

Towards MOFs' commoditisation: MOF Technologies' efficient and versatile one-step extrusion of shaped MOFs directly from raw materials.

José Casaban,^{*a} Yuancheng Zhang,^a Raul Pacheco,^a Ciaran Coney,^a Catherine Holmes,^a Emmajay Sutherland,^a Conor Hamill,^a John Breen,^a Stuart L. James,^{a,b} Diego Tufano,^a Dennis Wong,^a Efstratios Stavrakakis,^a Hamza Annath^{a,b} and Ashleigh Moore.^a

^a MOF Technologies Ltd, 63 University Road, Belfast, BT7 1NF, United Kingdom.

Email: j.casaban@moftechnologies.com

General Aspects

Extrusion

Twin screw extrusion (TSE) was carried out using either a Thermo Fisher Process 11 mm Parallel co-rotating twin screw extruder, a Three-Tec 12 mm co-rotating twin screw extruder or a Berstoff ZE25R 25 mm co-rotating twin screw extruder.

N₂ isotherms measurement

In-situ activation of MOFs prior to BrunauerEmmett-Teller (BET) analysis involved heating at 200°C under vacuum overnight. N₂ adsorption isotherms were obtained at 77K between relative pressures (p/p_0) of 0.005 to 0.995, using a Belsorp Mini II.

Determination of Bulk Crush strength of MOF pellets

The Tensile strength (crushing strength) of pellets were analysed using a Texture Analyser (TAXT2i model, Stable Micro Systems, UK) fitted with a 5 kg load cell and the cylindrical probe with a flat surface of 3.5 cm in diameter. The distance of the probe from the platform where the single pellet was mounted to apply the force was set at 100 mm. 30 to 35 pellet samples with an average length of 3mm were tested individually. The probe and the force were calibrated prior to measurement and test was conducted at ambient laboratory condition. The distance of the probe to move apart was set at 100 mm. Following settings were used for measuring the maximum force in Newton at which the pellets get crushed or cracked: Measure force in tension (analysing mode); Return to start (option); 3.0 mm/s (pre-test speed); 3.0 mm/s (test speed); 5mm/s (post-test speed); 100mm (probe moving distance).

PXRD analysis

XRD measurements were carried out on a PANanalytical Aeris diffractometer. Copper was used as the Xray source with a wavelength of 1.5405 Å. All experiments were carried out ex-situ using a spinning stage. Diffractograms were typically obtained from 5–50° with a step size of 0.0167°.

TGA analysis

TGA measurements were carried out on a TG 209 F3 Tarsus thermogravimetric analyser. Samples were heated up 750 °C at a rate of 5 °C/min under an air flow of 30 mL/min.

Synthesis of HKUST-1 (Cu₃(BTC)₂) 2 mm pellets at 12.2 kg/h

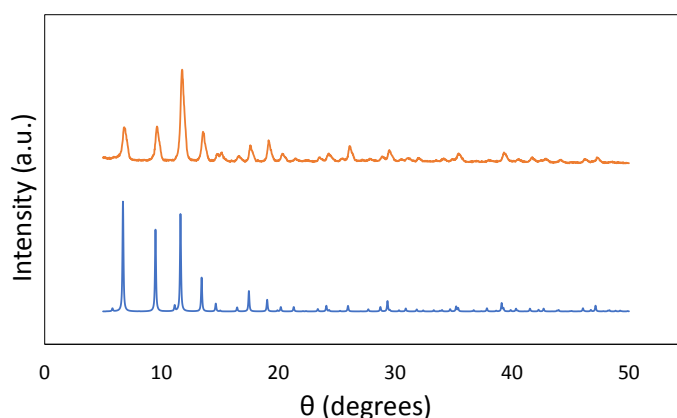


Figure S1. PXRD patterns for Cu₃(BTC)₂ (HKUST-1) 2 mm pellets synthesised by TSE and the simulated PXRD pattern for HKUST-1 (CSD code FIQCEN).

