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ELECTRONIC SUPPLEMENTARY INFORMATION

Confinement of alcohols to enhance CO_2 capture in MIL-53(Al)

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1. Materials and measurements

All reagents and solvents were used as received from commercial suppliers without further purification. Powder X-ray diffraction (PXRD) data were collected under ambient conditions on a Bruker AXD D8 Advance diffractometer operated at 160 W (40 kV, 40 mA) for Cu Kα_1 (λ= 1.5406 Å). Thermal gravimetric analysis (TGA) was performed under N_2 at a scan rate of 2 °C/min using a TA Instruments Q500HR analyser.

2. TGA plot

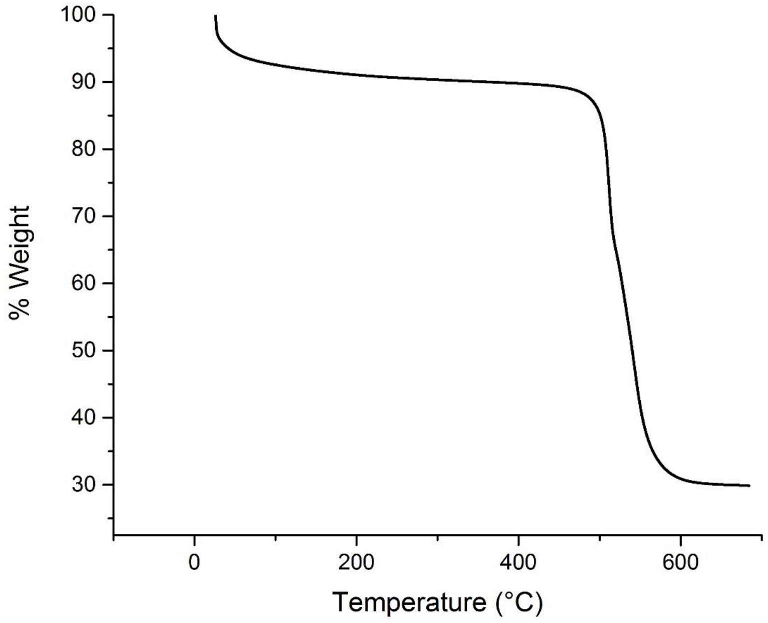

Fig. S1: TGA analysis of calcined MIL-53(Al).

3. Powder X-ray diffraction patterns of MIL-53(Al)

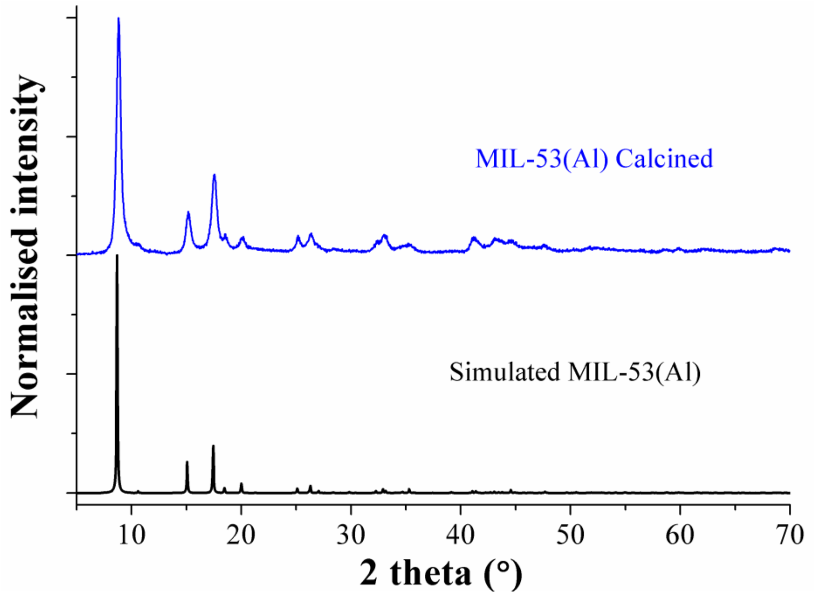

Fig. S2: PXRD patters of simulated (black) and calcined (blue) MIL-53(Al).

