Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

MOF-based heterogeneous catalysis in continuous flow via. incorporation onto polymer based spherical activated carbon supports

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Contents

1.1 Flow setup

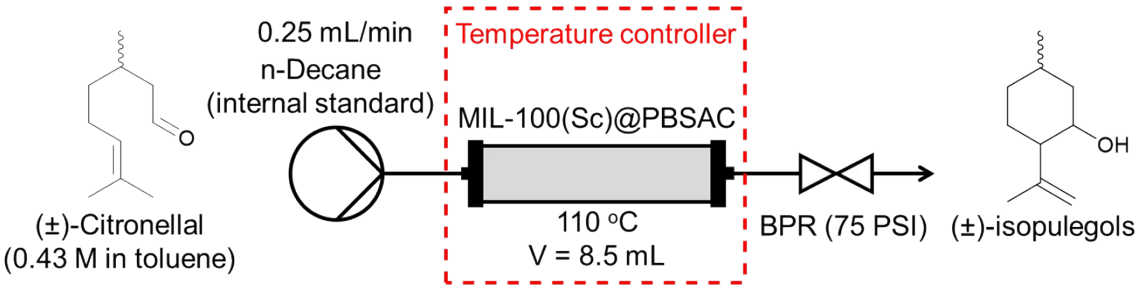

Figure SI 1: Flow setup used in this work.

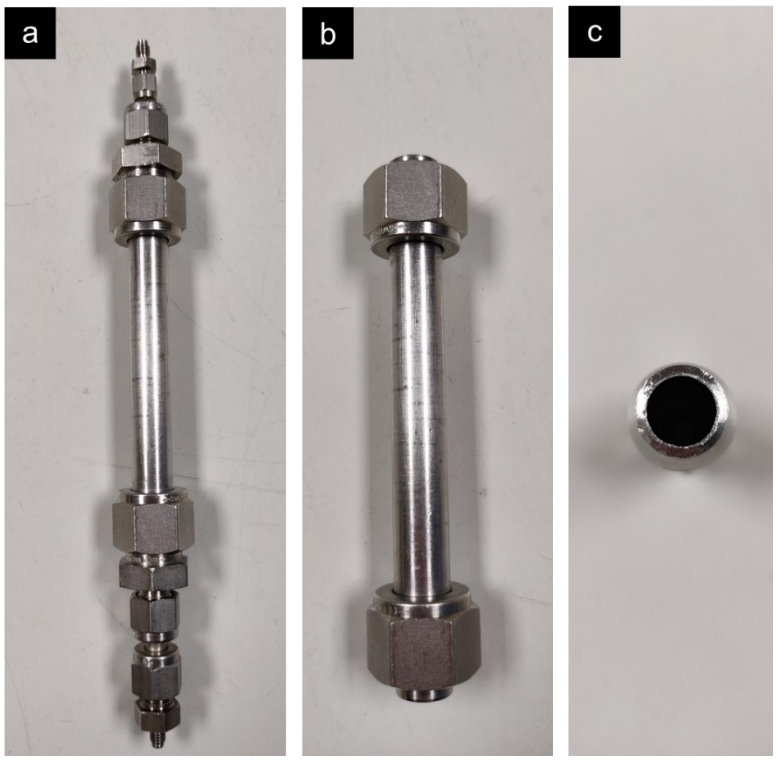

Figure SI 2: a) Packed-bed reactor used in this work with adapters connected. b) Packed-bed reactor used in this work without adapters connected. c) Top-view of packed-bed reactor used in this work.

1.2 Gas chromatography analysis

Table 1: GC method used for off-line experiment analysis

Column	DB-624 (Length: 30 m, Diameter: 0.25 m, Film Thickness: 1.40 µm)
Injection Volume	1 µL
Inlet Temperature	250 °C
Detector Temperature	300 °C
Split Ratio	25:1
Detection	FID

Table 2: Temperature program used for off-line GC chromatography.

Oven	**Rate (°C/min)**	**Value (°C)**	**Hold Time (mins)**	**Run Time (mins)**
Initial		40	1	1
Ramp 1	25	180	1	7.6
Ramp 2	2.5	190	1	12.6
Ramp 3	20	200	0	13.1

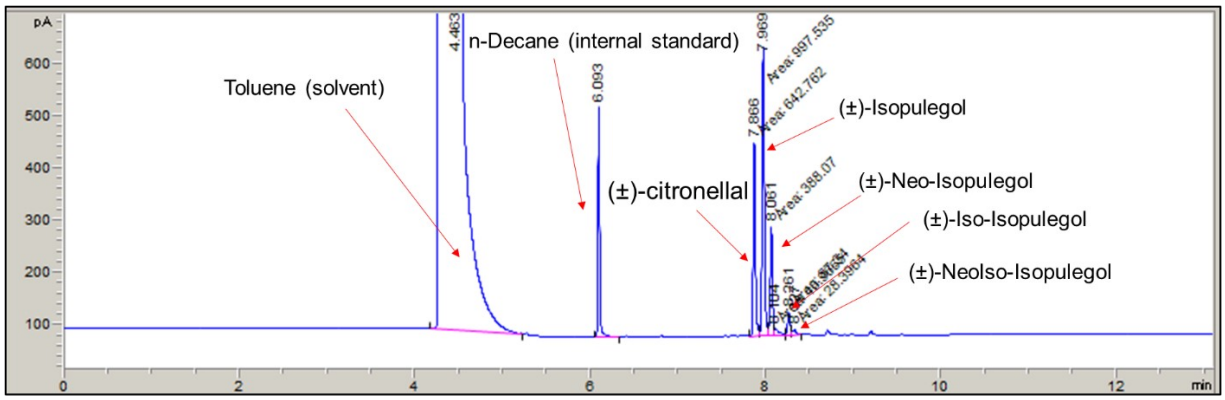

Figure SI 3: Example of typical GC chromatogram obtained in this work, the figure above was obtained after five hours.