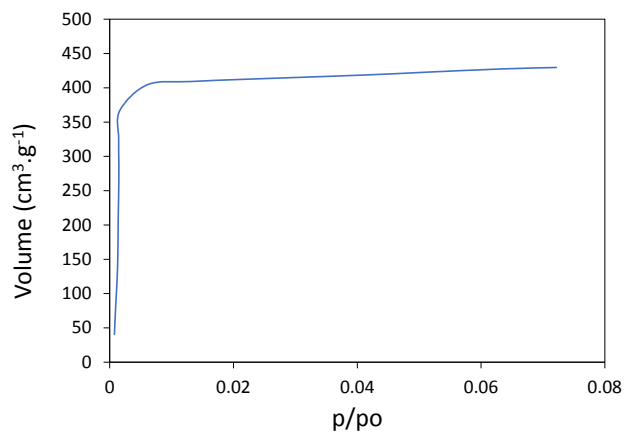


Figure S2. N₂ adsorption isotherm at 77K for Cu₃(BTC)₂ (HKUST-1) 2 mm pellets synthesised by TSE.

TGA analysis of MOF shaped samples

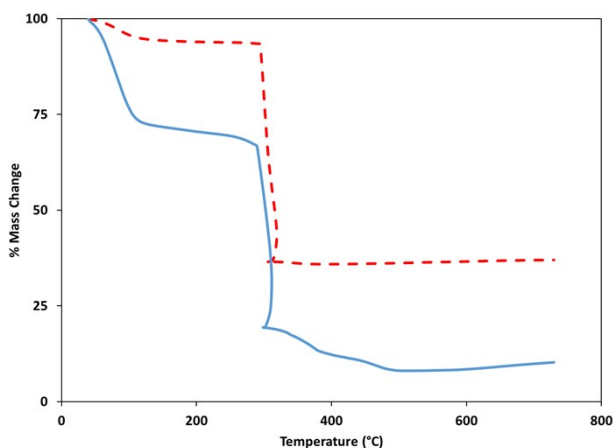


Figure S3. TG curves of (—) Cu₃(BTC)₂ pellets prepared by traditional extrusion of Cu₃(BTC)₂ powder in the presence of polyvinyl butyral (*Sample-A*) and (---) Cu₃(BTC)₂ powder prepared by a conventional multistep approach.

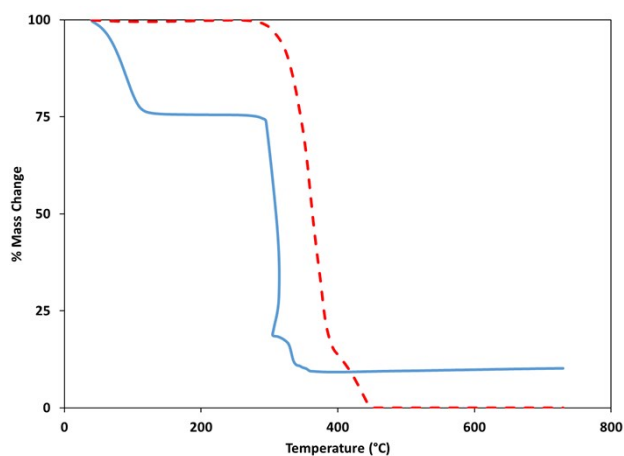


Figure S4. TG curves of (—) Cu₃(BTC)₂ pellets prepared by MOF Technologies binderless TSE process (*Sample-B*) and (---) trimesic acid.

Dynamic Breakthrough Performance Evaluation

Dynamic gas breakthrough performance tests were conducted using a bespoke continuous gas flow adsorption test rig. All tests were performed at $25\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ using a split tubular Carbolite Gero to maintain a constant MOF bed temperature during adsorption studies. A fixed volume of adsorbent pellets were loaded into a specially designed stainless steel container, in which dead volume was minimised. A type K thermocouple was positioned in a radially centred location at the entrance of the MOF powder bed to verify internal temperature.

All gases were sourced from BOC Ltd. and certified to $\pm 2\%$ of reported concentration values 5 v/v% Ne/N₂ (CP grade), 3.6 v/v% CO₂/N₂ (CP grade), 100 v/v% O₂ (N5.0) and 100 v/v% N₂ oxygen-free. Dry gas supply was controlled via a series of Bronkhorst EL-FLOW Select mass flow controllers, operating with an accuracy of $\pm 0.5\%$ reading plus $\pm 0.1\%$ full scale. Humidity control was achieved by passing a precisely metered flow of N₂ gas through a temperature-controlled saturator $\pm 0.1\text{ }^{\circ}\text{C}$. Dry and humid gas supplies were subsequently combined prior to entering the gas adsorption container, ensuring all gas lines were maintained at temperatures greater than H₂O dew point at 45 %RH.

