Supplementary Information

Experimental Details

A typical profile for P and T vs time for batch reactions is shown in Figure S1.

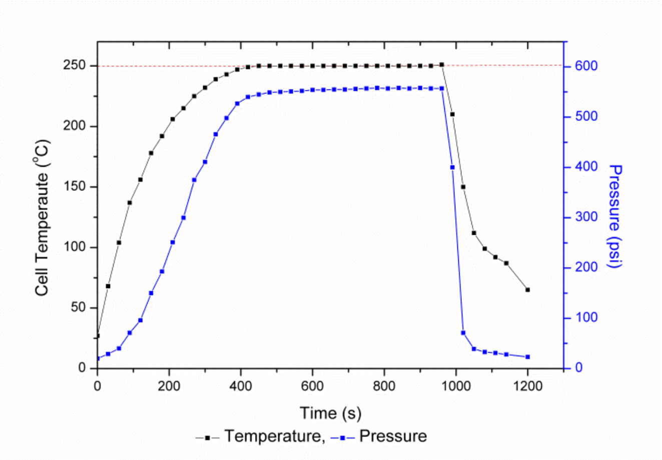

Figure S1 Plot of reactor internal temperature (black) and pressure (blue) against time for a typical batch reaction for 10 min at 250 °C to form MIL-53(Al). Red dotted line shows target reaction temperature.

Flow reactions: A back pressure regulator (BPR, Tescom, model no. 26-1762-24-043) was used in the flow systems (Figure 1). For the reactions carried out at 200 °C, 225 °C, 275 °C and 300°C the same conditions as at 250 °C were used except the reactor heater was set to these temperatures. All yields are based on the target phase $[Al(OH)(L^1)]_n$. The crude yield is quoted before removal of free H_2L^1 for the pores; the pure yield refers to the overall yield after removal of in-pore H_2L^1. The collection of samples at steady state also allows accurate determination of the yield, Y, using the equation:

$$Y = \frac{m}{C_L F_L t M}$$

where *m* is mass collected, *t* is time of collection, C_L and F_L are the molar concentration and flow rate of the ligand solution, respectively. *M* is the molecular weight for $[Al(OH)(C_6H_4(CO_2)_2)]$.

scEtOH Extractions: As-synthesised MIL-53(Al) (100 mg) containing H_2L^1 both internally in the pores and externally as discrete crystals was loaded into reactor 1. The extraction was run for 2 hr with reactor 1 held at 250 °C and reactor 2 cooled with water and with a liquid ethanol flow rate of 0.5 ml min^{-1} and a back pressure of 100 bar. Figure 2 shows a schematic of this extraction rig.

Volumetric Gas Adsorption

N_2 isotherms were carried out on a Quantachrome Autosorb-1 (model no. As1-GYTKXL11, software ver. 1.61). Samples were degassed overnight, MIL-53(Al) material at 125°C and HKUST-1 at 100°C. The BET pressure range for the batch sample was 7.0×10^{-3} to 2.9×10^{-3} P/P_0 and for the continuous process sample 2.5×10^{-3} to 5.3×10^{-2} P/P_0, consistent with criteria used by Snurr and co-workers.[1,2]

Gravimetric Gas adsorption

CO_2 and CH_4 adsorption experiments were carried out using a Hiden Isochema Intelligent Gravimetric Analyzer (model no. IGA-003 system) at the University of Nottingham under ultra-high vacuum in a clean system with a diaphragm and turbo pumping system. IGASwin system software v.1.03.143 (Hiden Isochema, 2004) was used to fit all isotherm data points. All changes in sample weight were corrected for buoyancy effects.

PXRD

X-ray powder diffraction patterns were collected on a Pananalytical X'Pert Pro diffractometer operating at 160 W (40 kV, 40 mA) CuK_α (λ= 1.5406 Å). High resolution powder diffraction data were collected on Beamline I11 at Diamond Light Source using multi-analysing-crystal detectors (MACs) and an *in situ* gas cell system.[3]

TGA

Thermogravimetric analyses were performed on a Perkin Elmer Thermogravimetric analyzer Pyris 1 TGA (model no. R1R151 TGA, software Ver. 11.0.0.0449). A heating rate of 5 °C min^{-1} was used from room temperature up to 700 °C.

Infrared (ATR-FTIR)

Attenuated total reflectance (ATR) Fourier transformed Infrared (FTIR) was used to collect IR spectra for MOF samples. The data were collected using a Fisher Thermo Scientific Nicolet iS5 with iD5-ZnSe ATR attachment and Ominic (software ver. 8.2.0.387) using 16 scans with a data spacing of 0.482 cm^{-1} over a range of 600-4000 cm^{-1}.