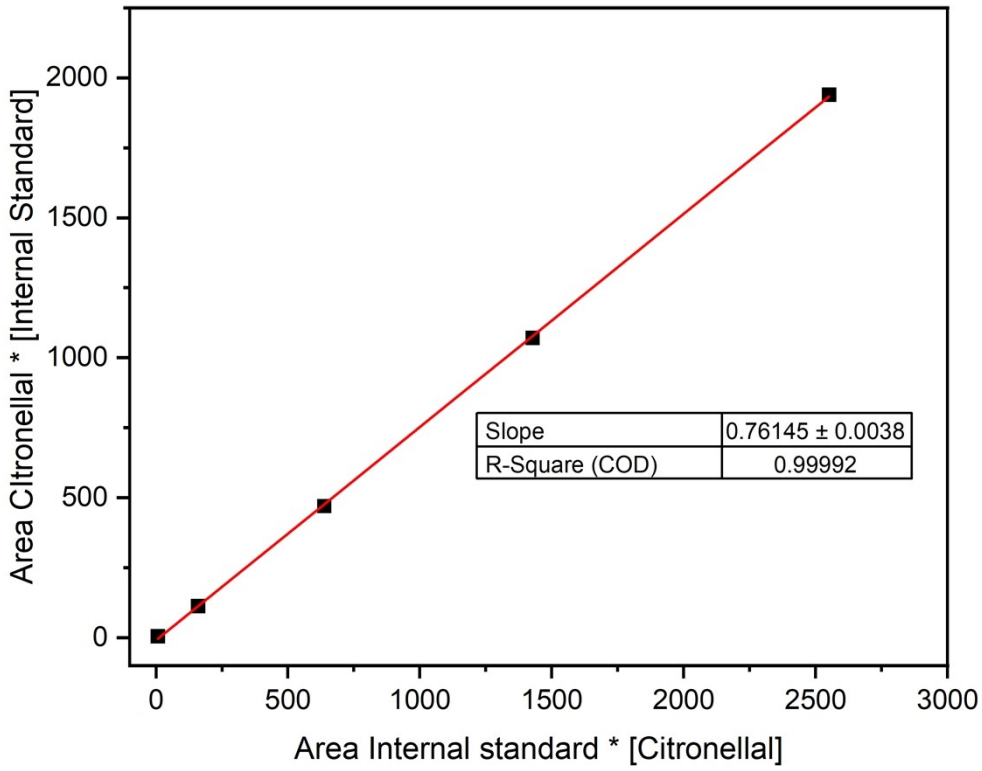

Figure SI 4: Calibration curve of (±)-citronellal and response factor (slope).

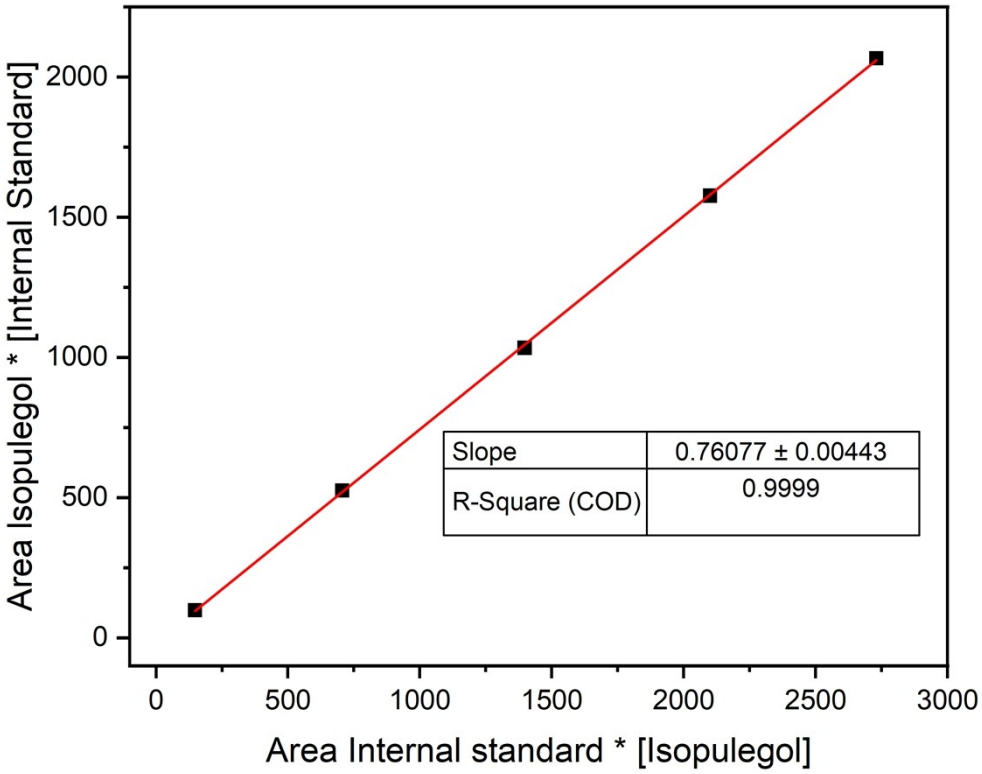

Figure SI 5: Calibration curve of Isopulegol and response factor (slope).

1.3 TGA profiles of PBSAC-trimesic acid control and trimesic acid

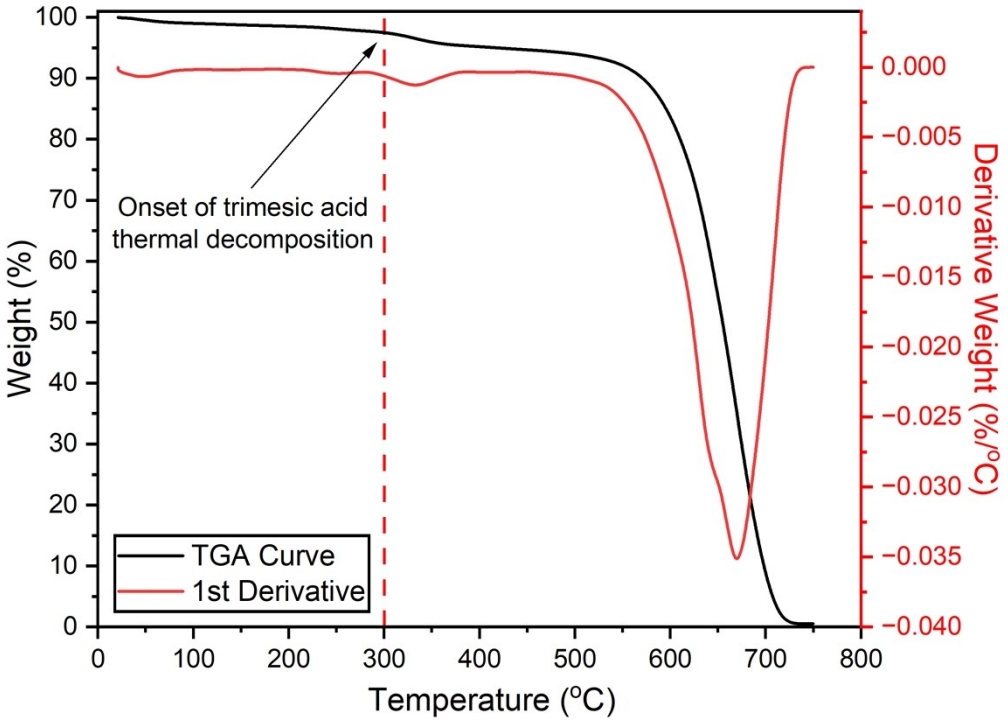

Figure SI 6: TGA profile of PBSAC-trimesic acid control sample. There is a small weight loss beginning at approximately 300 °C corresponding to the thermal decomposition of adsorbed trimesic acid.

