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ELECTRONIC SUPPLEMENTARY INFORMATION

Confinement of H_2O and EtOH to enhance CO_2 capture in MIL-53(Al)-TDC

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1. Dynamic CO_2 capture

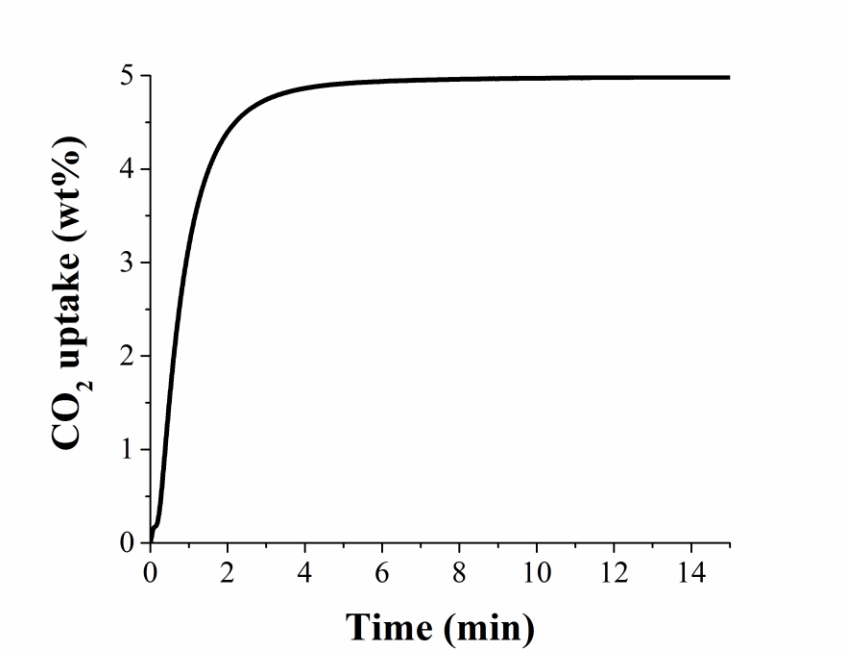

Fig. S1. MIL-53(Al)-TDC dynamic CO_2 adsorption at 30 °C.

2. Dynamic CO_2 capture under humidity conditions

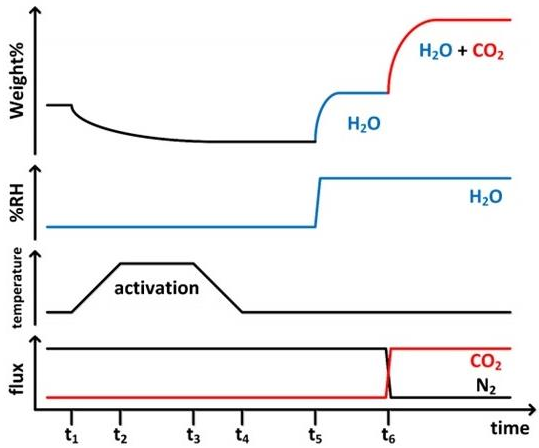

Fig. S2. Experimental variables diagram over the time for the CO_2 capture experiment. First the sample activation step at 180 °C under N_2 atmosphere (t_1 to t_3), then a stabilization step at 30 °C (t_4), after relative humidity setting (t_5), and capture of CO_2 under controlled humidity (t_6).