MIL-53(Al)

The phase referred to as MIL-53(Al)*op* (CDS ref. code SABVUN) and MIL-53(Al)*hy* (CDS ref. code SABWAU) were first reported by Loiseau *et al.*[4] The phase referred to as MIL-53(Al)*ta* (CDS ref. code SABVOH01) was reported by Vougo-Zanda *et al*,[5] and the phase referred to as H_2L^1 (CDS ref. code TEPHTH) was first reported by Bailey and Brown,[6] with the phase referred to as γ-AlO(OH) (ICSD collection code Collection Code 59609) reported by Bokhimi *et al.*.[7] The simulated PXRD patterns were generated using Mercury 3.1.[8]

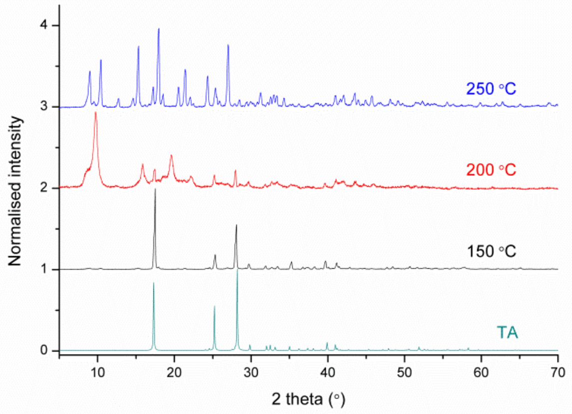

Figure S2 PXRD pattern of the reaction product MIL-53(Al) prepared by batch reaction at 150 °C (black), 200 °C (red) and 250 °C (blue) and simulated pattern for H_2L^1 (green).

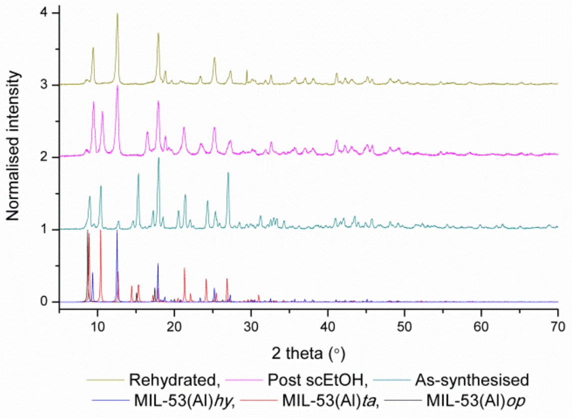

Figure S3 PXRD patterns for MIL-53(Al) produced in batch at 250 °C; as-synthesised (green), after treatment with scEtOH (pink), and after degassing and rehydration (yellow). The rehydrated material can be seen to match MIL-53(Al) hydrate (blue) by comparison with the simulated pattern. The small shoulder on the first peak is due to incomplete rehydration.

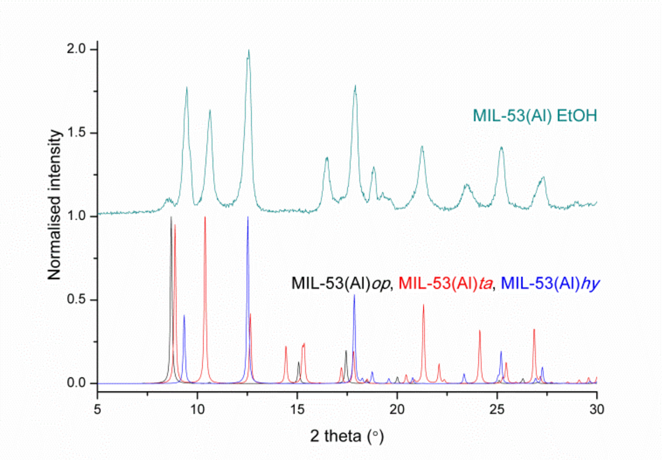

Figure S4 PXRD pattern of MIL-53(Al) after washing with scEtOH. The shift in peak positions and absence of peaks from 14-16° confirms that this phase does not match previously reported phases, consistent with the formation of MIL-53(Al).xEtOH. MIL-53(Al) was produced in batch at 250 °C, before being washed with scEtOH for 2h.

