

Experimental Details

Samples were synthesised using the continuous-flow-reactor designed by the Lester group which uses a counter-current mixing reactor to induce rapid reaction and crystallisation of the dissolved precursors.

All chemicals were purchased from Sigma Aldrich and Fisher Scientific and used without further purification.

ZIF-8

A 0.06 M aqueous solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was used in the upflow (room temperature, 10 mL min^{-1}) and a 0.06 M aqueous solution of 2-methylimidazole (2-HMIm) was used in the downflow (room temperature- $400 \text{ }^\circ\text{C}$, 20 mL min^{-1}). To improve the rate of deprotonation of the acid, ammonium hydroxide (NH_4OH) was also added to the organic solution in the ratio 1:8 (HMIm: NH_4OH). Final ratio of reagents is 1:2:16 (Zn: HMIm: NH_4OH).

X-ray Diffraction

Powder X-ray Diffraction (PXRD) was performed on a Bruker D8-Advance diffractometer using Cu K_α radiation, $\lambda = 1.5415 \text{ \AA}$ over a 2θ range of $5 - 40^\circ$.

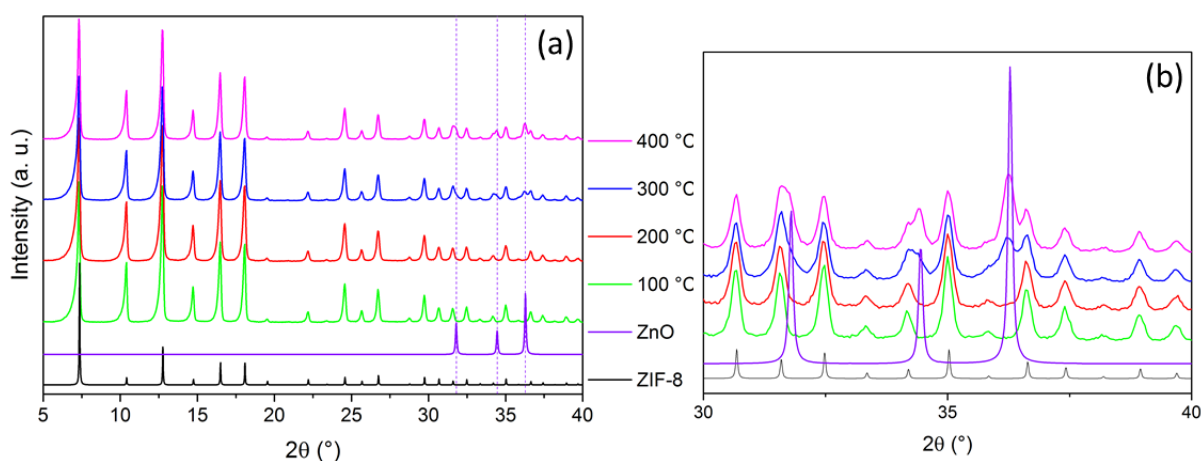


Figure A PXRD patterns for the ZIF-8 products synthesised using $\text{N}(\text{Et})_3$ at RT, 100, 200, 300 and 400 $^\circ\text{C}$. ZnO impurities can be seen in the product produced at 300 and 400 $^\circ\text{C}$. The simulated patterns for ZIF-8 and ZnO are shown in black and purple respectively.