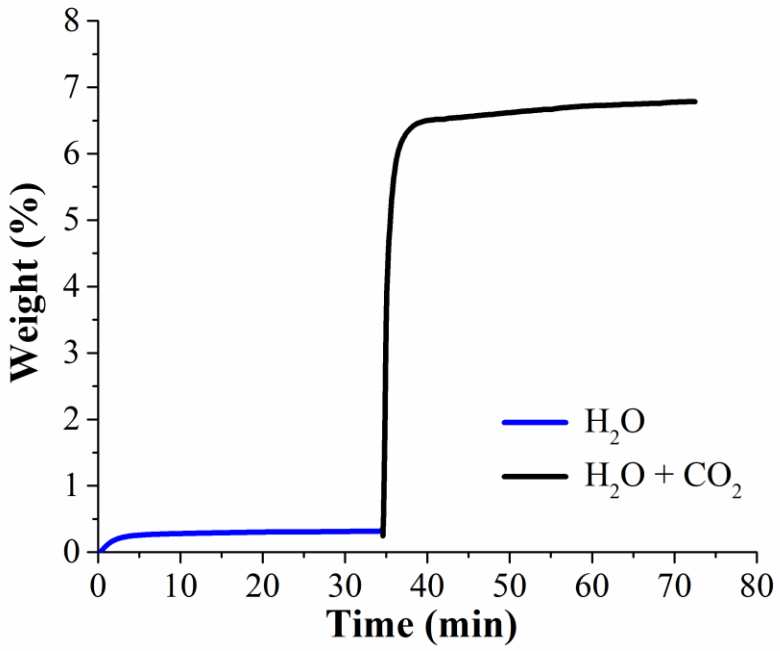

Fig. S3. MIL-53(Al)-TDC dynamic CO_2 adsorption at 30 °C under 5 %RH.

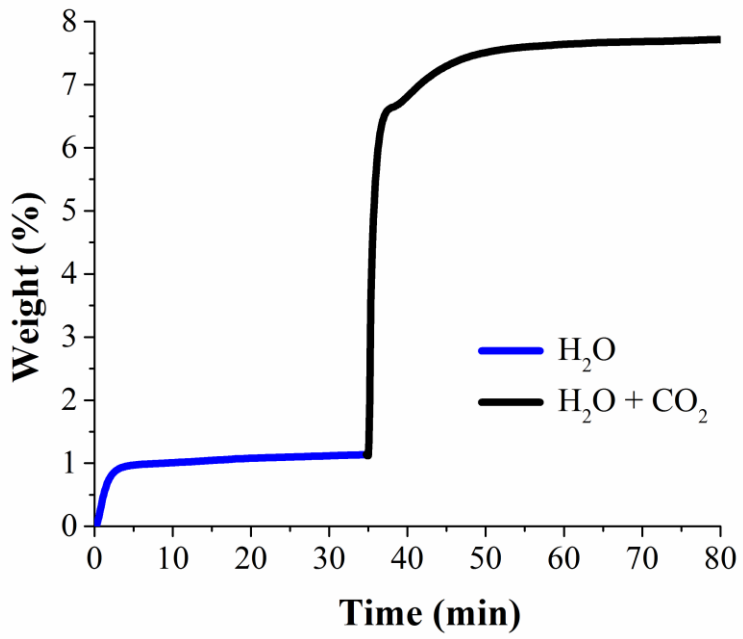

Fig. S4. MIL-53(Al)-TDC dynamic CO_2 adsorption at 30 °C under 15 %RH.

3. Loading of small amounts of EtOH (activation protocol)

Pre-adsorption of EtOH (saturation of EtOH). Samples of activated MIL-53 (Al)- TDC were placed in a quartz cell inside a BELPREP activation module and activated at 180 °C for 8 hours. After that time, these samples were cooled down to room temperature (under N_2) and immediately immersed in ethanol for 10 minutes. After that time, the samples were recovered by filtration and kept in a desiccator for 8 hours. Then, this saturated samples with the alcohols were placed in a thermobalance (Q500 HR, from TA) and heated up from room temperature to 300 °C (under N_2) in order to desorb all the alcohol molecules inside the micropores of MIL-53(Al).

Different activation conditions (heating ramps to reach maximum temperatures) were used in order to desorb (in a controlled manner) the amounts of ethanol that we determined. Thus, when saturated samples of ethanol were heated from room temperature to 170 °C, with a ramp of 10 °C/min, and immediately cooled down to 30 °C (under N_2), the residual amount of ethanol was determinated. This procedure was repeated 5 times in order to ensure the reproducibility of the experiment. For the best EtOH confinement result the values were: 2.10, 2.06, 1.99, 2.20, 2.03 wt%. Average = 2.076 wt%.