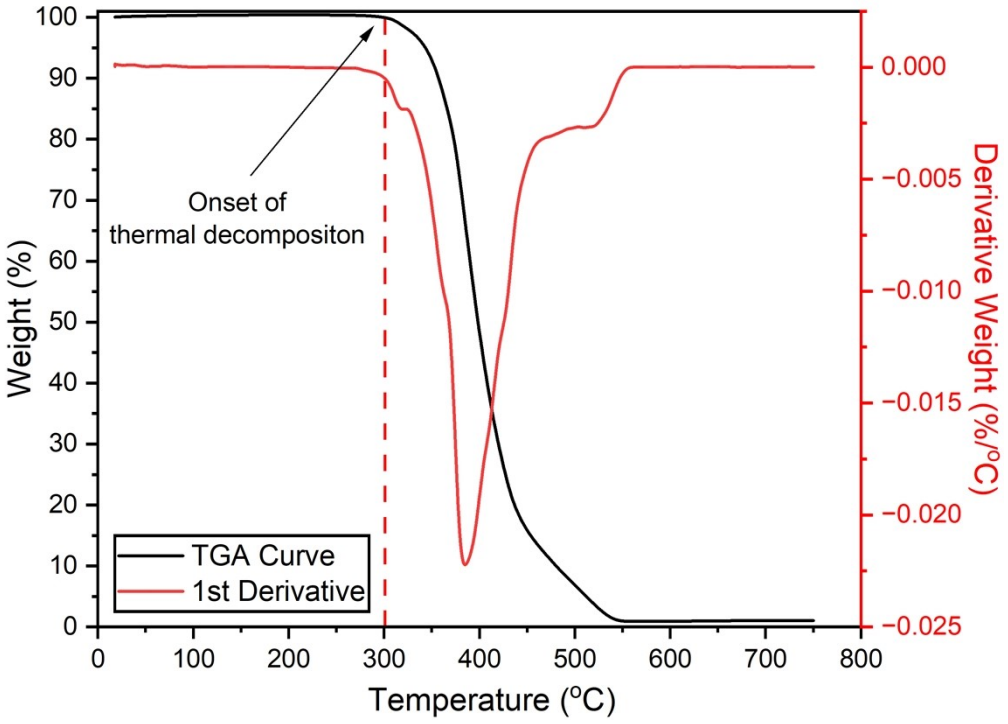

Figure SI 7: TGA profile of trimesic acid. Thermal decomposition begins to occur at approximately 300 °C.

1.4 PXRD pattern of loose powdered MIL-100(Sc) formed during MIL-100(Sc)@PBSAC synthesis

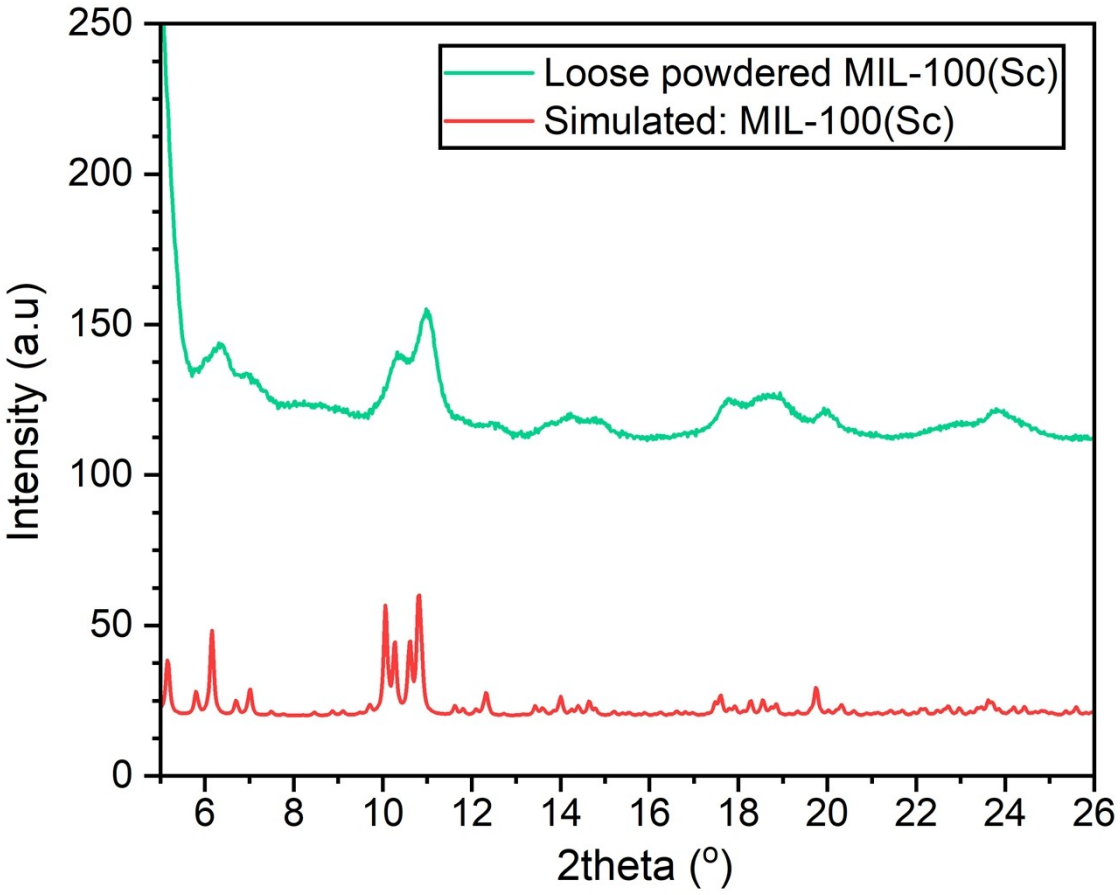

Figure SI 8: PXRD pattern of loose powdered MIL-100(Sc) (green) that was formed in the reaction vessel during MIL-100(Sc)@PBSAC synthesis compared with the simulated pattern of MIL-100(Sc). The data was acquired on a D2 Phaser (Bruker).