Prior to each test, samples were activated at temperatures of $150\text{ }^{\circ}\text{C}$ for 10 hours, under N₂ gas flow. Upon cooling to the preselected isothermal adsorption temperature of $25\text{ }^{\circ}\text{C}$, samples were subjected to the challenge gas mixture and end-pipe analysis was performed using a combination of mass spectrometry. The Hiden HPR20 Mass Spectrometry provided continuous sampling of gases and vapours between 0 and 200 amu, with triple filtering resulting in an ultimate sensitivity of 5 ppb. A heated inlet capillary and ionization chamber prevented condensation of low boiling species prior to the detector and a gaseous species detection frequency of 1 Hz permitted one recording to be made every second.

Table S1. Dynamic Breakthrough testing conditions.

Parameters	Starting Input Conditions
Dry bulb Temperature	25 °C
Relative Humidity	45 %
Pressure	101 kPa
Gas Hourly Space Velocity	1500 h ⁻¹
Inlet H ₂ O Concentration	1.46 v/v%
Inlet O ₂ Concentration	21 v/v%
Inlet CO ₂ Concentration	1.3 v/v%

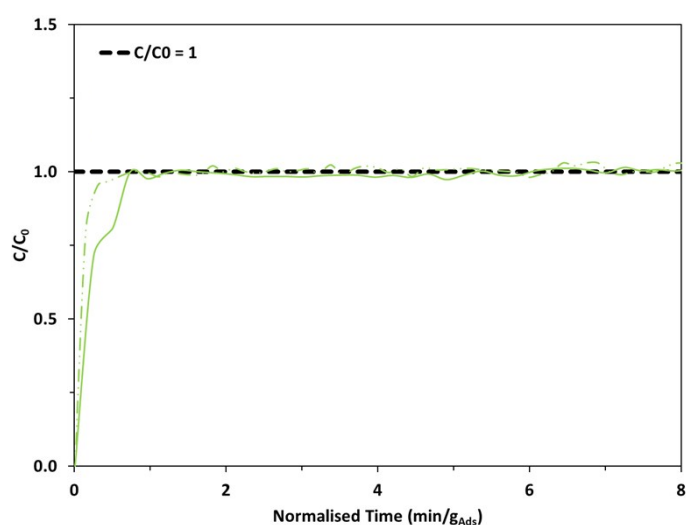


Figure S5. O₂ breakthrough profiles of 1mm Cu₂(BTC)₃ pellets: (—) Sample-A and (.....) Sample-B and as a function of normalised time. Adsorbents subjected to a gas flow of 1 L.min⁻¹ consisting of 1.3 v/v% CO₂, 21 v/v% O₂, 1.46 v/v% H₂O and balance N₂ at a temperature of $25\text{ }^{\circ}\text{C}$ and pressure of 101kPa.

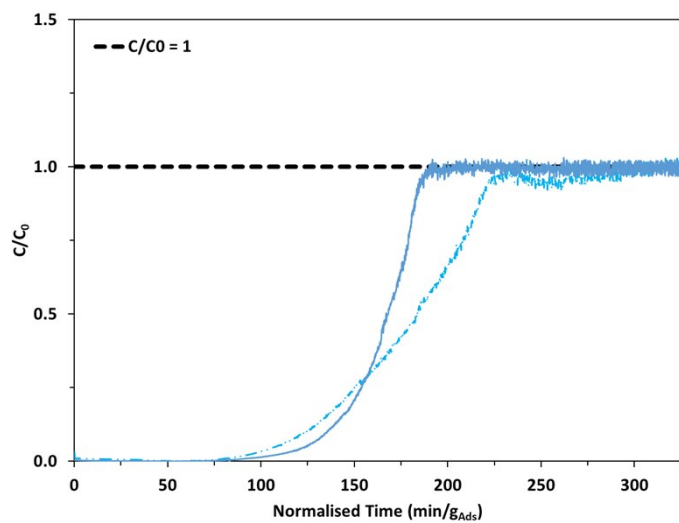


Figure S6. H₂O breakthrough profiles of 1mm Cu₂(BTC)₃ pellets: (—) Sample-A and (---) Sample-B and as a function of normalised time. Adsorbents subjected to a gas flow of 1 L.min⁻¹ consisting of 1.3 v/v% CO₂, 21 v/v% O₂, 1.46 v/v% H₂O and balance N₂ at a temperature of 25 °C and pressure of 101kPa.