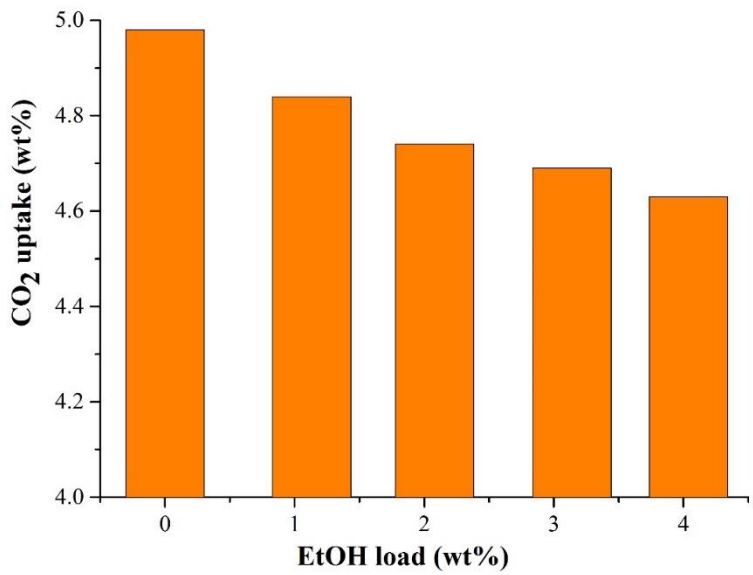

Fig. S5. MIL-53(Al)-TDC dynamic CO_2 adsorption at 30 °C under different ethanol loads.

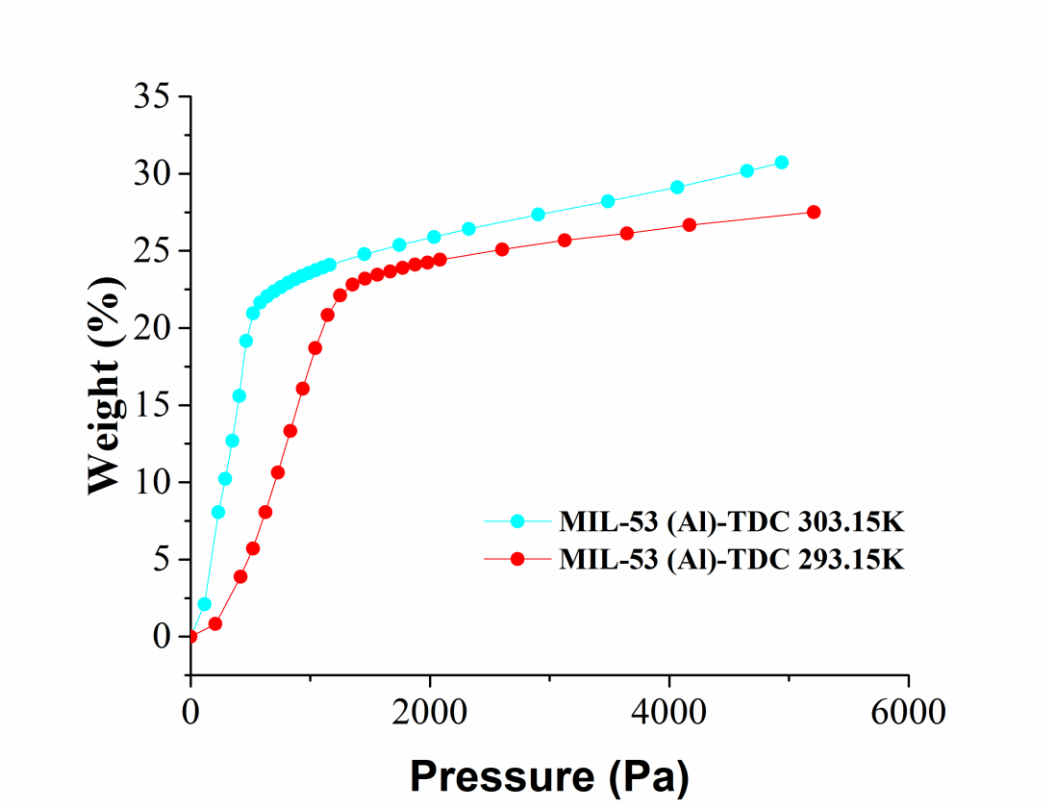

Fig. S6. MIL-53 (Al)-TDC ethanol adsorption isotherms at 293.15 K and 303.15 K.