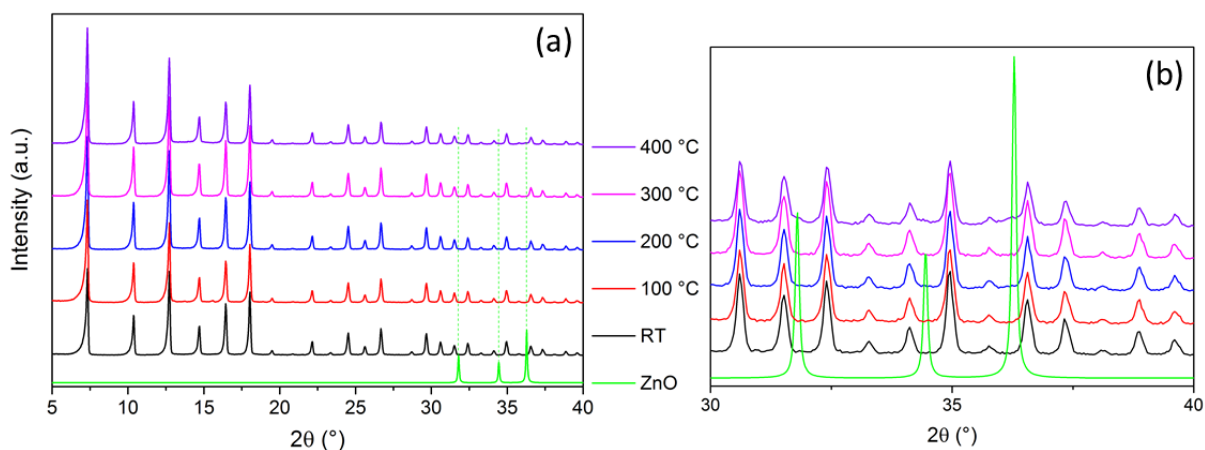


Figure B PXR D patterns for the ZIF-8 products synthesised using NH_4OH at RT, 100, 200, 300 and 400 °C. ZnO impurities can be seen in the product produced at 400 °C. The simulated patterns for ZIF-8 and ZnO are shown in black and green respectively.

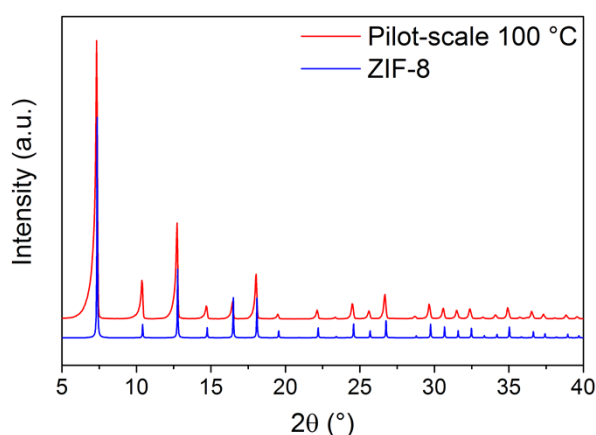


Figure C PXR D pattern for ZIF-8 synthesised at 100 °C, 0.06 M using the pilot-scale reactor. The simulated pattern for ZIF-8 is shown in blue.