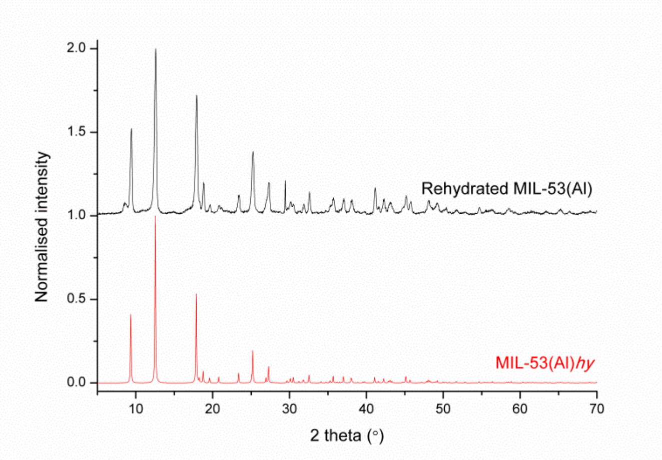

Figure S5 PXRD pattern of MIL-53(Al) prepared in batch (250 °C), activated with scEtOH, degassed, and then and exposed to air (black). The sample matches the MIL-53(Al)*hy* (red).

Treatment of as-synthesised MIL-53(Al) with scEtOH produced new phases which do not match the known phases MIL-53(Al)*ta*, MIL-53(Al)*hy* or MIL-53(Al)*op* phase. Rehydration of the material affords MIL-53(Al) hydrate by comparison with the simulated pattern. The small shoulder on the first peak (Figure S6) is due to incomplete rehydration. None of the MIL-53(Al)*ta* phase is present after scEtOH treatment confirming that H_2L^1 has been removed from the pores.

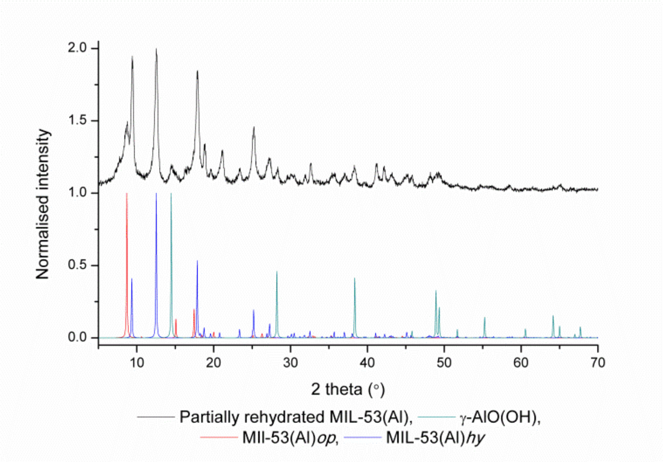

Figure S6 PXRD pattern of MIL-53(Al) prepared in continuousflow, treated with scEtOH, degassed and then partially rehydrated upon exposure to air (black).The sample matches the phases MIL-53(Al)*op* (red) and MIL-53(Al)*hy* (blue), and a minor phase γ-AlO(OH)(green) is present.

A Le Bail refinement was performed on PXRD data for the degassed sample of MIL-53(Al) produced in batch at 250 °C. The refinement confirms that the bulk material matches with the known phase MIL-53(Al)*op*.

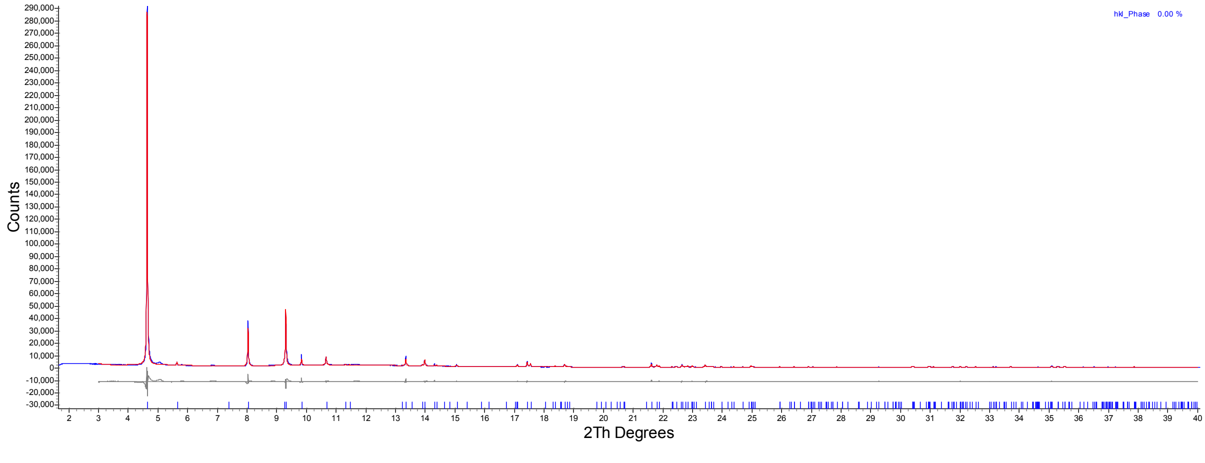

Figure S7 Le Bail profile fitting of MIL-53(Al) after degassing showing peaks at 2θ = 0-40° shown, r_wp = 9.06, r_p = 6.24, gof = 5.53, cell parameters: *Imma*, V = 1423.87(11), *a* = 6.63198(25), *b* = 16.75117(61), *c* = 12.81691(69). The material was produced in batch at 250 °C, treated with scEtOH, and degassed *in situ*.