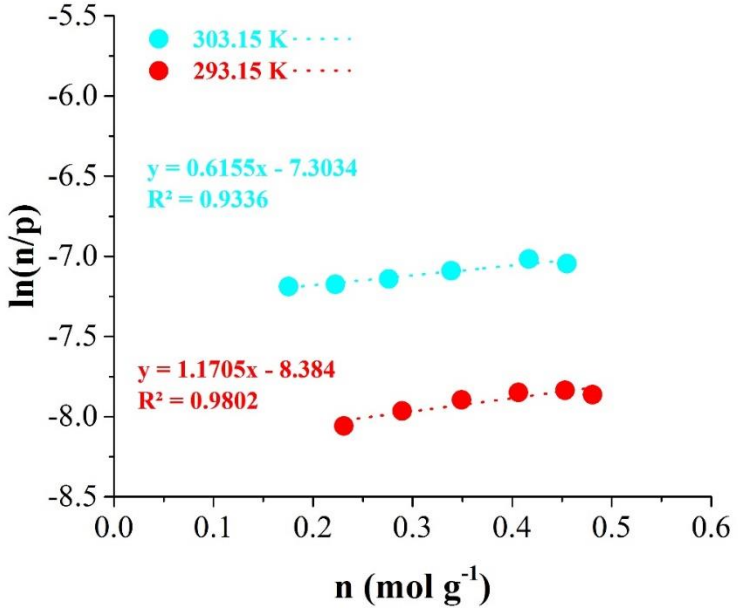

Fig. S7. Linear fit from the MIL-53 (Al)-TDC data.

From the regression data, we take the intercept (A_0) and slope (A_1) to estimate the isosteric heat of adsorption.

$$Q_{st} = R\left[A_0^{T_2} - \mathbf{A_0^{T_1}} + \left(\mathbf{A_1^{T_2}} - \mathbf{A_1^{T_1}}\right)n\right]\left(\frac{T_1 T_2}{T_1 - T_2}\right)$$

$$Q_{st} = 69.6 \text{ kJ } mol^{-1}$$

4. Computational details.

Calculations related to geometries optimisation were undertaken using Gaussian 09 implementation.[1] The geometry of the model was fully optimised at B3LYP/LANL2DZ level.[2,3] Harmonic analyses were performed and local minima were identified (zero negative values)

	d(H…A)	Angle	$\rho(BCP)$	$\nabla^2\rho(BCP)$	G(r)	V(r)	H(r)	-G(r)/V(r)	E_{int}
[AL$_2$(μ_2-OH)] /H_2O/CO_2									
$Al_2OH…OH_2$	1.36	179.93	0.10499	0.08156	0.07674	-0.13309	-0.05635	0.57660	-41.76
$H_2O..OCO$	1.78	177.13	0.02839	0.11087	0.02434	-0.02095	0.00338	1.16144	-6.57
$AlO…H_2O$	2.06	172.98	0.01866	0.06877	0.01647	-0.01574	0.00072	1.04600	-4.94
$Al_2OH…OH_2$	5.14	178.97	0.00013	0.00052	0.00008	-0.00003	0.00005	2.67358	-0.01
[AL$_2$(μ_2-OH)] /$EtOH/CO_2$									
$Al_2OH…$ EtOH	1.29	179.63	0.12974	-0.07790	0.08465	-0.18877	-0.10412	0.44842	-59.23
EtOH..OCO	1.79	178.63	0.02817	0.10845	0.02398	-0.02085	0.00313	1.15010	-6.54
$EtOHCH_3…S$	3.80	178.64	0.00104	0.00321	0.00056	-0.00031	0.00025	1.78377	-0.10
$EtOHCH_3…S$	4.02	175.19	0.00070	0.00217	0.00039	-0.00023	0.00016	1.67324	-0.07

Table S1. Analysis of Quantum Theory Atoms in Molecules. Distances (d) in angstroms, angles in degrees, energy interaction (Eint) in kcal/mol, and other quantities in au. B3LYP/6-31++G**.

5. References

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