1.5 SEM-EDX images of unfunctionalised PBSAC spheres

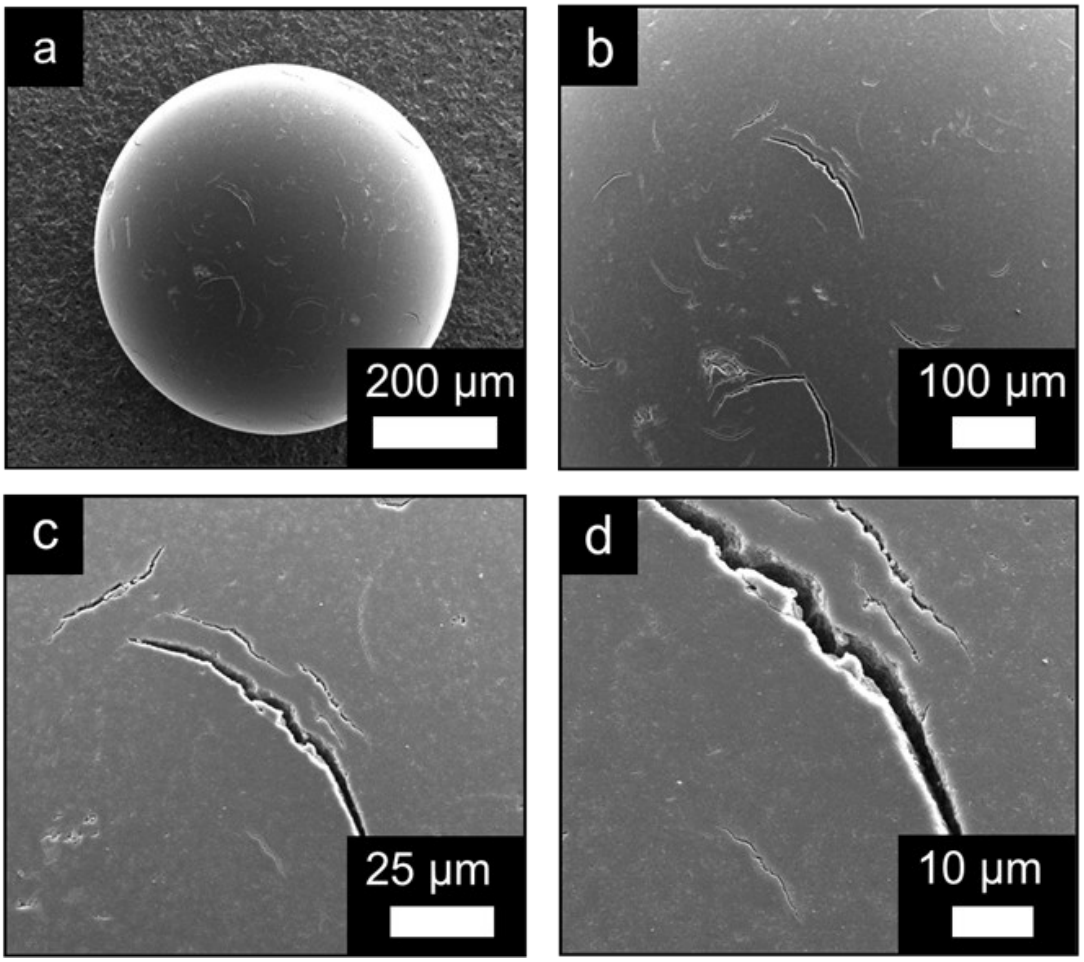

Figure SI 9: SEM images of a PBSAC bead showing; a) the whole bead and (b-d) a crack located on surface of a PBSAC bead (all images, detector: ETD, mode: SE).

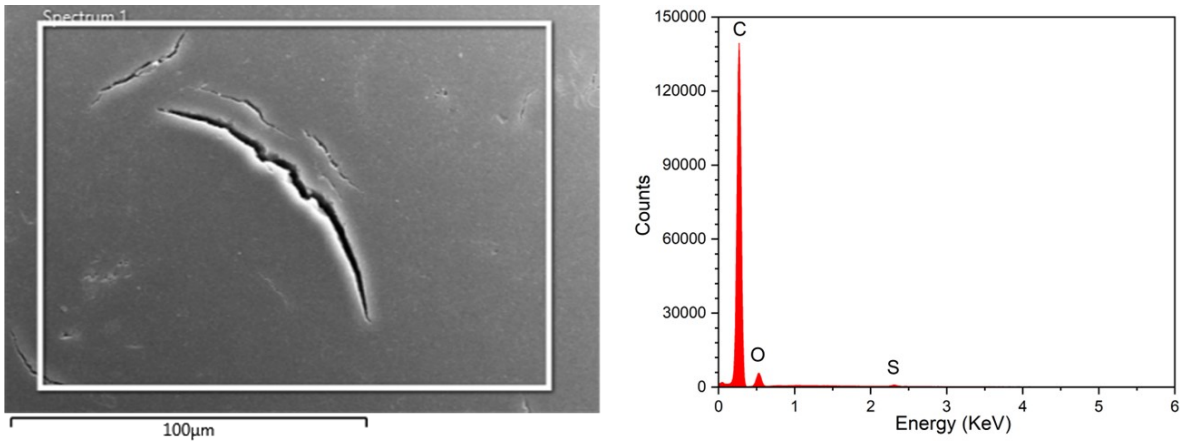

Figure SI 10: Left: Region of PBSAC sphere where EDX spectra was obtained. Right: Resultant EDX spectra, unfunctionalised PBSAC spheres contain carbon, oxygen and small amounts of sulphur (which may be attributed to the presence of residues from the initial polymer bead synthesis).

