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ELECTRONIC SUPPLEMENTARY INFORMATION

CO_2 capture under humid conditions in NH_2-MIL-53(Al): the influence of the amine functional group

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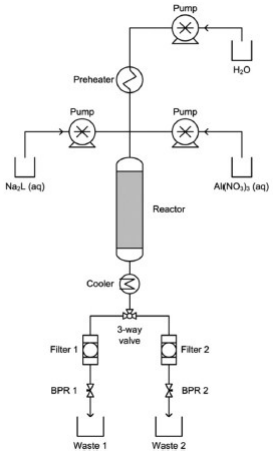
1. Materials and measurements

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 $K\alpha_1$ (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. N_2 adsorption was carried out in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer. The surface area was calculated using the BET method based on adsorption data in the partial pressure (p/p_0) range 0.01 to 0.04. Dynamic and isothermal experiments were performed using a humidity-controlled thermobalance (TA Instruments, model Q5000SA) at 30 °C and relative humidities (RH) of 5, 10 and 30%. Fourier transform Infrared (FTIR) spectroscopy spectra were obtained on a Bruker Alpha spectrometer equipped with an attenuated total reflectance (ATR) accessory. The samples MIL-53(Al) and NH_2-MIL-53(Al) were synthesised using a continuous flow approach[1] and calcined (extraction of terephtalic and 2-amino-terephthalic acid from the pores) in an oven at 330 °C for 3 days. Thus, both samples are labelled as post-synthesised.

Continuous process for the synthesis of materials MIL-53(Al) and NH_2-MIL-53(Al). A total flow rate of 3.0 mL min^{-1} of water was adjusted and the pressure of the system was set at 230 bar. The temperature of the pre-heater (and the reactor) was set to 300 °C and 250 °C, respectively. Once the temperature was stable, the streams were changed to metal salt and ligand solutions and the flows passed through Filter 1 for 20 min. Then, the 3-way valve was switched to Filter 2 and next batch of product collected for 20 min, while product in Filter 1 was collected and a new filter inserted. After 20 min, the 3-way valve was turned to Filter 1, new reaction conditions set and while the product in Filter 2 was collected in the filter, more product was collect in Filter 1. (See Scheme S1).[1]



Scheme S1: Schematic representation of the continuous process.[1]

2. TGA plots

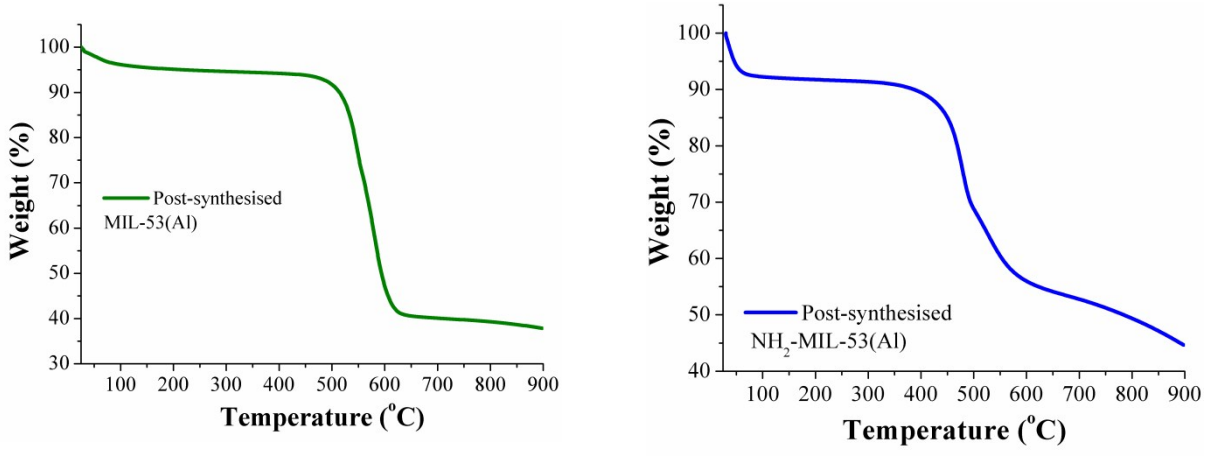


Fig. S1: TGA analyses of: (right) post-synthesised MIL-53(Al) and (left) post-synthesised NH_2-MIL-53(Al).