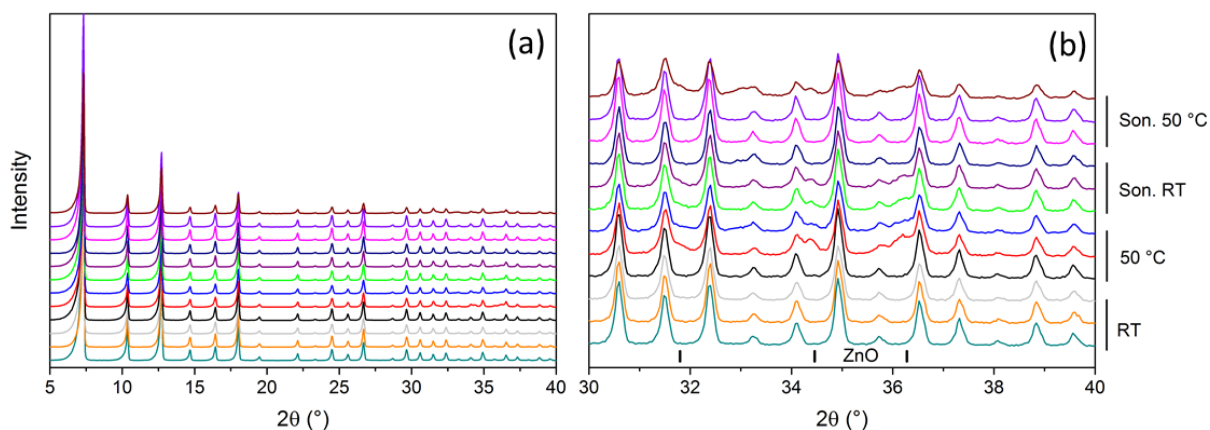


Figure D PXR D patterns for the ZIF-8 activated using the coil reactor. Sample method for activation, in ascending order, room temperature and dilutions of 1:1, 1:2 and 1:3, using a water bath at 50 °C and dilutions of 1:1, 1:2 and 1:3, sonicated water bath at room temperature and dilutions of 1:1, 1:2 and 1:3 and a sonicated water bath at 50 °C and dilutions of 1:1, 1:2 and 1:3. Synthesis conditions- Zn^{2+} 0.06 M, reagent ratio 1:2:16 (zinc acetate: 2-methylimidazole: ammonium hydroxide), 100 °C.

Thermogravimetric Analysis

Thermogravimetry data was recorded using a Q500 TA instruments thermogravimetric analyser. All material profiles were recorded between room temperature and 800 °C in air.

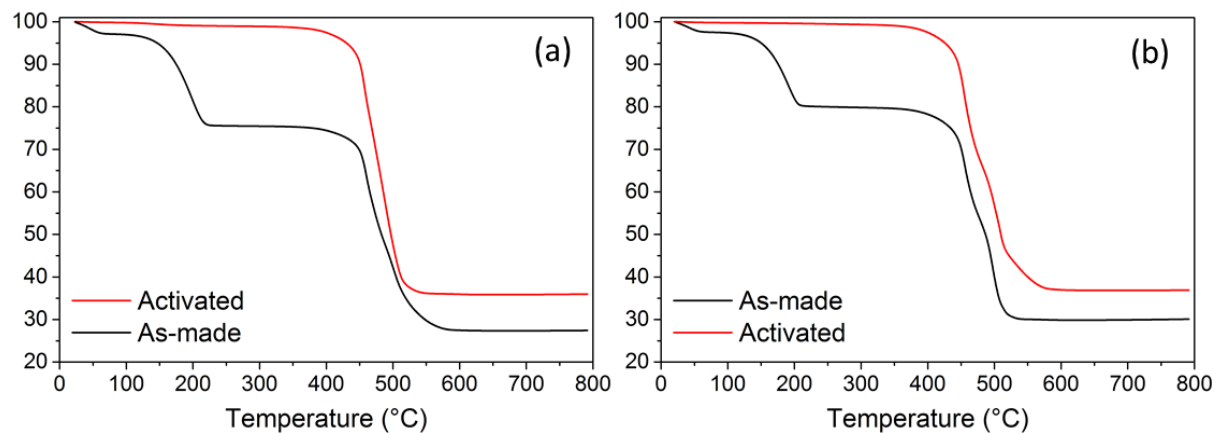


Figure E Thermogravimetric analysis of the as-made and activated products from the room temperature (a) and 400 °C (b) experiments.

Surface Area Analysis

Nitrogen isotherms were recorded using a Micromeritics Tristar II 3020 surface area analyser. Partial pressure range was 0.01 – 0.99. The Microactive software, which uses the Rouquerol method, was used for determining the BET range for each dataset independently.