4. Differential Scanning Calorimetry (DSC)

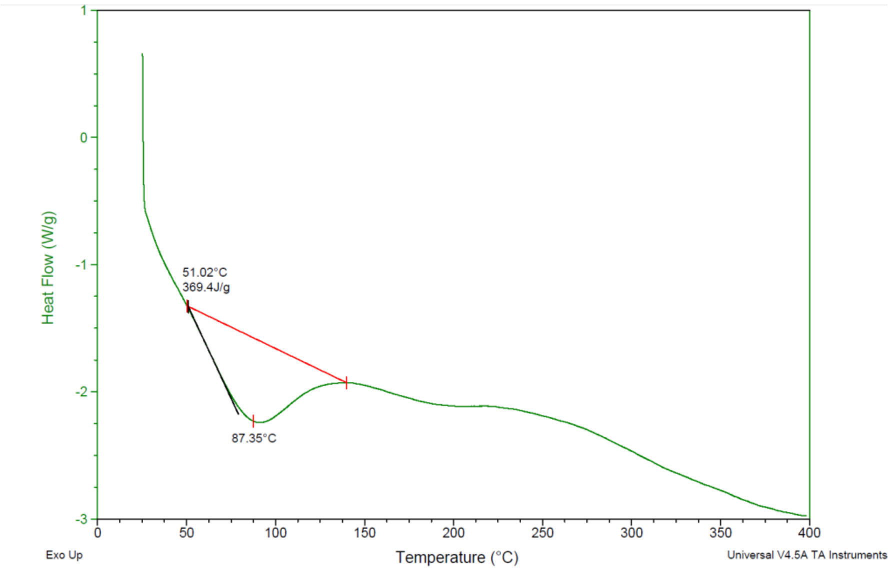

Figure S3. DSC for MeOH@MIL-53(Al) sample.

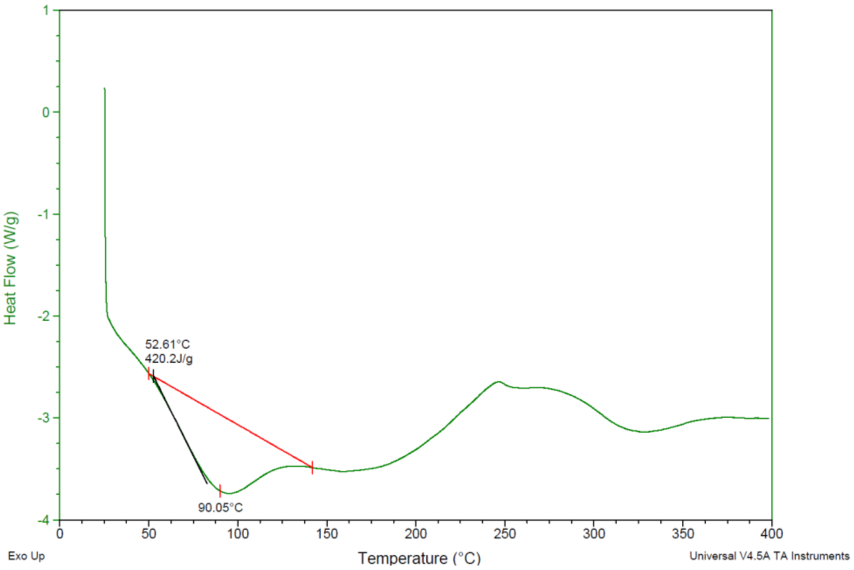

Figure S4. DSC for *i*-PrOH@MIL-53(Al) sample.

5. Loading of small amounts of alcohols (activation protocol)

Pre-adsorption of alcohols (saturation of the alcohols). Samples of calcined MIL-53 (Al) 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 one of the alcohols (methanol or isopropanol) 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 ^{o}C (under N_2) in order to desorb all the alcohol molecules inside the micropores of MIL-53(Al). The maximum loads of alcohols were: 26 wt% for MeOH and 24 wt% for *i*-PrOH. These results were in good agreement with both alcohols isotherms.

Once the maximum amounts of alcohols were established for MIL-53(Al), more saturated samples were prepared. Then, different activation conditions (heating ramps to reach maximum temperatures, from 40 to 180 ^{o}C) were used in order to desorb (in a controlled manner) the amounts of alcohols that we determined. Thus, when saturated samples of both alcohols were heated from room temperature to 170 ^{o}C, with a ramp of 10 ^{o}C/min, and immediately cooled down to 30 ^{o}C (under N_2), the residual amount of the alcohols was approximately 2 wt%. This procedure was repeated 5 times in order to ensure the reproducibility of the experiment.

In addition, in order to corroborate the exact amount of residual alcohol in MIL-53(Al), another experiment was carried out. Diagram S1 shows the activation of a saturated sample with MeOH followed by a kinetic CO_2 adsorption experiment and the final desorption of the sample.

