Probing the origins of *in situ* Generated Nanoparticles as Sustainable Oxidation Catalysts

Christopher S. Hinde[a], Sivan Van Aswegen[a], Gillian Collins[bc], Justin D. Holmes[bc], T. S. Andy Hor[d] and Robert Raja*[a]

[a] *Faculty of Natural and Environmental Science (Chemistry), University of Southampton, Southampton, UK, SO17 1BJ. Tel: (+44)23 8059 2144; E-mail: R.Raja@soton.ac.uk*
[b] *Department of Chemistry and Tyndall National Institute, University College Cork, Cork, Ireland.*
[c] *Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland*
[d] *Institute of Materials Research and Engineering (IMRE), A*STAR, 3, Research Link, Singapore 117602*

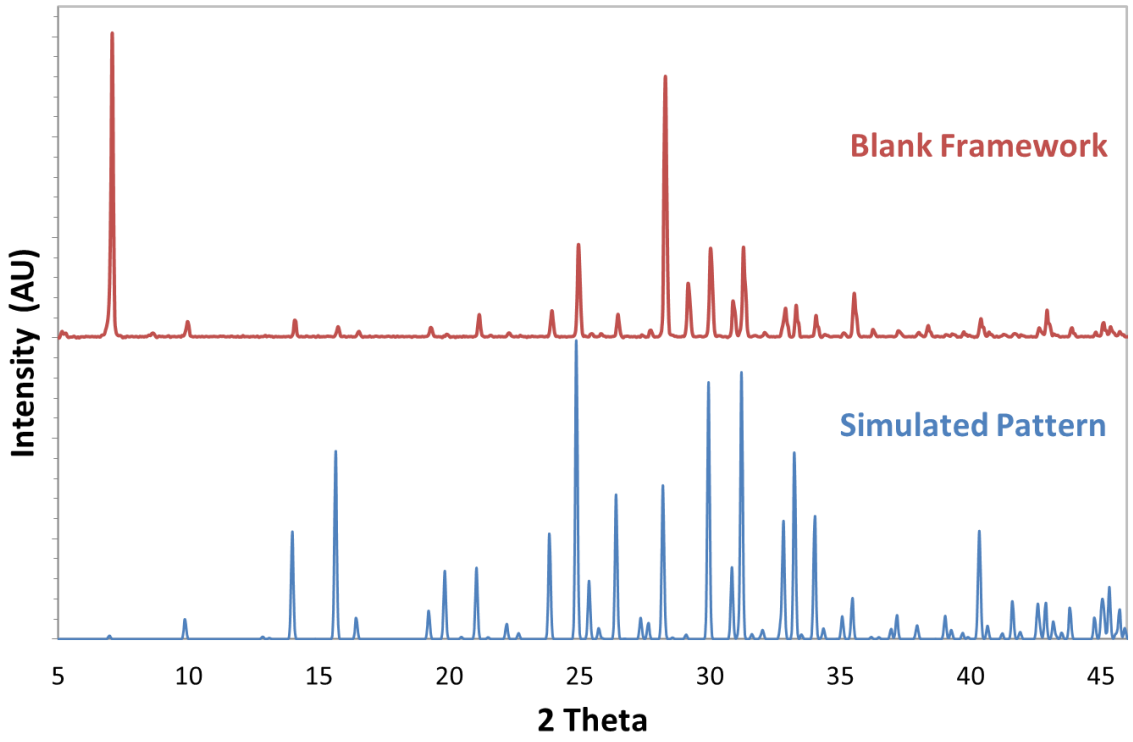
Electronic Supplementary Information (ESI)