3. Powder X-ray diffraction patterns of MIL-53(Al) and NH_2-MIL-53(Al)

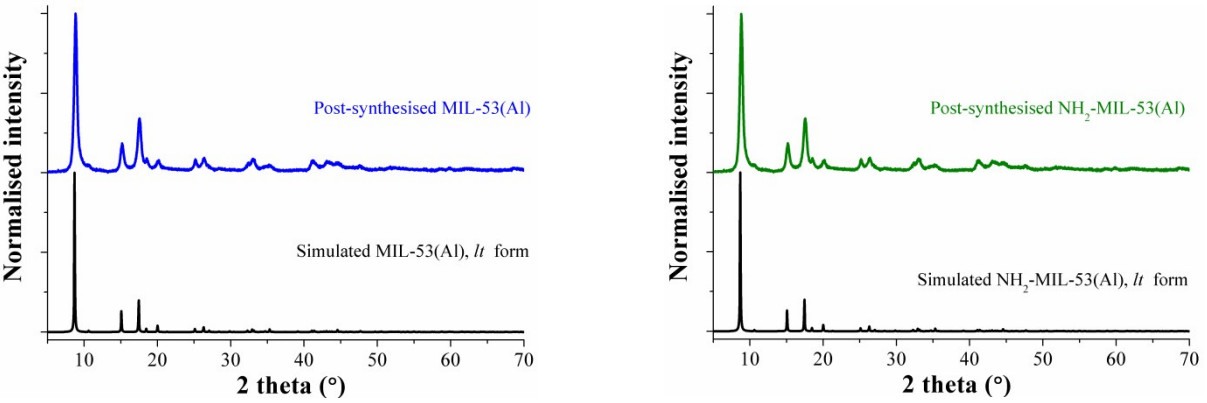
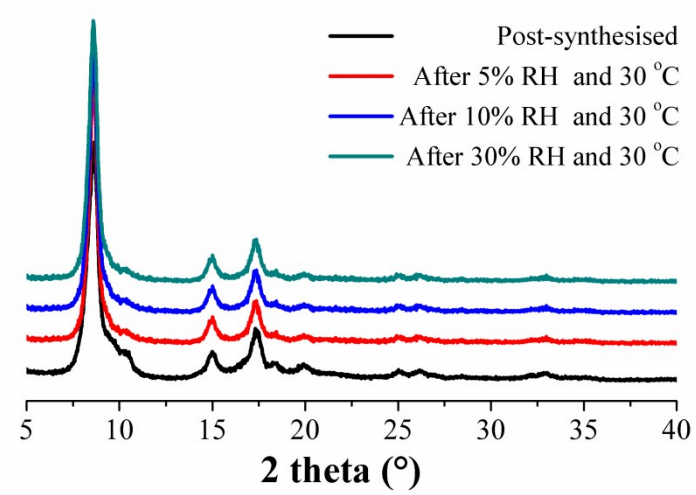


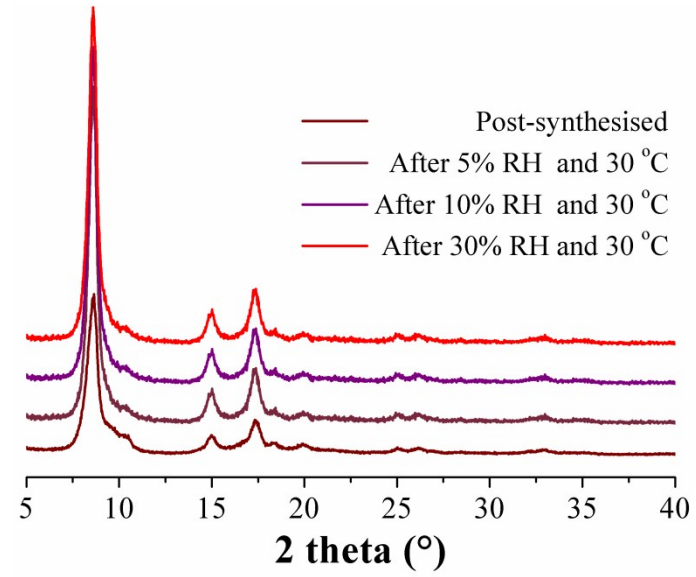
Fig. S2: PXRD patters of: (left) simulated, *lt* form, (black) and post-synthesised (blue) MIL-53(Al) and (right) simulated, *lt* form, (black) and post-synthesised (green) NH_2-MIL-53(Al).

4. PXRD and BET surface areas of each MIL-53(Al) and NH_2-MIL-53(Al) samples after the kinetic CO_2 isotherms.



Sample	BET area ($m^2 g^{-1}$)
Post-synthesised	1096
After 5% RH and 30 °C	1089
After 10% RH and 30 °C	1093
After 30% RH and 30 °C	1088

Fig. S3: (left) PXRD patters of each MIL-53(Al) samples after the kinetic CO_2 isotherms were carried out at different relative humidities; (right) BET areas of each MIL-53(Al) samples after the kinetic CO_2 isotherms were carried out at different relative humidities.



Sample	BET area ($m^2 g^{-1}$)
Post-synthesised	780
After 5% RH and 30 °C	777
After 10% RH and 30 °C	781
After 30% RH and 30 °C	779

Fig. S4: (left) PXRD patters of each NH_2-MIL-53(Al) samples after the kinetic CO_2 isotherms were carried out at different relative humidities; (right) BET areas of each MIL-53(Al) samples after the kinetic CO_2 isotherms were carried out at different relative humidities.

References

1. P. A. Bayliss, I. A. Ibarra, E. Pérez, S. Yang, C. C. Tang, M. Poliakoff and M. Schröder, *Green Chem*., 2014, **16**, 3796.