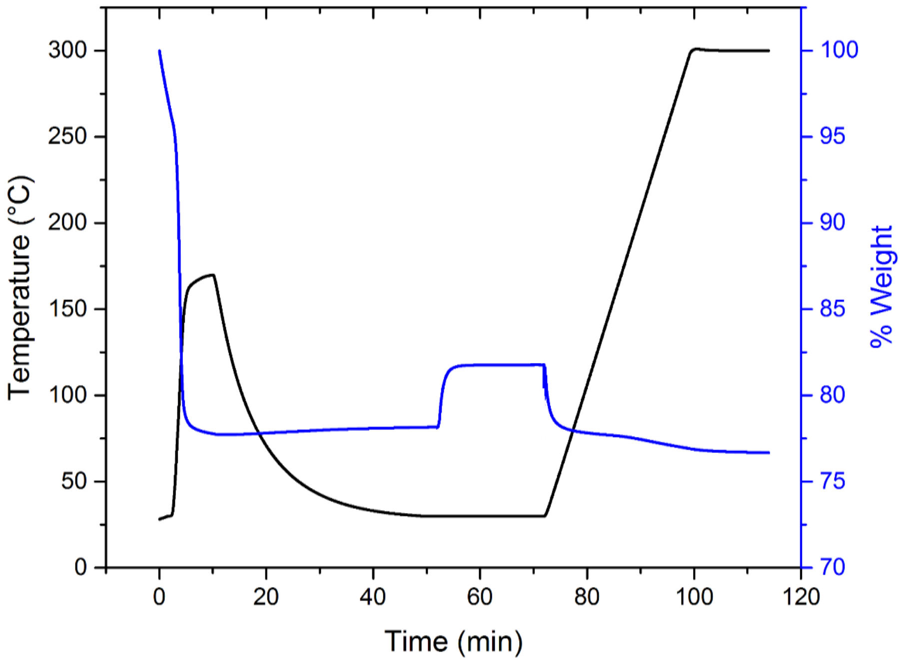

Diagram S1. Description of a kinetic CO_2 uptake experiment. First, a saturated sample of MIL-53(Al) with methanol was heated from room temperature to 170 °C (10 ºC/min) under N_2, form 0 min to 10 min. Immediately, the sample was cooled down to 30 °C and when the sample was stabilised (after 50 min) the flow of N_2 was changed for CO_2 and a quick weight gain was observed. Then, from 55 min to 70 min this weight was constant and there was another gas switching (this time from CO_2 to N_2) and the CO_2 desorption was recorded: from 70 min to approximately 75 min. Finally the sample was heated up to 300 °C and all the residual alcohol was completely removed. The residual amount of MeOH was estimated to be 1.93 wt%.

6. Derivation of the isosteric enthalpy of adsorption for CO_2

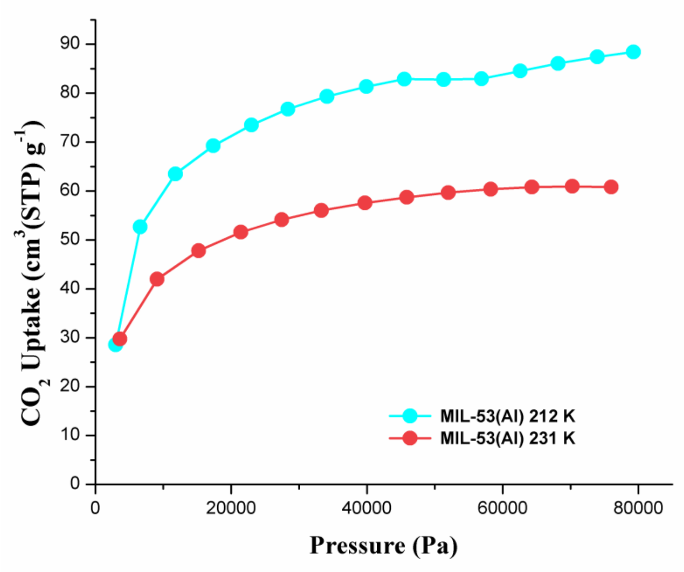

Figure S5. MIL-53(Al) CO_2 adsorption isotherms at 212 and 231 K.