Contents

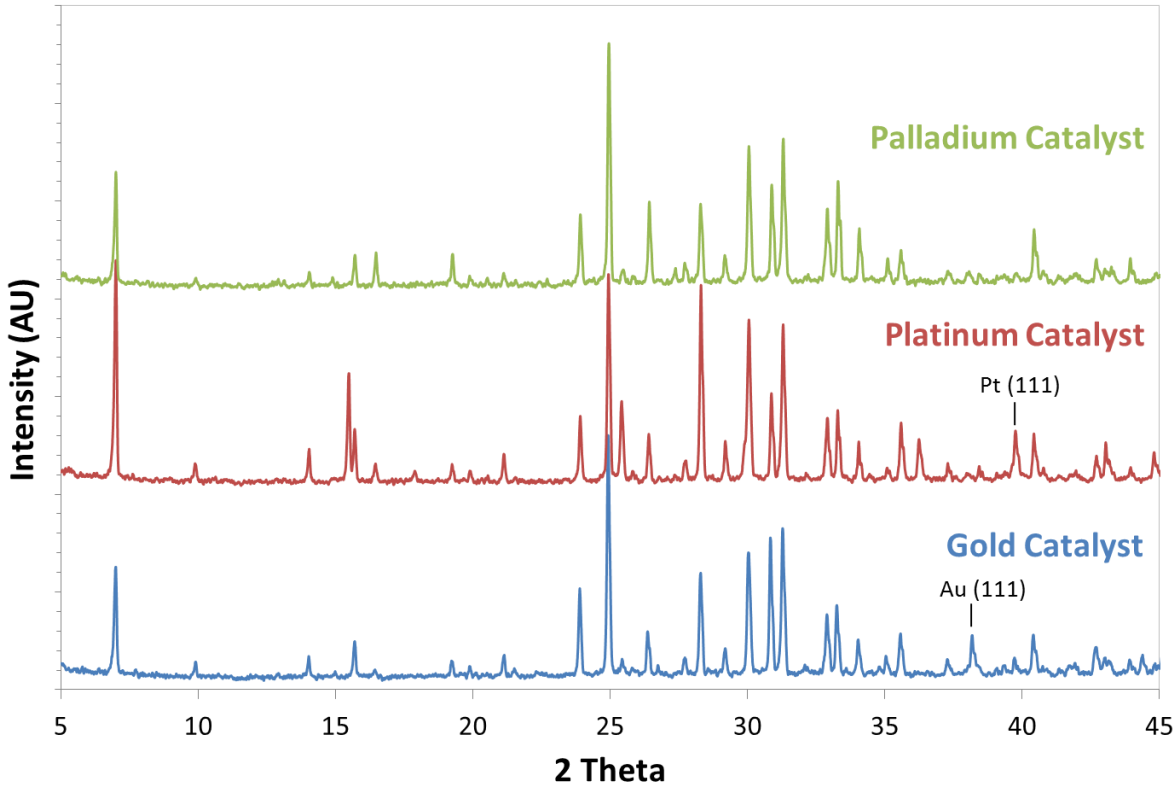
Abbreviations

XRD	X-Ray Diffraction	PVA	Polyvinyl Alcohol
SEM	Scanning Electron Microscopy	PVP	Polyvinyl pyrrolidone
TEM	Transmission Electron Microscopy	PTFE	Polytetrafluoroethylene
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy	FID	Flame-Ionisation Detector
EDX	Energy Dispersive X-Ray Spectroscopy	TON	Turnover Number
NP	Nanoparticle		
MOF	Metal-Organic Framework		

1. Powder XRD Patterns of Catalyst Materials



ESI Figure 1.1 – Simulated powder XRD pattern (blue line) and experimental XRD of the blank framework (red line), showing the structural integrity of the uncalcined framework