1.6 SEM-EDX of MIL-100(Sc)@PBSAC composites

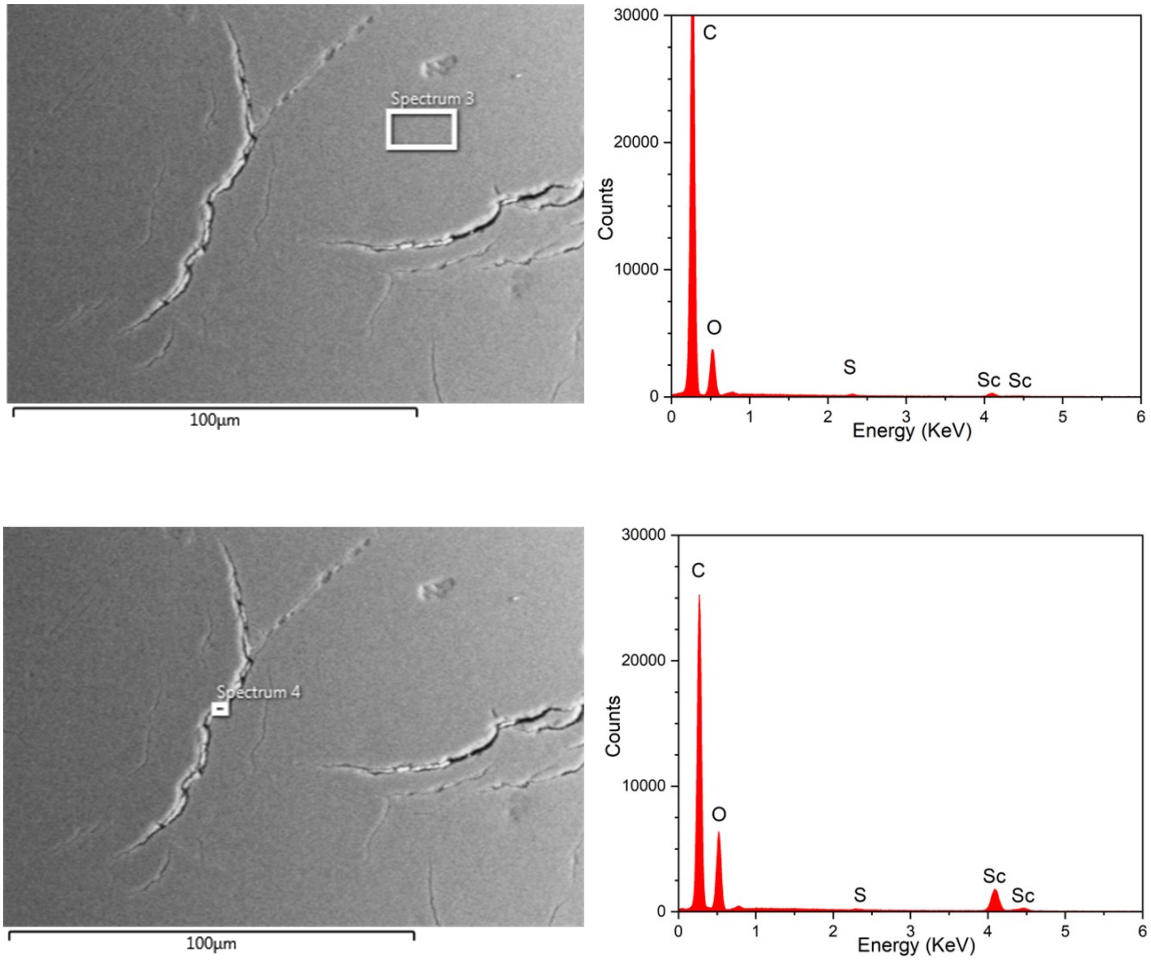

Figure SI 11: Left: SEM image of a MIL-100(Sc)@PBSAC sphere with the region where EDX spectra was obtained highlighted. Right: Resultant EDX spectra.

1.7 Calculation of MIL-100(Sc) stoichiometry and loading onto PBSAC spheres by TGA

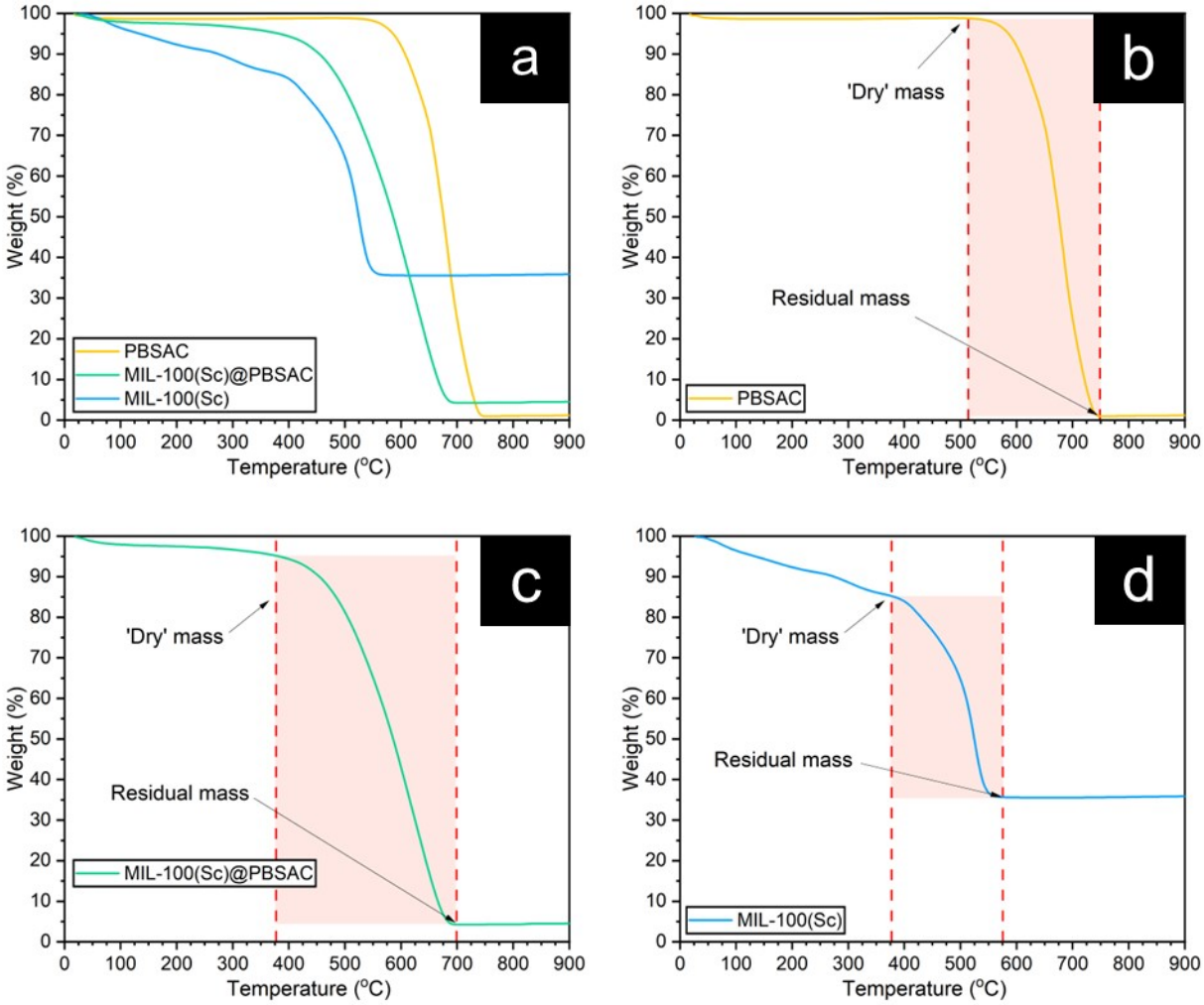

Figure SI 12: a) TGA profiles of PBSAC spheres (yellow), MIL-100(Sc)@PBSAC (green) and MIL-100(Sc) (blue). b) TGA profile of PBSAC spheres showing the dry mass (≈515 °C) and residual mass following frameowrk decomposition at ≈740 °C. c) TGA profile of MIL-100(Sc)@PBSAC showing the dry mass (≈380 °C) and residual mass following frameowrk decomposition at ≈700 °C. d) TGA profile of MIL-100(Sc) showing the dry mass (≈380 °C) and residual mass following frameowrk decomposition at ≈580 °C.