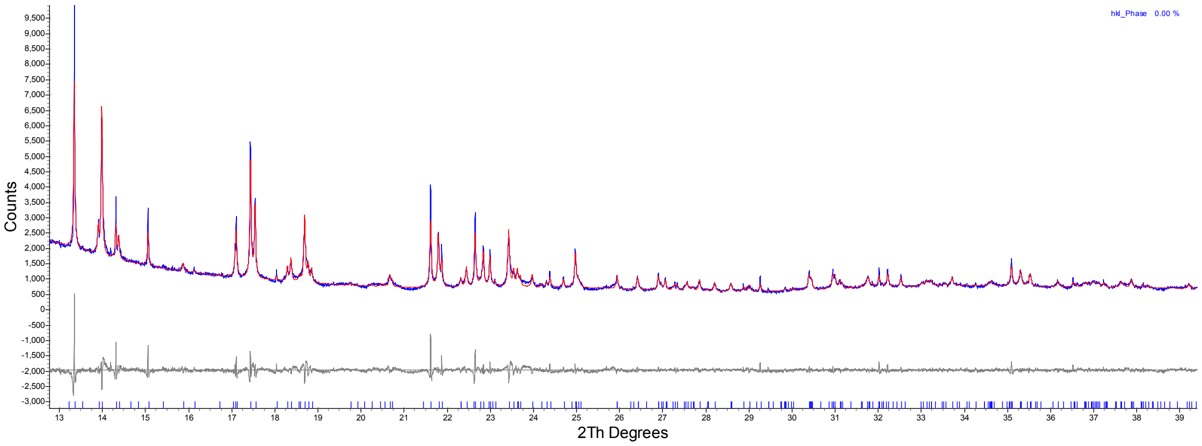

Figure S8 Le Bail profile fitting of PXRD data for MIL-53(Al) after degassing showing higher angle peaks with 2θ = 13-39°.

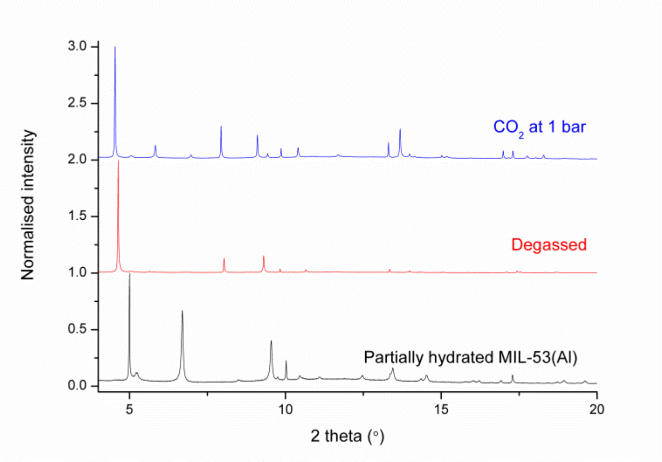

Figure S9 High resolution PXRD pattern (λ = 0.827107 Å) of partially hydrated MIL-53(Al) (black), degassed *in situ* (red) and CO_2 loading at 1 bar (blue). The material was produced in batch at 250 °C before treatment with scEtOH and drying. The PXRD data confirm that MIL-53(Al) exhibits the expected flexibility on degassing and CO_2 adsorption.