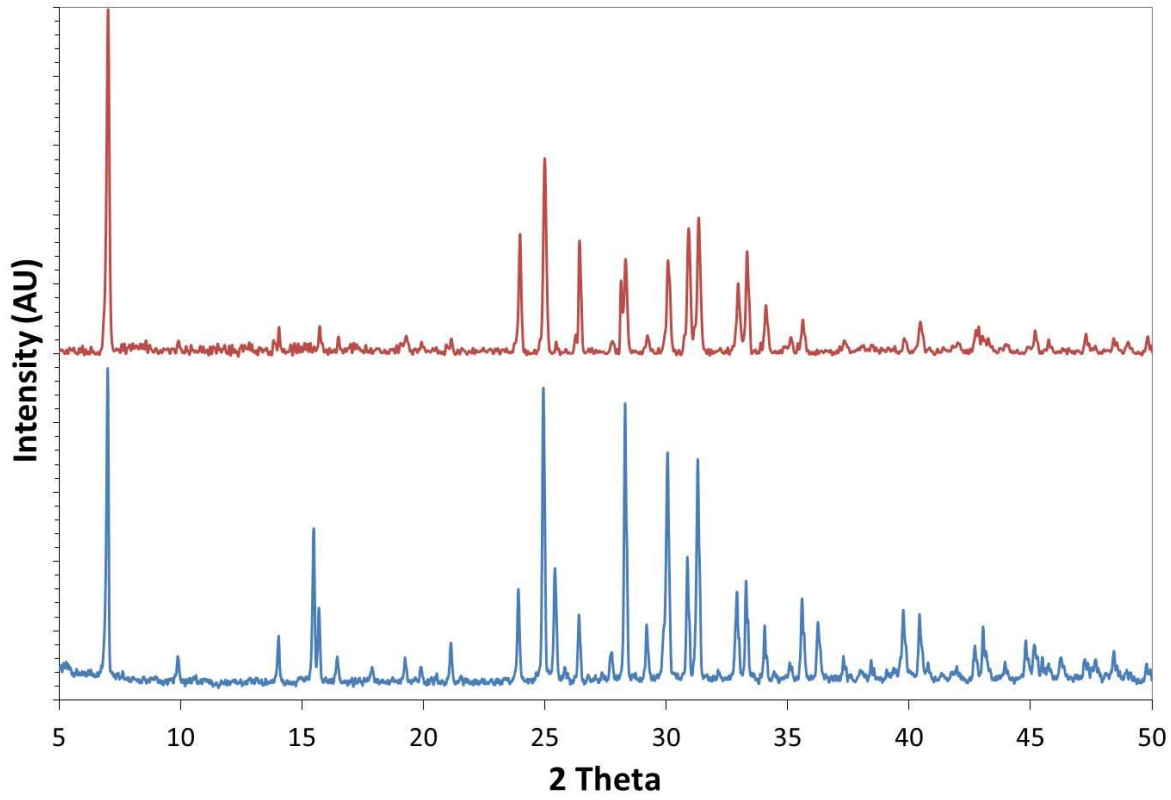


ESI Figure 1.2 Powder XRD patterns of each catalyst material calcined @ 500°C (Blue line – Au catalyst; Red line – Pt catalyst; Green line – Pd catalyst)