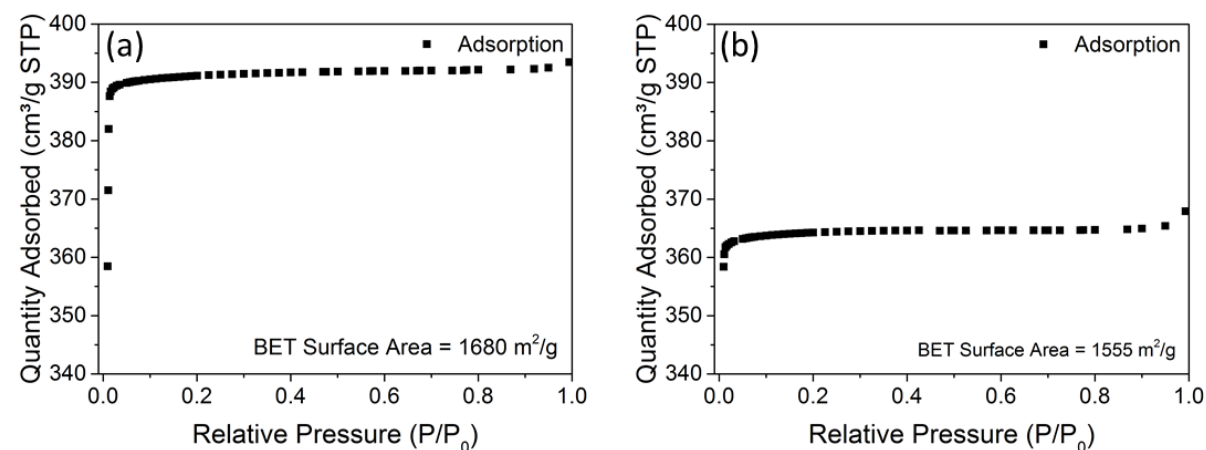


Figure F Nitrogen adsorption isotherms for the products produced at room temperature (a) and 400 °C (b). BET surface areas for each product are given.

Table A synthesis conditions and corresponding surface areas for various ZIF-8 materials. All products were synthesised with the reagent ratio of 1:2:16 (Zn²⁺:HMIm:NH₄OH). [†]Bench batch-reaction performed for comparison, [§] reagent ratio was 1:4:16, * pilot-scale reactor used for synthesis, a = reaction was performed under autogenous pressure created internally within the equipment.

Synthesis Conditions				Characterisation
Temperature (°C)	Pressure (bar)	Zn ²⁺ concentration (M)	Product	BET Surface Area (m ² g ⁻¹)
[†] RT	(Bench)	0.06	ZIF-8	1654
RT	a	0.06	ZIF-8	1713
RT	240	0.06	ZIF-8	1680
100	a	0.06	ZIF-8	1806
100	240	0.06	ZIF-8	1741
100	240	0.24	Unknown impurity	938
100	240	0.015	ZIF-8	1805
400	240	0.06	ZIF-8	1555
[§] 100	a	0.24	ZIF-8	1741
*100	a	0.06	ZIF-8	1780

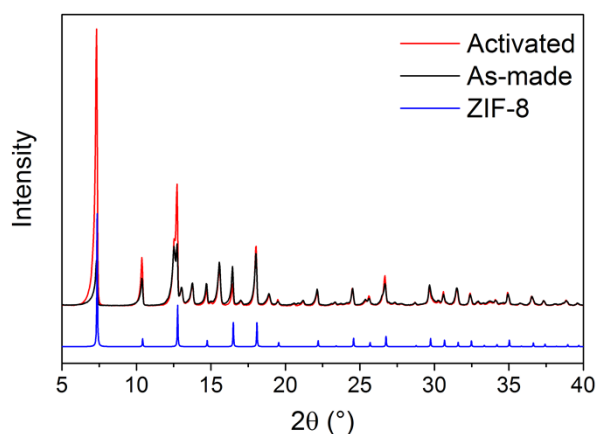


Figure G PXRD pattern of ZIF-8 before and after activation, synthesised at 100 °C and 0.24 M (Zn²⁺), showing the presence of an unidentified impurity phase. The simulated pattern for ZIF-8 is shown in blue.

Space-Time Yield

Space-time yields were calculated based on the highest concentration reactions (Zn²⁺ = 0.24 M) using the product concentration and the total internal volume of the reactor.

$$\sigma_p = \frac{m_p}{Vt}$$

Metal salt concentration = 0.24 M

units

Internal reactor volume (total pressurised pipework) 0.000055 m⁻³

	Total flow rate	30	mL min ⁻¹
	Product concentration	0.0148	kg L ⁻¹
	Production rate (per hr)	0.027	kg hr ⁻¹
(σ_p)	Production rate (per day [8 hours])	0.213	kg d ⁻¹
	Space-time yield (total pressurised pipework)	3874.9	kg m⁻³ d⁻¹