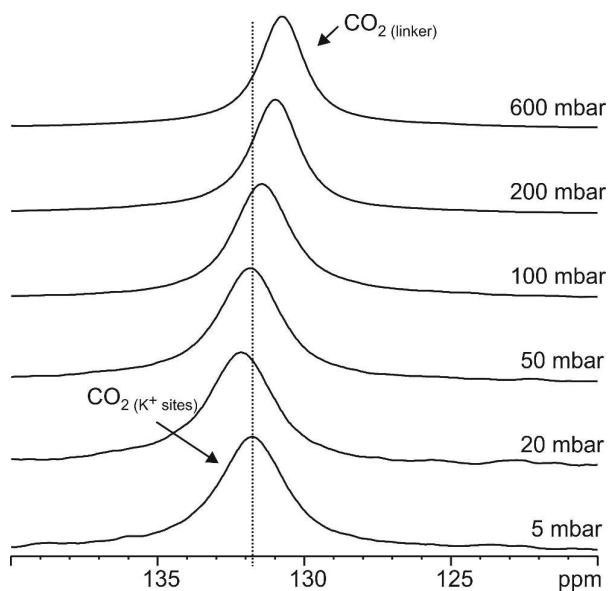


Fig. S2 ^{13}C (100.65 MHz) MAS spectra with relevant assignments of UTSA-16 loaded with different pressures of $^{13}\text{CO}_2$ (from 5 to 600 mbar) recorded with a spinning speed of 12 kHz at 298 K.

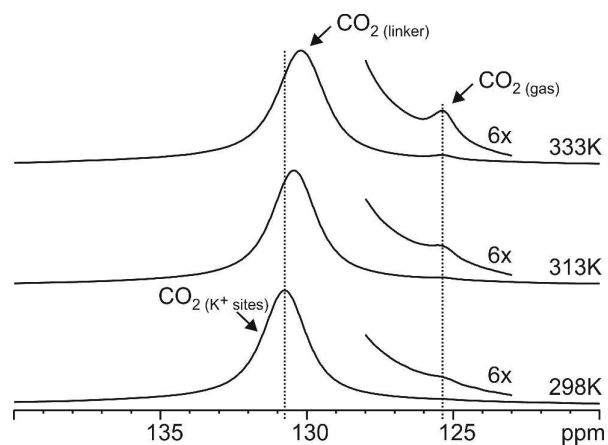


Fig. S3 ^{13}C (100.65 MHz) MAS spectra with relevant assignments of $^{13}\text{CO}_2$ -loaded UTSA-16 at 600 mbar in the temperature range from 298 to 333 K recorded with a spinning speed of 12 kHz.

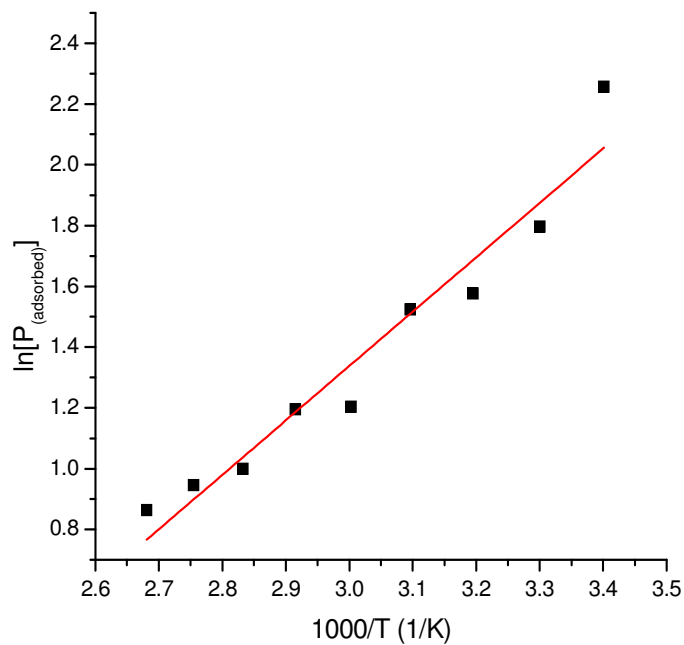


Fig. S4 Dependence of $\ln(P_{(K^+ \text{ sites})})$ on the reciprocal temperature (1000/K) for the sample at 200 mbar ($R^2=0.937$).