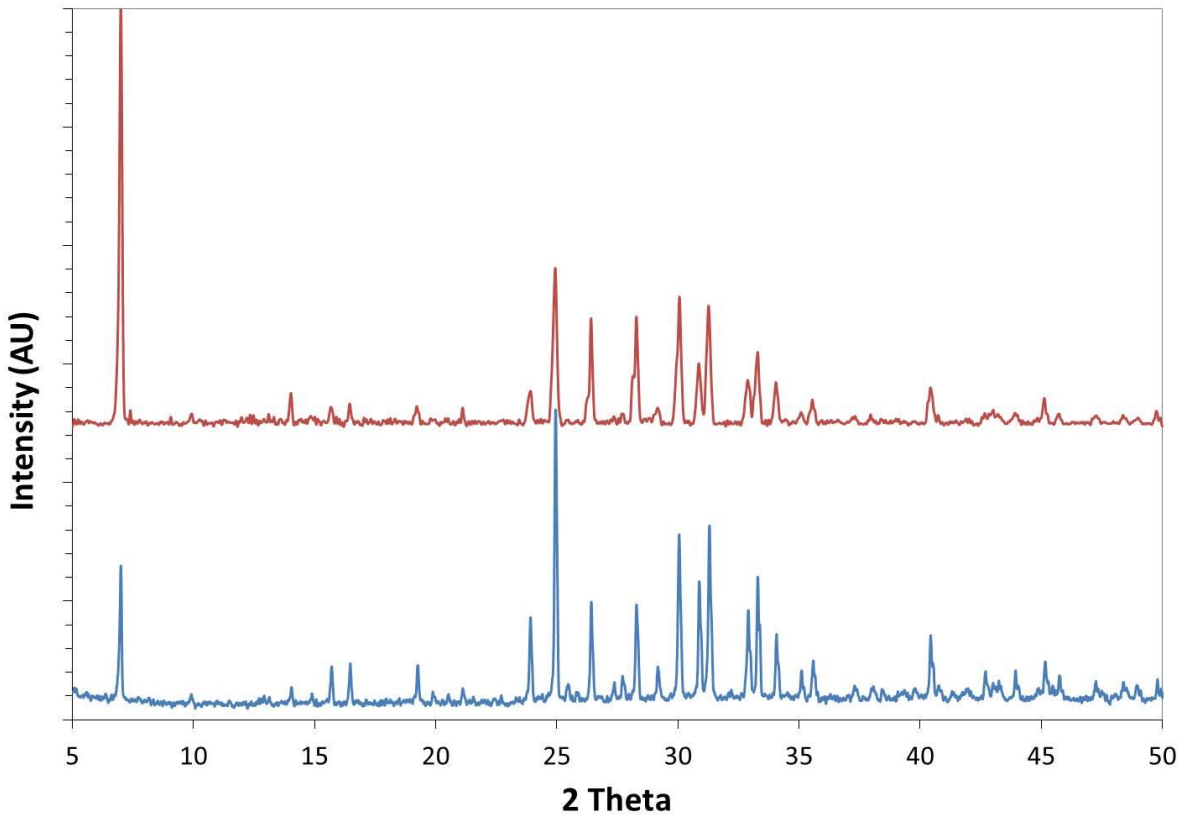
ESI Table 1.2 – Indexed powder XRD data with associated hkl and d-spacings for each reflection observed for parent $Rb_9Cu_6(P_2O_7)_4Cl_3$ framework

h	k	l	d(hkl)	2-Theta
1	1	0	12.64	6.99
0	2	0	8.94	9.89
1	2	1	6.88	12.86
0	0	2	6.74	13.12
2	2	0	6.32	14.00
1	1	2	5.95	14.88
1	3	0	5.65	15.66
0	2	2	5.38	16.46
2	3	1	4.65	19.06
2	2	2	4.61	19.24
0	4	0	4.47	19.85
1	3	2	4.33	20.49
3	3	0	4.21	21.07
1	4	1	4.13	21.51
2	4	0	4.00	22.22
1	2	3	3.92	22.68
0	4	2	3.72	23.87
3	3	2	3.57	24.90
1	5	0	3.51	25.39
3	4	1	3.46	25.76
2	4	2	3.44	25.89
0	0	4	3.37	26.42
2	3	3	3.33	26.75
1	2	5	2.55	35.10
1	7	0	2.53	35.48
4	6	0	2.48	36.21
1	6	3	2.46	36.50
1	5	4	2.43	36.97
2	7	1	2.42	37.19
4	5	3	2.37	37.91
2	3	5	2.37	37.96
1	7	2	2.37	37.98
3	7	0	2.35	38.32
1	1	4	3.26	27.37
2	5	1	3.22	27.65
4	4	0	3.16	28.22
0	2	4	3.15	28.28
1	4	3	3.12	28.59
1	5	2	3.11	28.68
3	5	0	3.07	29.11
0	6	0	2.98	29.97
2	2	4	2.97	30.03
1	3	4	2.89	30.87
1	6	1	2.87	31.12
4	4	2	2.86	31.24
2	6	0	2.83	31.63
3	4	3	2.80	31.96
3	5	2	2.79	32.05
4	5	1	2.73	32.73
0	6	2	2.72	32.84
0	4	4	2.69	33.27
2	5	3	2.67	33.54
3	3	4	2.63	34.04
3	6	1	2.61	34.28
2	6	2	2.61	34.38
2	4	4	2.58	34.79
1	2	5	2.55	35.10
1	7	0	2.53	35.48
4	6	0	2.48	36.21
1	6	3	2.46	36.50
1	5	4	2.43	36.97
2	7	1	2.42	37.19
4	5	3	2.37	37.91
2	3	5	2.37	37.96
1	7	2	2.37	37.98
3	7	0	2.35	38.32
4	6	2	2.33	38.67
4	4	4	2.31	39.04
3	6	3	2.29	39.28
1	4	5	2.29	39.32
3	5	4	2.27	39.71
5	6	1	2.26	39.92
0	0	6	2.25	40.10
0	8	0	2.23	40.33
0	6	4	2.23	40.38
3	7	2	2.22	40.67
1	1	6	2.21	40.76
1	8	1	2.19	41.23
0	2	6	2.18	41.40
2	8	0	2.17	41.63
2	6	4	2.17	41.67
2	7	3	2.15	41.89
3	4	5	2.15	41.94
0	8	2	2.12	42.59
2	2	6	2.12	42.68
6	6	0	2.11	42.90
2	5	5	2.09	43.19
1	3	6	2.09	43.30
5	7	0	2.08	43.52
3	8	1	2.07	43.75
2	8	2	2.06	43.84
5	6	3	2.04	44.38
1	7	4	2.02	44.78