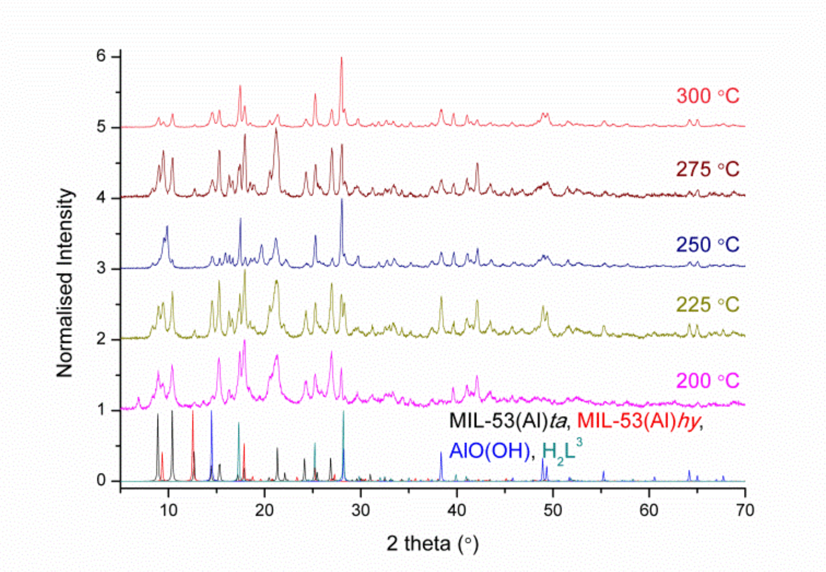

Figure S10 Comparison of PXRD patterns for products isolated from continuous flow reactions at 200 °C, 225 °C, 250 °C, 275 °C and 300 °C. PXRD patterns for MIL-53(Al)*ta*, MIL-53(Al)*hy*, H_2L^1 and AlO(OH) are shown for comparison.

In the TGA for $[Al(OH)(L^1) + xH_2L^1]_n$, the step of 38.5% between 215°C and 440°C is attributed to the loss of in-pore H_2L^1 (Figure S11). From this it has been calculated the as-synthesised product contains 0.8 equivalents of H_2L^1. The step of 39.2% from 540 °C to 665 °C corresponds to loss of terephthalate linker and structure decomposition of the framework to aluminium oxide. For as-synthesised MIL-53(Al) Loiseau *et al* reported two steps in the range of 275-420 °C for the sublimation of H_2L^1 removal and the loss of 0.7 H_2L^1 equivalents.[3] Here the additional steps between 200-300 °C may also include direct sublimation of amorphous H_2L^1 located outside of the pores. This is plausible since we have used a higher H_2L^1:Al ratio in the synthesis of the material.

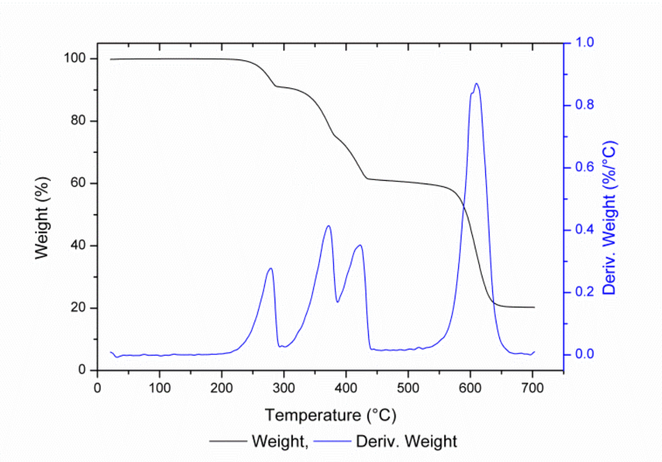

Figure S11 TGA of the as-synthesised batch sample $[Al(OH)(L^1) + 0.8H_2L^1]_n$ (black) with derivative plot (blue) showing the rate of change of % weight loss with temperature.

TGA for the as-synthesised MIL-53(Al) from the continuous flow process has a step of 23.6% between 215 °C and 440 °C attributed to the loss of in-pore H_2L^1 and is divided into three steps (Figure S12). From this it has been calculated that the as-synthesised product contains 0.41 H_2L^1 equivalents. The step of 36.4% from 500 °C to 690 °C corresponds to loss of ligand and structure decomposition of the framework to aluminium oxide.

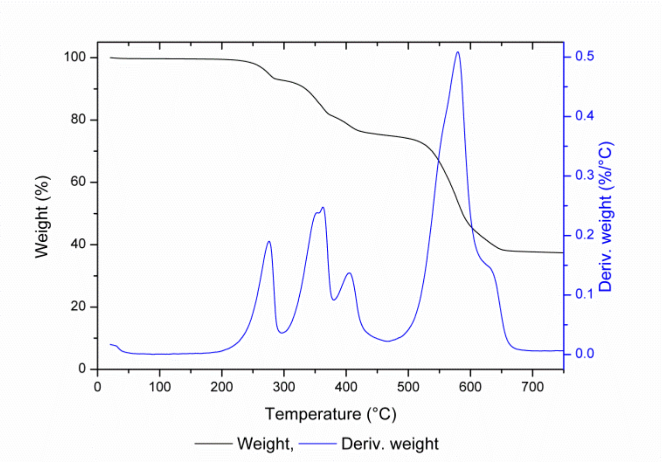

Figure S12 TGA under N_2 of as-synthesised MIL-53(Al) produced using the continuous flow process; the derivative plot (blue) shows the rate of change of % weight loss with temperature.