1.7.1 Calculation of MIL-100(Sc) stoichiometry

In the TGA profile of powdered, reflux prepared MIL-100(Sc) (Figure 8 c), the residual mass (e.g. following framework decomposition at 700 °C) corresponds to Sc_2O_3 and thus allows for determination of the stoichiometry of this framework. By mass, scandium oxide (Sc_2O_3) is 65.2 % scandium, thus of the 3.61 mg residual mass in an experiment involving 10.17 mg MIL-100(Sc), 2.35 mg was scandium (Equation 1).

$$Mass\ of\ scandium\ in\ MIL-100\ (Sc)\ (mg) = \frac{3.61\ mg}{100} \times 65.2 = 2.35\ mg \qquad \text{(Equation 1)}$$

The residual mass as a percentage of the 'dry' mass (i.e. the mass following solvent removal but before structure thermal decomposition, e.g. at ≈ 380 °C in the TGA profile of MIL-100(Sc), Figure 8 c) was calculated according to equation 2.

$$Residual\ mass\ (\%) = \frac{mass\ present\ following\ material\ decomposition\ (mg)}{'Dry'\ mass\ (mg)} \times 100$$

(Equation 2)

For an experiment involving 10.17 mg MIL-100(Sc), with a 'dry' mass of 8.65 mg (at 380 °C) (Figure 8 c), the residual mass of MIL-100(Sc) was 3.61 mg and so the amount of scandium present was 2.35 mg. Thus, the powdered MIL-100(Sc) was 27.2 % scandium by weight (Equation 3).

$$Residual\ mass\ of\ powdered\ MIL-100(Sc)(\%) = \frac{2.35\ mg}{8.65\ mg} = 27.2\% \quad \text{(Equation 3)}$$

The literature reported formula of MIL-100(Sc) is $[Sc_3O(BTC)_2X]$ (where X = singly charged anion required to balance charge, assumed to be hydroxide (OH^-)) which has a scandium weight percentage of 23.2% w/w, below the calculated value of 27.2% w/w for powdered MIL-100(Sc) in this work. Due to this difference in value, a new stoichiometry of MIL-100(Sc) was calculated, ensuring a neutral framework by balancing the charge with the relevant number of hydroxide (OH^-) ions. A formula of $[Sc_3O(BTC)_{1.45}(OH)_{2.65}]$ was calculated and thus was also used for the determination of MIL-100(Sc) loading onto PBSAC spheres.

Table 3: Previously reported formula of MIL-100(Sc) and stoichiometry that was calculated in this work.

Formula	Scandium % w/w
$[Sc_3O(BTC)_2(OH)]$ (reported formula)	23.2
$[Sc_3O(BTC)_{1.45}(OH)_{2.65}]$	27.2

1.7.2 Calculation of MIL-100(Sc) loading onto PBSAC spheres

For MIL-100(Sc)@PBSAC composites (Figure 8 c) and PBSAC spheres (Figure 8 b), an average residual mass of 4.05 ± 0.80 % and 1.37 ± 0.40 % and was determined respectively (calculated using Equation 2). The residual mass of PBSAC was subtracted from the residual mass of MIL-100(Sc)@PBSAC composites which gave the amount of Sc_2O_3 present in MIL-100(Sc)@PBSAC composite samples following framework decomposition. This value was then used to calculate the loading of scandium on PBSAC spheres (Equation 4).

$$Sc\ loading\ (\%\ w/w) = \frac{Resid.\ mass\ MIL-100(Sc)@PBSAC(\%) - Resid.\ mass\ PBSAC(\%)}{100} \times 65.2$$

(Equation 4)

$$Sc\ loading\ (\%\ w/w) = \frac{4.05\ (\%) - 1.37(\%)}{100} \times 65.2 = 1.75\%\ w/w \pm 0.52\%\ w/w$$ (Equation 5)

The MIL-100(Sc) loading was calculated assuming that the framework had the stoichiometry $[Sc_3O(BTC)_{1.45}(OH)_{2.65}]$ (as determined in section 1.7.1) with a 27.2 % w/w scandium loading. The loading of MIL-100(Sc) onto PBSAC spheres was calculated to be 6.42% w/w ± 1.93%.

$$MIL-100(Sc)\ loading\ \left(\%\frac{w}{w}\right) = \frac{1.75}{\left(\frac{27.2}{100}\right)} = 6.42\ \%\ w/w\ \pm 1.93\%\ w/w$$ (Equation 6)

1.8 TGA derivative weight loss plot

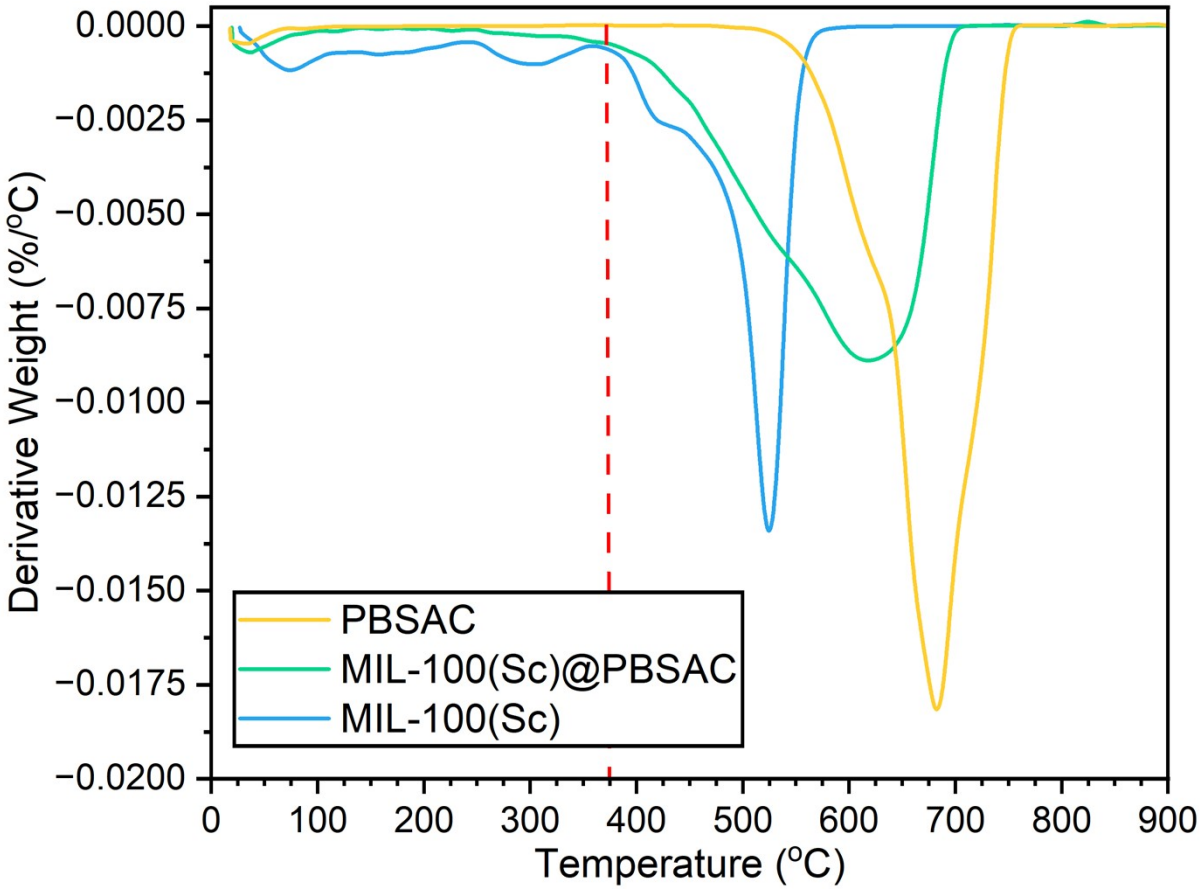

Figure SI 13: TGA derivative weight loss plot for PBSAC, MIL-100(Sc)@PBSAC and MIL-100(Sc). Material decomposition begins at a similar temperature (≈380 °C).