2. Powder XRD of materials before and after catalytic runs

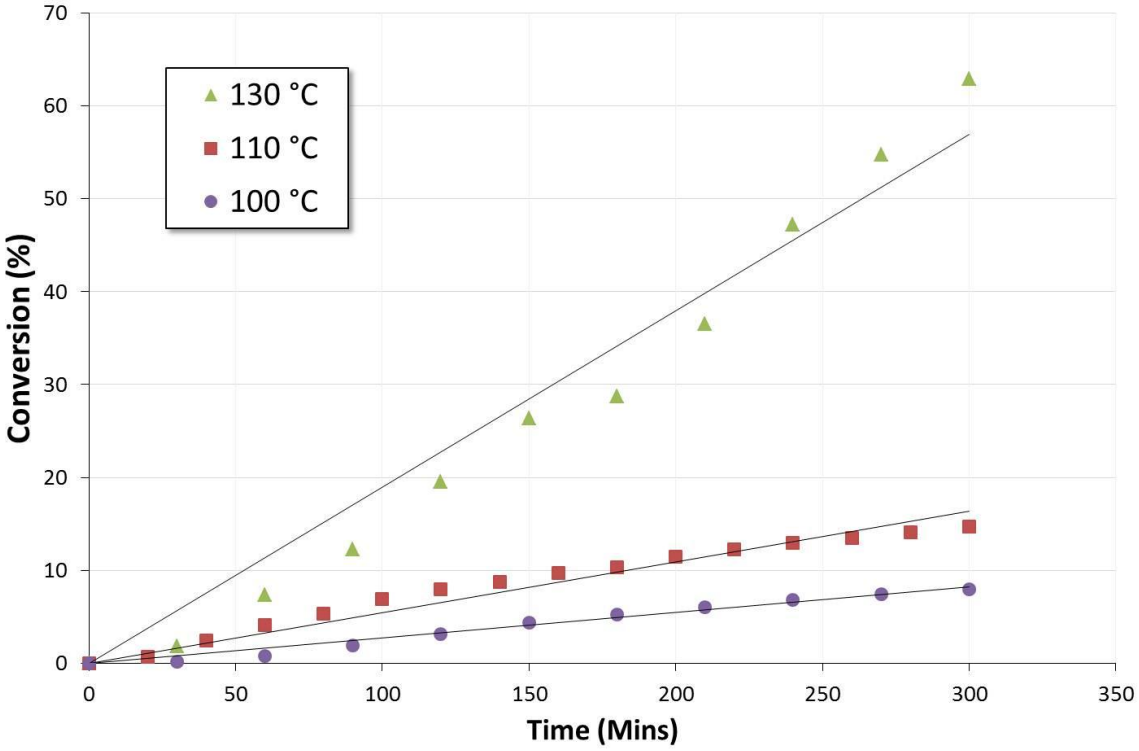


ESI Figure 2.1 – Powder XRD of calcined (blue line) and used (red line) platinum catalyst