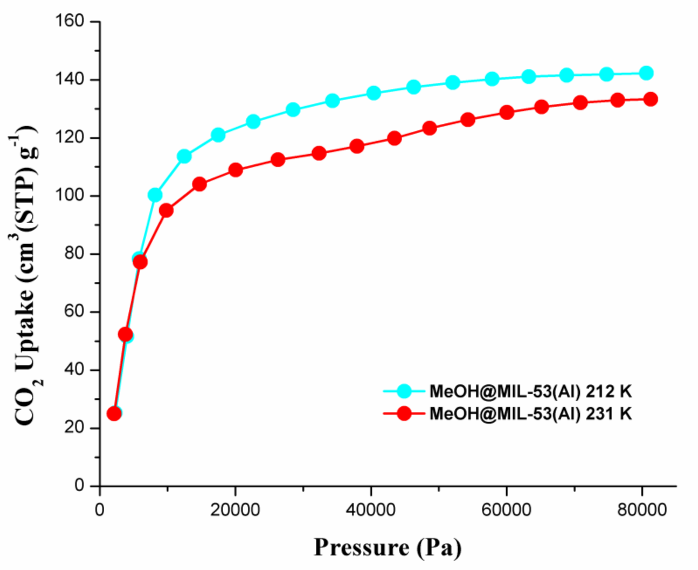

Figure S6. MeOH@MIL-53(Al) CO_2 adsorption isotherms at 212 and 231 K.

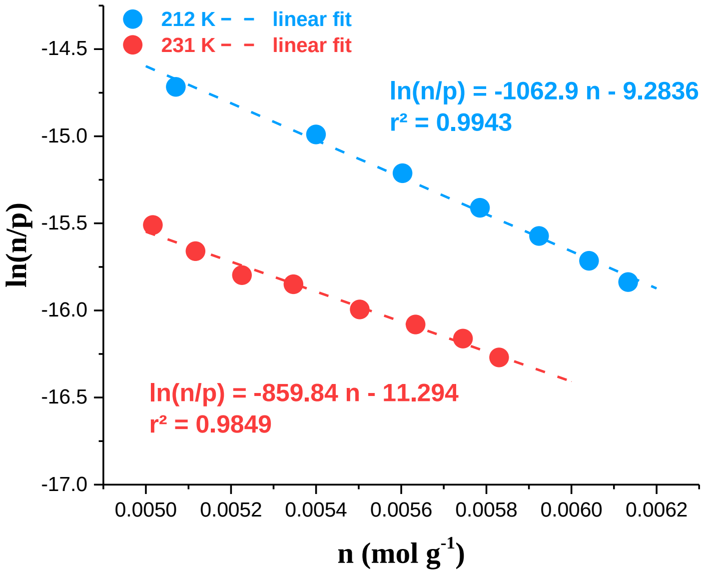

Figure S7. Linear fit from the MIL-53(Al) data.

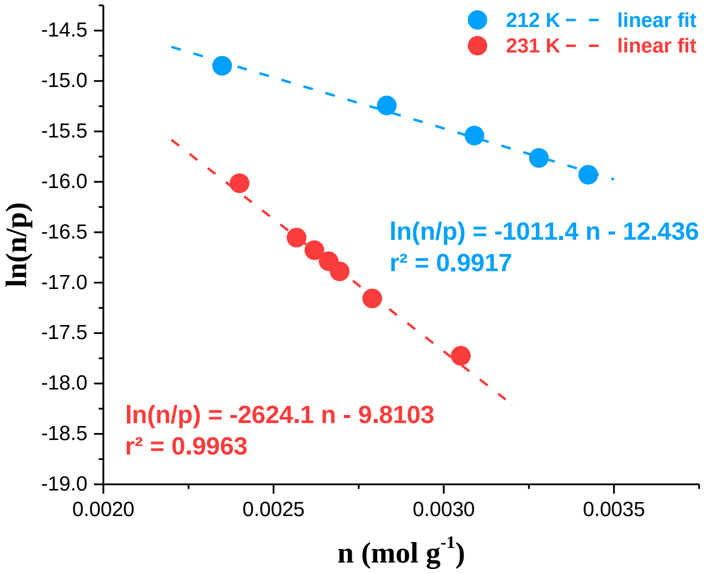

Figure S8. Linear fit from the MeOH@MIL-53(Al) data.

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

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

Table S1. Heat of adsorption values.

Material	Q_{st} kJ mol^{-1}
MIL-53(Al)	42.1
MeOH@MIL-53(Al)	50.3

7. Theoretical calculations.

Density functional approximation[1-3] as implemented in Gaussian 03[4] was used for all calculations. Full geometry optimisations without symmetry constrains and frequency analysis were carried out for all the stationary points using the three parameters B3LYP[5-7] density functional and the LANL2DZ basis sets.[8-10] Harmonic frequency analyses allowed us to verify optimised minima. Small model of the reactive site was used to analyse structural differences with and without the presence of MeOH and i-PrOH.

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