1.9 Volume size distribution of PBSAC spheres

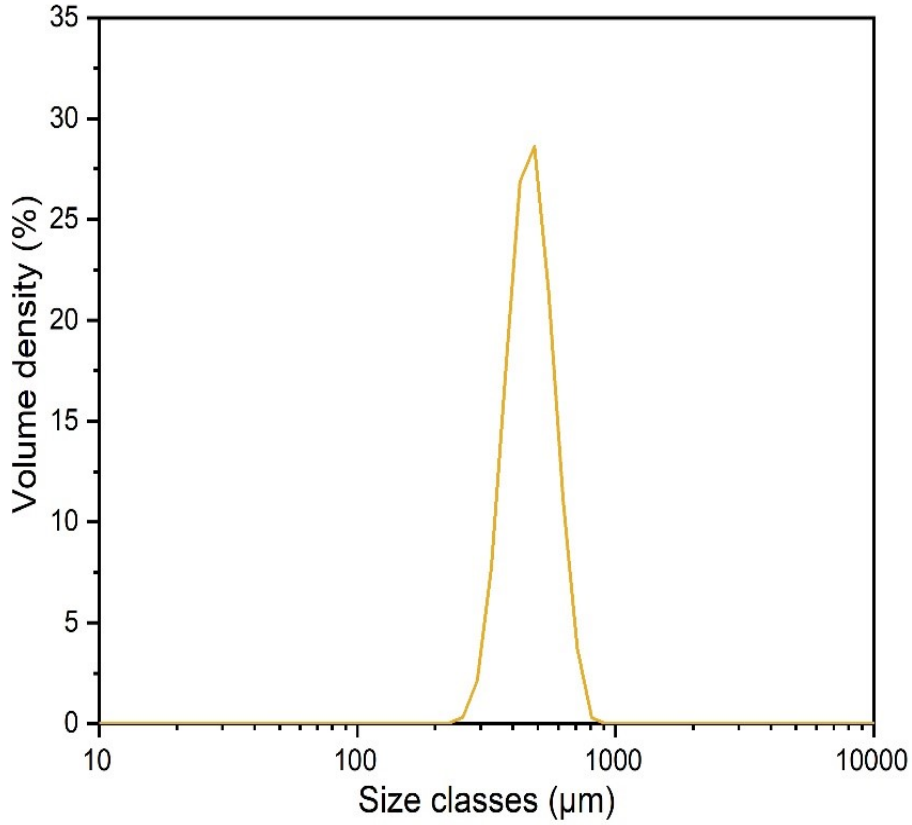

Figure SI 14: Volume distribution of PBSAC spheres obtained from Mastersizer 3000 laser diffraction analysis.

2.0 Calculation of reaction metrics

$$Convrerison\ (\%) = \frac{[(\pm) - Citronellal]_0\ (M) - [(\pm) - Citronellal]_t (M)}{[(\pm) - Citronellal]_0\ (M)} \times 100$$

$[(\pm) - Citronellal]_0 = (\pm) - Citronellal\ concentration\ at\ start\ of\ reaction$

$[(\pm) - Citronellal]_t = (\pm) - Citronellal\ concentration\ at\ a\ given\ time\ t$

$$Yield\ (\%) = \frac{[(\pm) - Isopulegols]_t\ (M)}{[(\pm) - Citronellal]_0\ (M)} \times 100$$

$[(\pm) - Isopulegols]_t = (\pm) - Isopulegols\ concentration\ at\ a\ given\ time\ t$

$[(\pm) - Citronellal]_0 = (\pm) - Citronellal\ concentration\ at\ start\ of\ reaction$

$$Selectivity\ to\ isopulegols\ (\%) = \frac{[(\pm) - Isopulegols]_t\ (M)}{[(\pm) - Citronellal]_0\ (M) - [(\pm) - Citronellal]_t (M)} \times 100$$

$[(\pm) - Isopulegols]_t = (\pm) - Isopulegols\ concentration\ at\ a\ given\ time\ t$

$[(\pm) - Citronellal]_0 = (\pm) - Citronellal\ concentration\ at\ start\ of\ reaction$

$[(\pm) - Citronellal]_t = (\pm) - Citronellal\ concentration\ at\ given\ time\ t$

$$Selectivity\ to\ isopulegol\ (\%) = \frac{[(\pm) - Isopulegol]_t}{[(\pm) - Isopulegols]_t} \times 100$$

$[(\pm) - Isopulegol]_t = (\pm) - Isopulegol\ concentration\ at\ a\ given\ time\ t$

$[(\pm) - Isopulegols]_t = (\pm) - Isopulegols\ concentration\ at\ a\ given\ time\ t$

$$Turnover\ number\ (TON) = \frac{moles\ of\ (\pm) - Isopulegols\ produced\ after\ x\ time}{moles\ of\ scandium\ used\ for\ reaction}$$

$$Turnover\ Frequency\ (TOF)\ (hr^{-1}) = \frac{TON}{time\ (hr)}$$

$$Productivity\left(g\ hr^{-1}\right) = \frac{mass\ of\ (\pm) - Isopulegols\ produced\ after\ 1\ hour\ (g)}{time\ (hr)}$$

$$Activity\left(mmol\ {g_{cat}}^{-1} hr^{-1}\right) = \frac{Average\ amount\ of\ (\pm) - citronellal\ converted\ (mmol)}{hour - on - stream\ (hr) \times gram\ of\ catalyst\ (g_{cat})}$$

2.1 Characterisation of MIL-100(Sc)@PBSAC after 26 hours on stream

2.1.1 Atomic absorption spectroscopy (AAS)

Table 4: Atomic absorption spectroscopy (AAS) data of fresh and used (26 hours time-on-stream) catalyst. A average 10.6 % loss of scandium was measured to have leached over the course of the reaction.