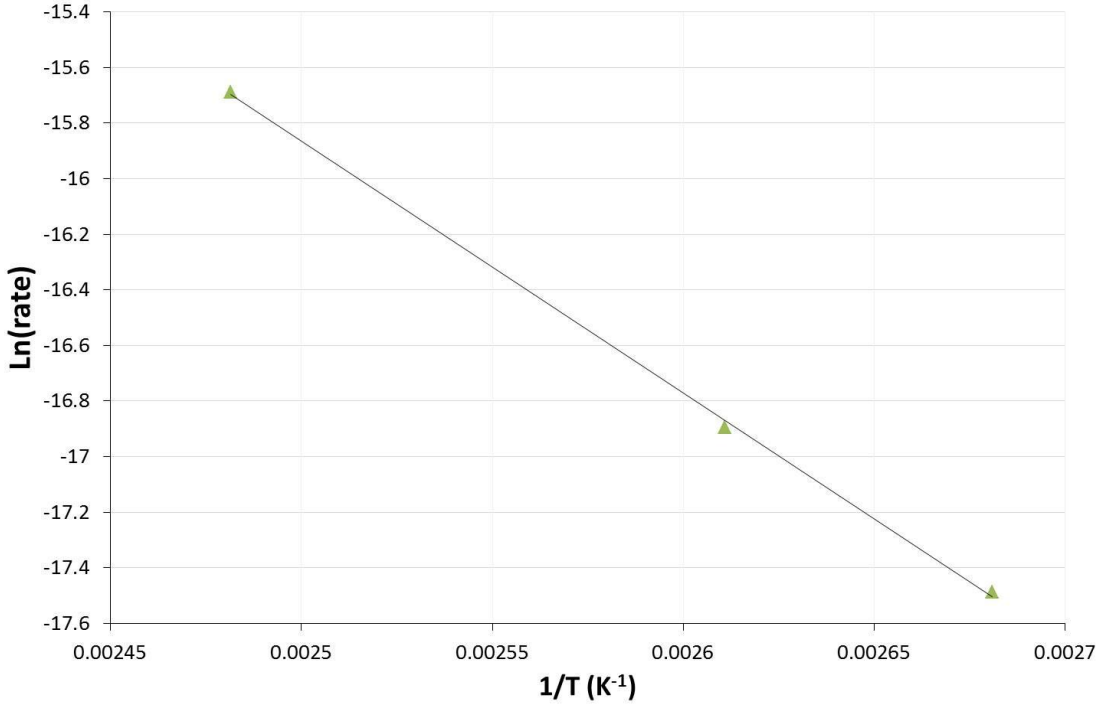


ESI Figure 2.2 – Powder XRD of calcined (blue line) and used (red line) palladium catalyst