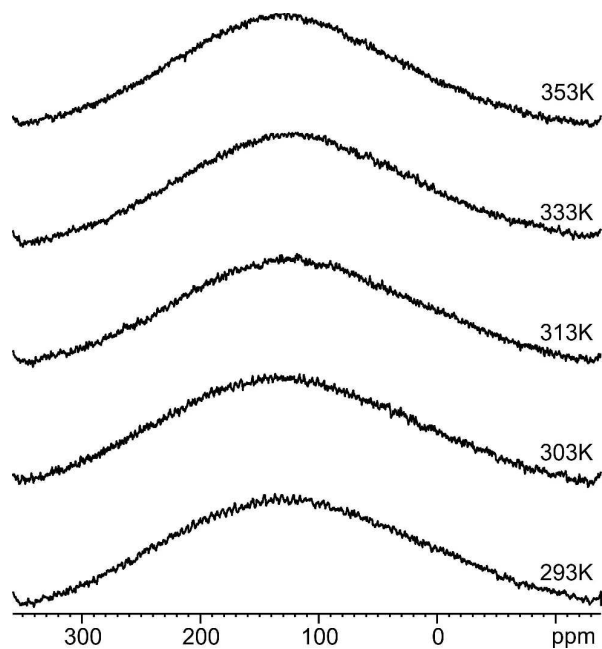


Fig. S5 ^{13}C (100.65 MHz) static spectra of $^{13}\text{CO}_2$ -loaded UTSA-16 at 200 mbar in the temperature range from 293 to 353 K.

4. Infrared spectroscopy and VTIR theory

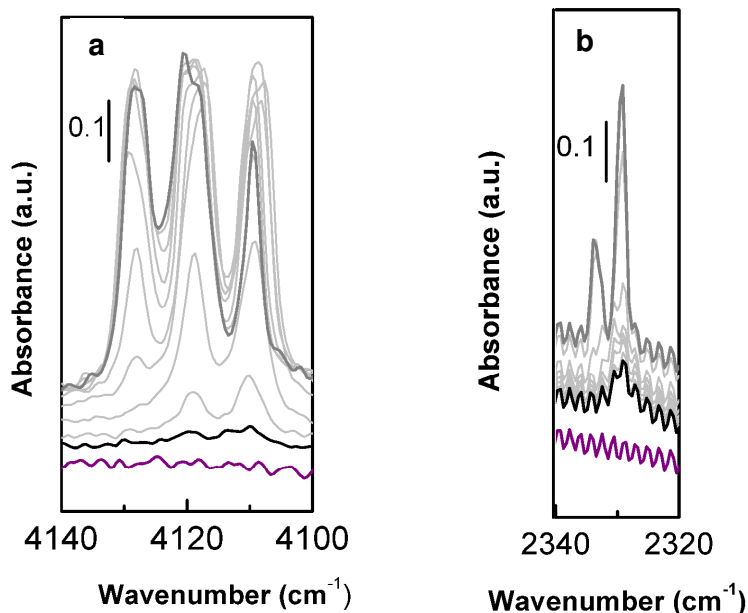


Fig. S6 VTIR spectra of (a) H₂ recorded at 20 mbar from temperature of 90 K (black line) to 15 K (grey line) and of (b) N₂ recorded at 40 mbar from temperature of 140 K (black line) to 60 K (grey line). Violet lines represent the zero-coverage UTSA-16 at 150 K.

Through the spectra of H₂ (Fig. S6,a) recorded in variable temperature mode, it was possible to apply the VTIR theory and calculate the enthalpy of hydrogen adsorption over UTSA-16:⁵ the integrated intensity, $A(T)$ of the IR absorption band is proportional to surface coverage, θ , at any given temperature T . $A(T)$ gives then information on the activity (in the thermodynamic sense) of both the adsorbed species and the empty adsorbing sites like the equilibrium pressure (p) does for the gas phase. An adsorption equilibrium constant, K , can be derived and the variation of K with temperature leads to the corresponding values of adsorption enthalpy and entropy. Assuming Langmuir-type adsorption, we have:⁶⁻⁸

$$\theta(T) = A(T) / A_M = K(T)p / [1 + K(T)(p/p_0)] \quad (1)$$

in eqn. 1, A_M is the integrated intensity corresponding to full coverage ($\theta = 1$), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and p_0 is the reference pressure (usually taken as 1 Torr or 1 mbar, while in few cases some authors have chosen 1 bar, *vide infra*). The equilibrium constant $K(T)$ can be obtained inverting eqn. 1:

$$K(T) = [A(T) / (A_M - A(T)) (p/p_0)] \quad (2)$$

when combining eqn. 2 with van't Hoff eqn. 3:

$$K(T) = \exp(-\Delta H^0 / RT) \exp(\Delta S^0 / R) \quad (3)$$

we obtain eqn. 4:^{6,7}

$$\ln[A(T) / (A_M - A(T))(p/p_0)] = (-\Delta H^0 / RT) + (\Delta S^0 / R) \quad (4)$$

Defining $Y = \ln[A(T) / (A_M - A(T))(p/p_0)]$:

$$Y = (-\Delta H^0 / RT) + (\Delta S^0 / R) \quad (5)$$

Eqn. 5 is the equation of a line in the (Y, T^{-1}) plane, so that different couples of (Y_i, T_i^{-1}) values obtained by VTIR experiments at different temperatures will allow to derive both ΔH_0 and ΔS_0 values through a standard linear fit procedure, ΔH_0 being related to the slope of the line Y and ΔS_0 related to its intercept with the ordinate axis. Obviously, this approach assumes a temperature independence of both ΔH_0 and ΔS_0 . Below, the linear fits made for H_2 IR signals at 4109, 4119 and 4128 cm^{-1} are reported in Fig. S7, S8, S9 respectively. The only parameter calculated was the enthalpy of adsorption ΔH_0 . ΔS_0 has been omitted. The few points used in the fit did not allowed an appropriate estimation of this quantity.