Scandium loading – fresh catalyst sample (% w/w)	Scandium loading – Used catalyst samples (26 hours time-on-stream) (% w/w)	% loss of scandium over course of reaction
1.68 ± 0.02	1.50 ± 0.03	7.5 – 13.6

2.1.2 Scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX)

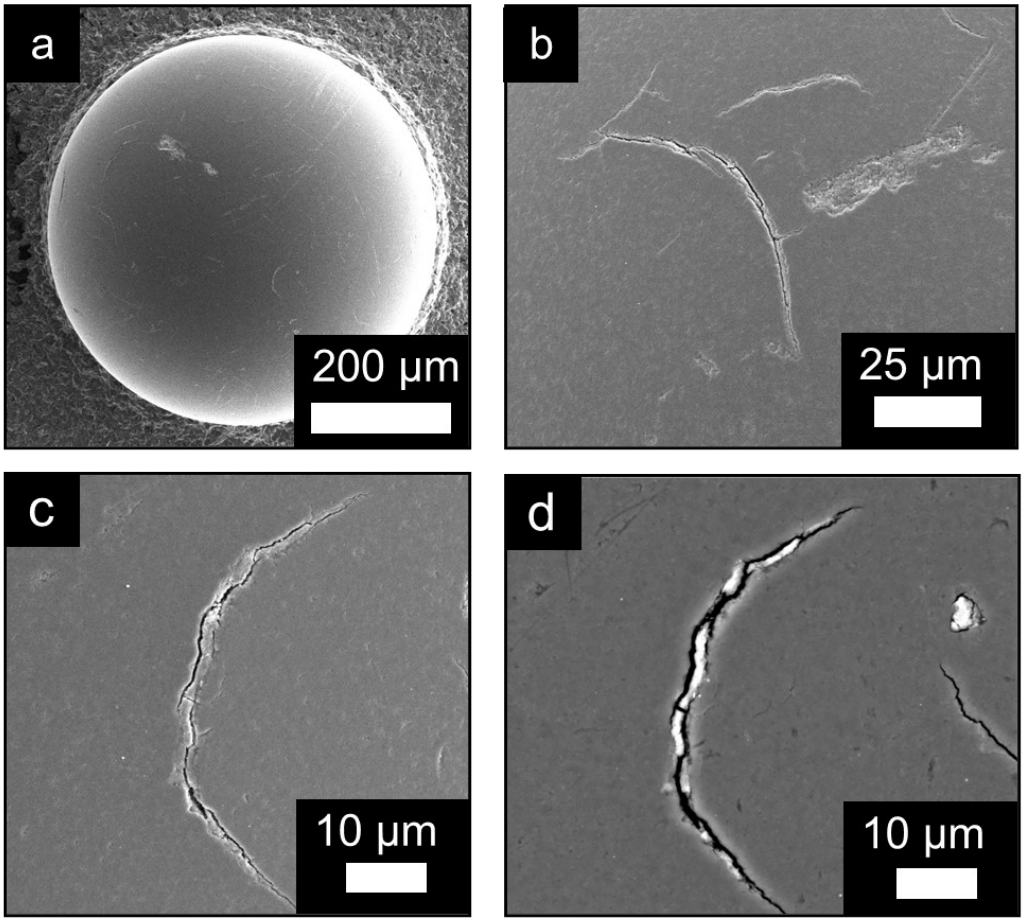

Figure SI 15: SEM images of MIL-100(Sc)@PBSAC after 26 hours on stream (a-c: detector: ETD, mode: SE; d: detector CBS, mode: all). The surface of the particle appears unchanged to MIL-100(Sc)@PBSAC spheres that have not been used for a reaction.

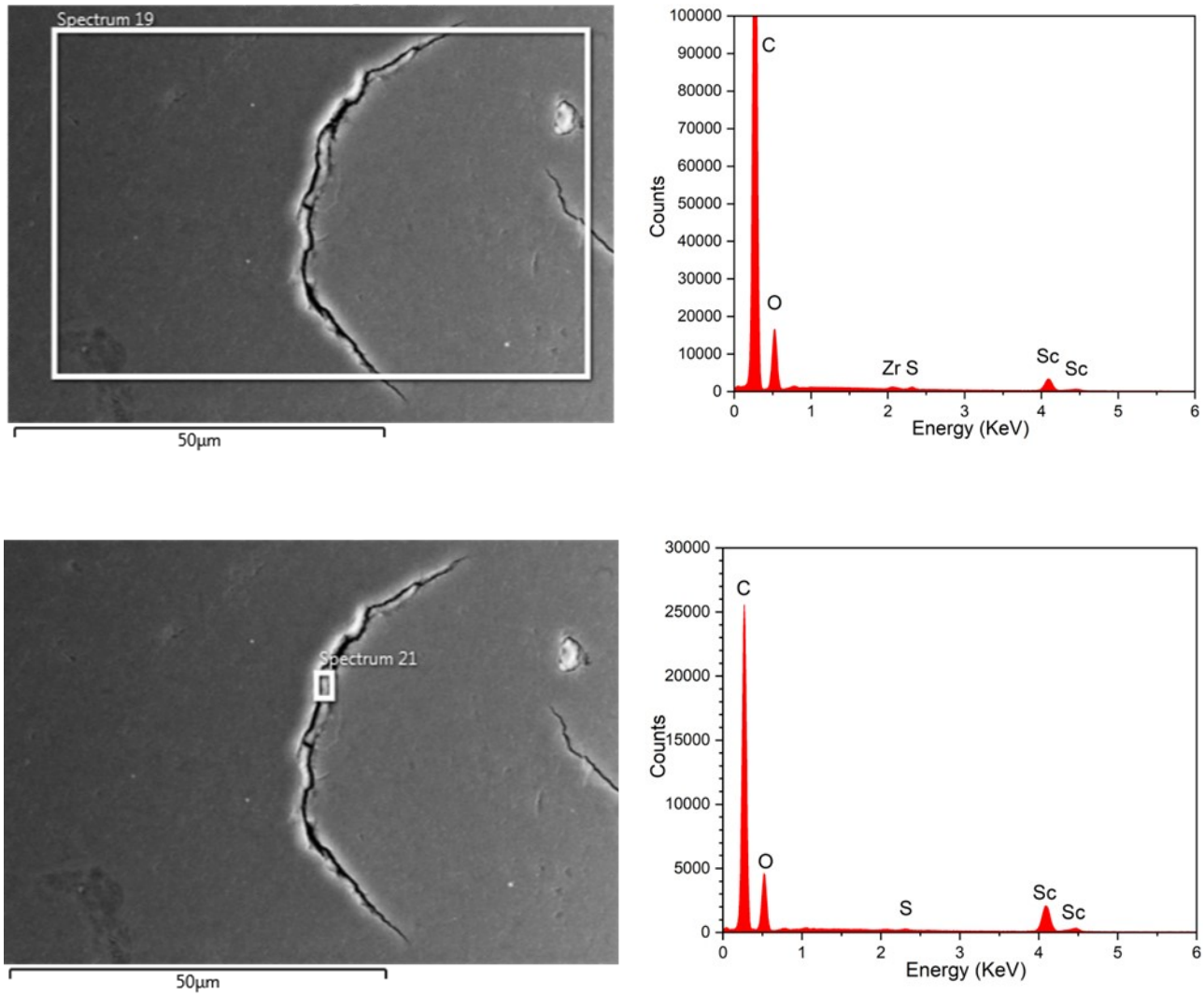

Figure SI 16: Left: SEM image of MIL-100(Sc)@PBSAC after 26 hours on stream. The labelled box in the images highlight where EDX spectra was obtained. Right: The resultant EDX spectra of the region stated. Zirconium is considered an impurity.