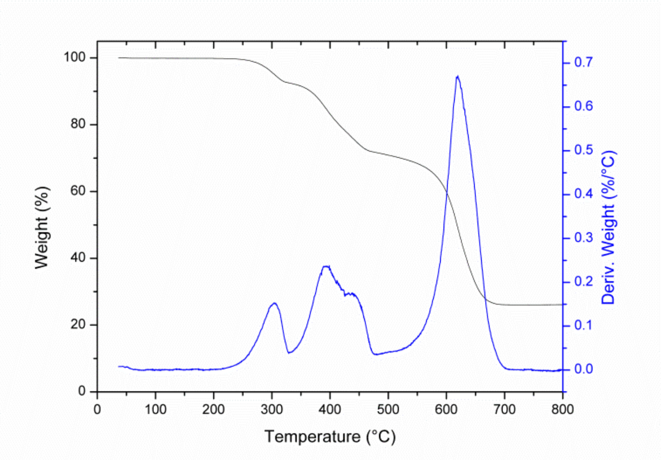

Figure S13 TGA under air of as-synthesised MIL-53(Al) produced using the continuous flow process; the derivative plot (blue) shows the rate of change of % weight loss with temperature.

The TGA for MIL-53(Al) produced in batch at 250 °C after treatment with scEtOH has an initial weight loss of 6.0% between 15 °C at 100 °C corresponding to loss of ethanol trapped in the pores (Figure S14). The TGA shows a weight loss of only 2.4% in the region of 215 °C to 475 °C, confirming that in-pore H_2L^1 has been removed. The second step of 63.6% between 500 °C and 700 °C is due to the decomposition of the material.

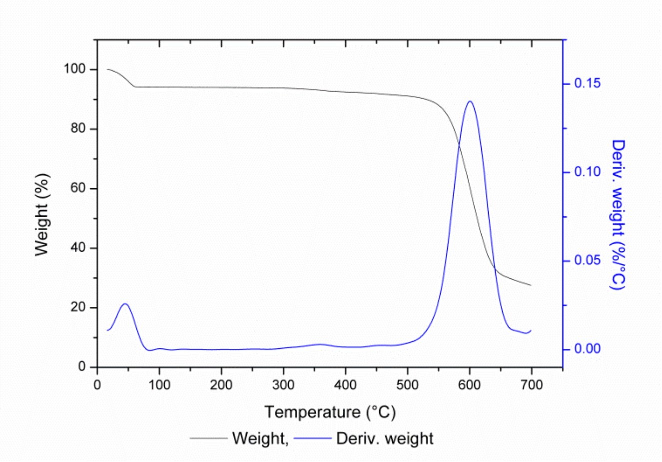

Figure S14 TGA of MIL-52(Al) produced in batch after treatment with scEtOH to remove uncoordinated H_2L^1 from within the pores.

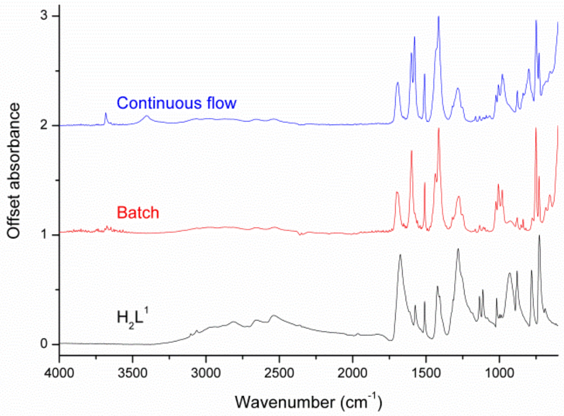

Figure S15 ATR-FTIR of MIL-53(Al) synthesised using HTW at 250 °C *via* batch (red) and continuous flow process (blue) and of H_2L^1 (black) for comparison.

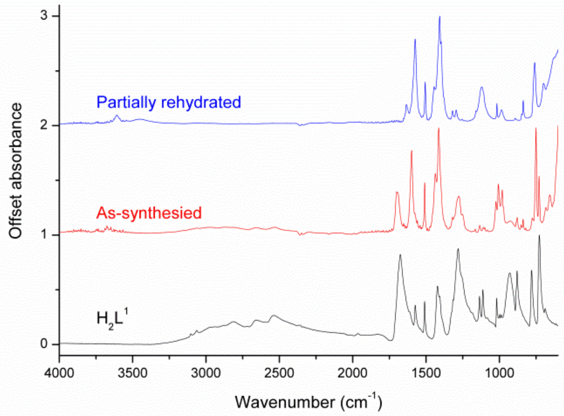

Figure S16 ATR-FTIR of MIL-53(Al) produced in batch; the as-synthesised (red) and partially rehydrated sample (blue). The partially rehydrated sample was first treated with scEtOH to remove H_2L^1 from the pores, followed by degassing at 120 °C overnight and then partial rehydration on exposure to air. The absence of the peak at 1695 cm^{-1} (uncoordinated) confirms that H_2L^1 is no longer present in the pores. The FTIR spectrum of H_2L^1 is shown for comparison.