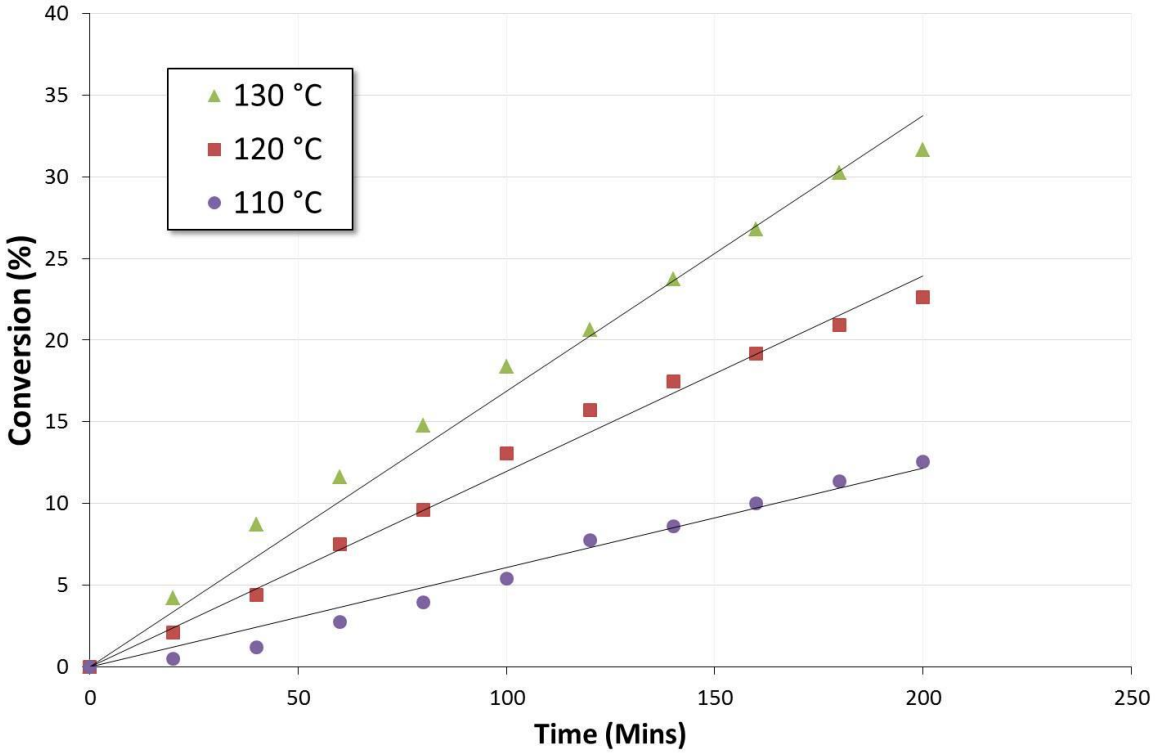
3. Kinetic profiles and Arrhenius plots



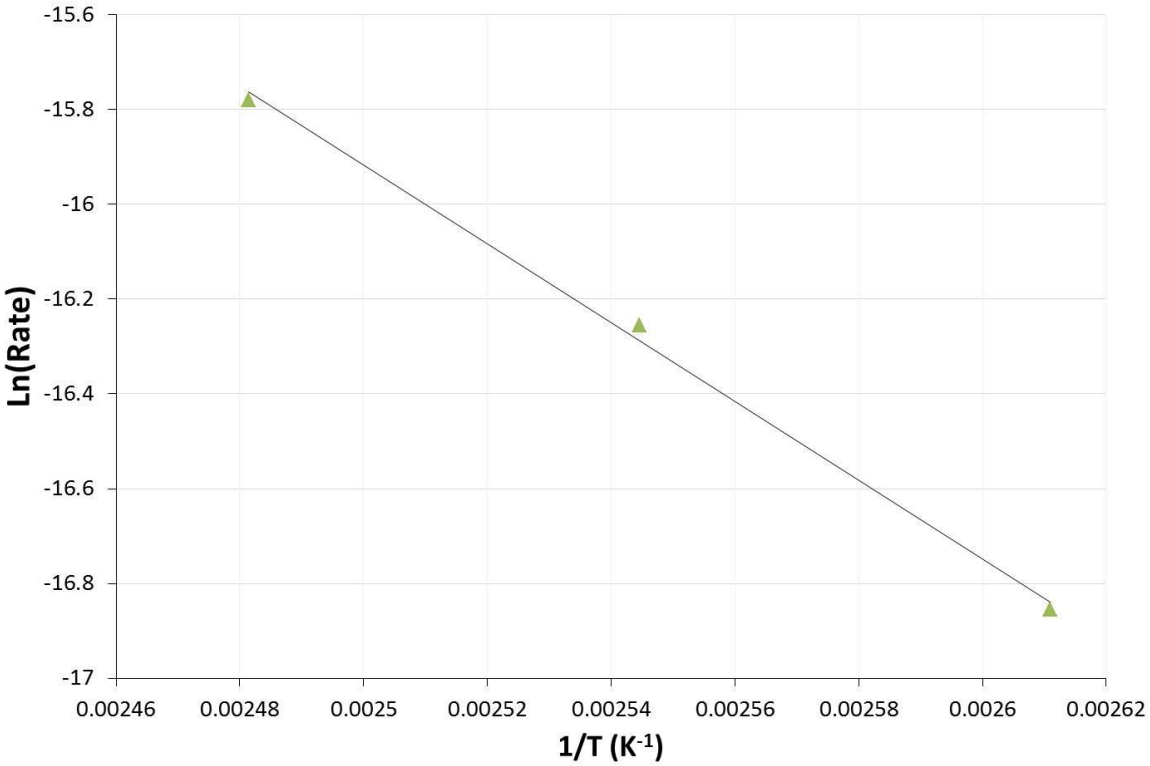
ESI Figure 3.1 - Kinetic plots for conversion of benzyl alcohol in aerobic oxidation with Au catalyst at varying temperatures