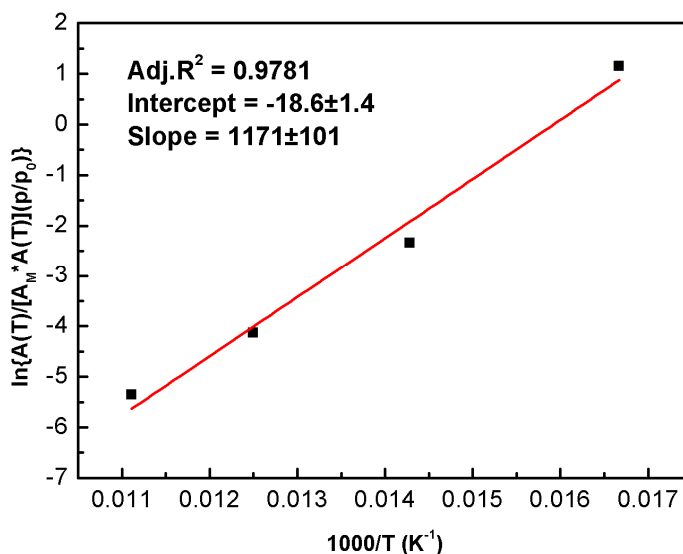


Fig. S7 van't Hoff plot obtained from the signal at 4109 cm^{-1} present in the H_2 VTIR spectra of Fig. S7,a. Reference pressure was $p_0 = 1$ mbar.

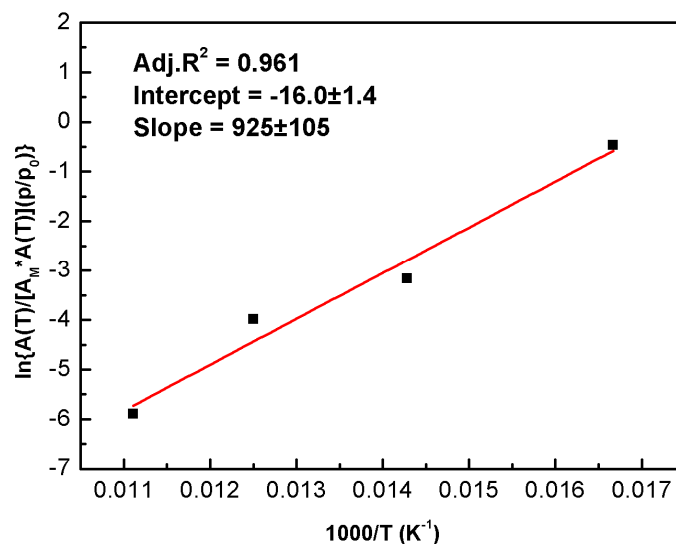


Fig. S8 van't Hoff plot obtained from the signal at 4119 cm⁻¹ present in the H₂ VTIR spectra of Fig. S7,a. Reference pressure was p₀ = 1 mbar.

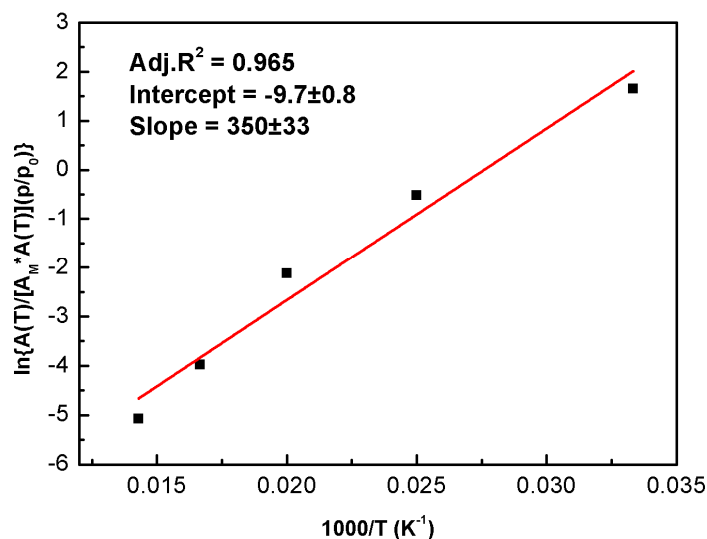


Fig. S9 van't Hoff plot obtained from the signal at 4128 cm⁻¹ present in the H₂ VTIR spectra of Fig. S7,a. Reference pressure was p₀ = 1 mbar.

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