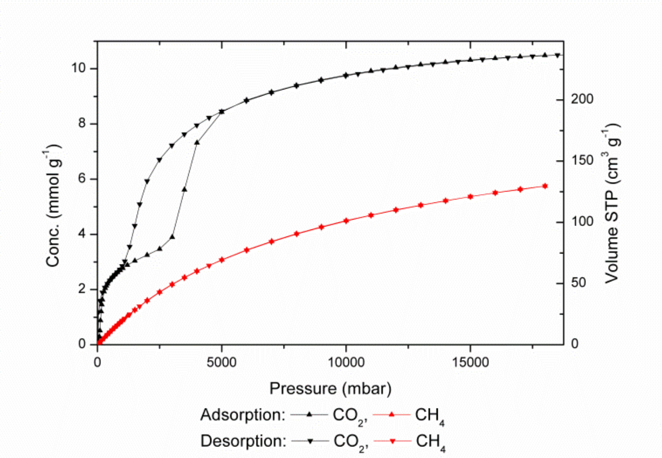

Figure S17 CO_2 and CH_4 isotherms at 10 °C for MIL-53(Al) produced in batch at 250 °C. The higher uptake of CO_2 indicates selectivity for CO_2 over CH_4.

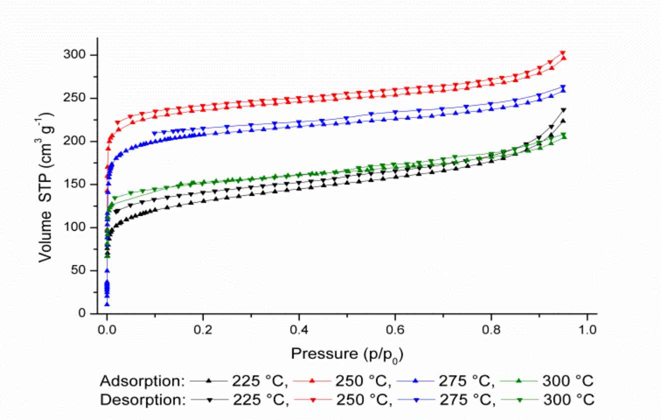

Figure S18 N_2 isotherms at 77 K for products of continuous flow reactions at 225 °C, 250 °C, 275 °C and 300 °C. Prior to gas adsorption scEtOH treatment was used to remove unreacted H_2L^1. Note that the yield of the reaction at 200 °C was too low to produce sufficient material for gas adsorption.

Independent measurements of the surface area and uptake of N_2 for the material produced by scaling up the reaction and for the commercial sample were performed by MCA Services, Unit 1A, Long Barn, North End, Meldreth, Cambs, SG8 6NT, UK. The results show our scale-up sample had a BET surface area of 1010 m^2 g^{-1} and the commercial sample 553 m^2 g^{-1}.

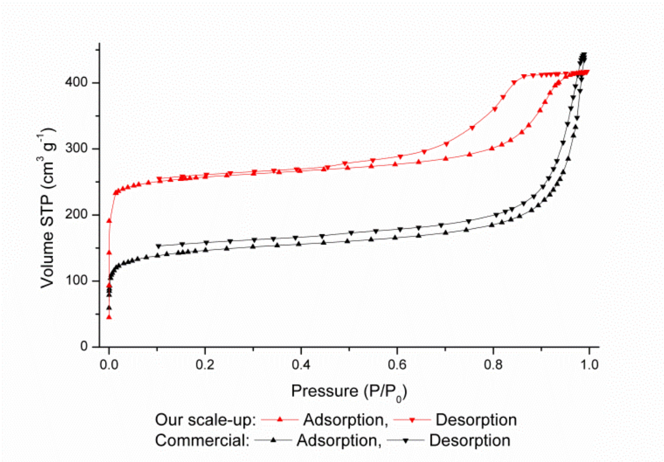

Figure S19 N_2 isotherm at 77K for our scaled-up sample of MIL-53(Al) and for a commercial sample. Uncoordinated H_2L^1 was removed from the scale-up sample by heating at 330 °C for 3 days.

HKUST-1

The synthesis of $[Cu_3(L^2)_2]_n$, HKUST-1, was achieved using the same procedure as with MIL-53(Al) except EtOH was used in place of water. Since both trimesic acid (H_3L^2) and $Cu(NO_3)_2$ are soluble in EtOH the use of ligand salts was not required. Thus, treatment of $Cu(NO_3)_2 \cdot 3H_2O$ (86.2 mg, 0.357 mmol) with H_3L^2 (50.0 mg, 0.238 mmol) in EtOH (5.0 ml) at 200 °C for 10 minutes afforded a material the PXRD of which matches that of HKUST-1 (Figure S16). No free H_3L^2 was recovered with the material and so a further purification step was not necessary. The material produced by continuous process had a surface area of 1554 m^2 g^{-1}, a maximum nitrogen uptake of 416.9 cm^3 g^{-1} (0.95 P/P$_0$), and a pore volume of 0.62 cm^3 g^{-1}. The space time yield of HKUST-1 in this process was 730 kg m^{-3} d^{-1}.

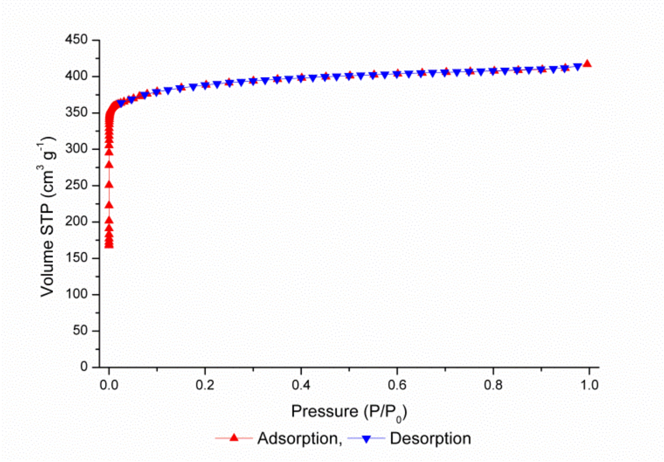

Figure S20 N_2 gas sorption isotherm of HKUST-1 prepared by continuous flow reaction in EtOH at 200 °C.

The TGA for as-synthesised HKUST-1 produced by continuous flow exhibits the expected thermal behaviour with three steps (Figure S21). The first of 11.4% between 20 and 70 °C is the result of loss of EtOH from the pores. The second step of 19.7% between 70 °C and 220 °C is attributed to the loss of coordinated solvents with a total solvent loss of 31.1%. The third step of 30.7% between 295 °C and 450 °C corresponds to decomposition of the material.

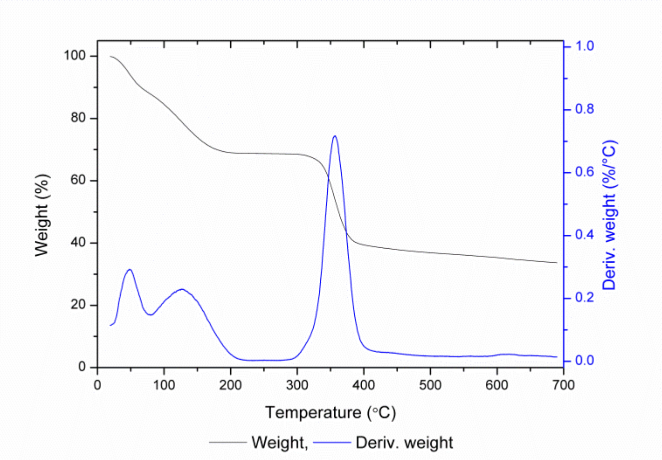

Figure S21 TGA of as-synthesised HKUST-1 prepared by continuous flow (black); the first derivative plot (blue) shows the rate of change of % weight loss with temperature.

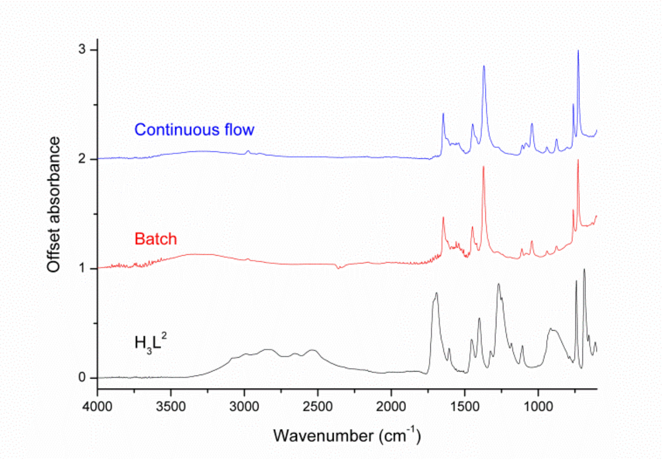

Figure S22 ATR-FTIR of as-synthesised of HKUST-1 *via* batch (red) and continuous flow process (blue) using EtOH at 200 °C, and of trimesic acid H_3L^2 (black).

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