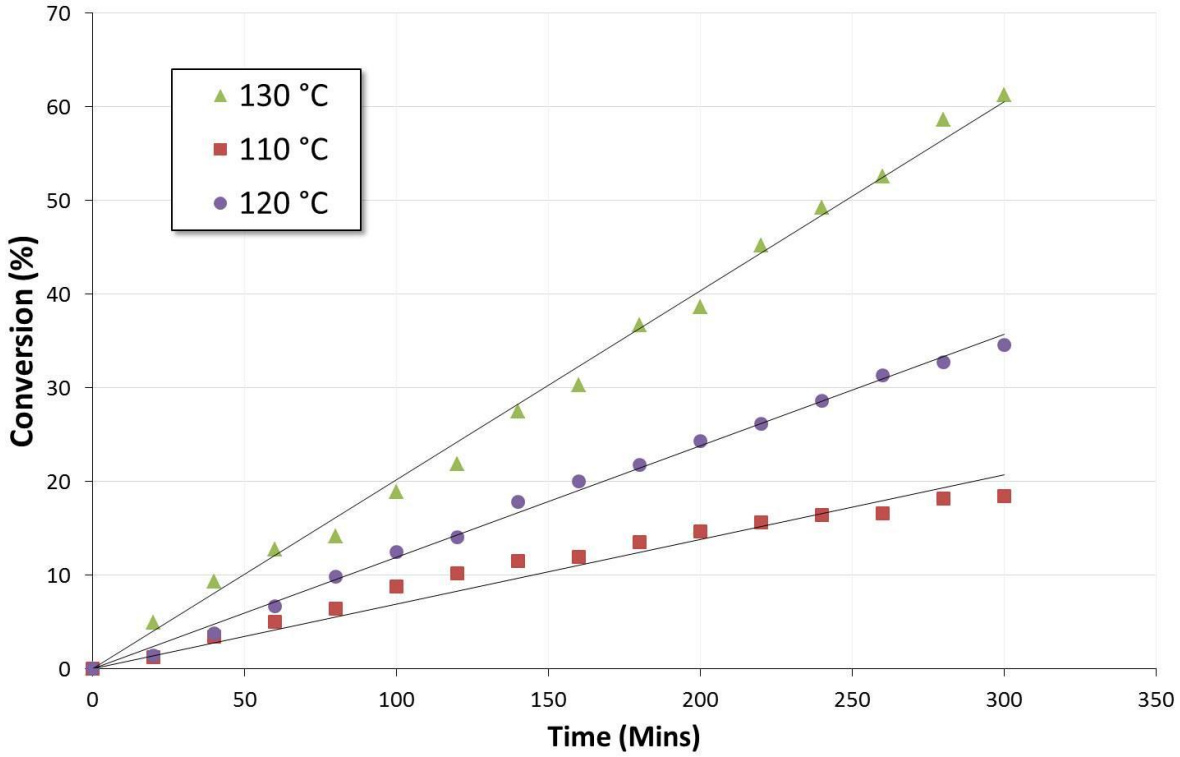
ESI Figure 3.2 - Arrhenius Plot for Au Catalyst



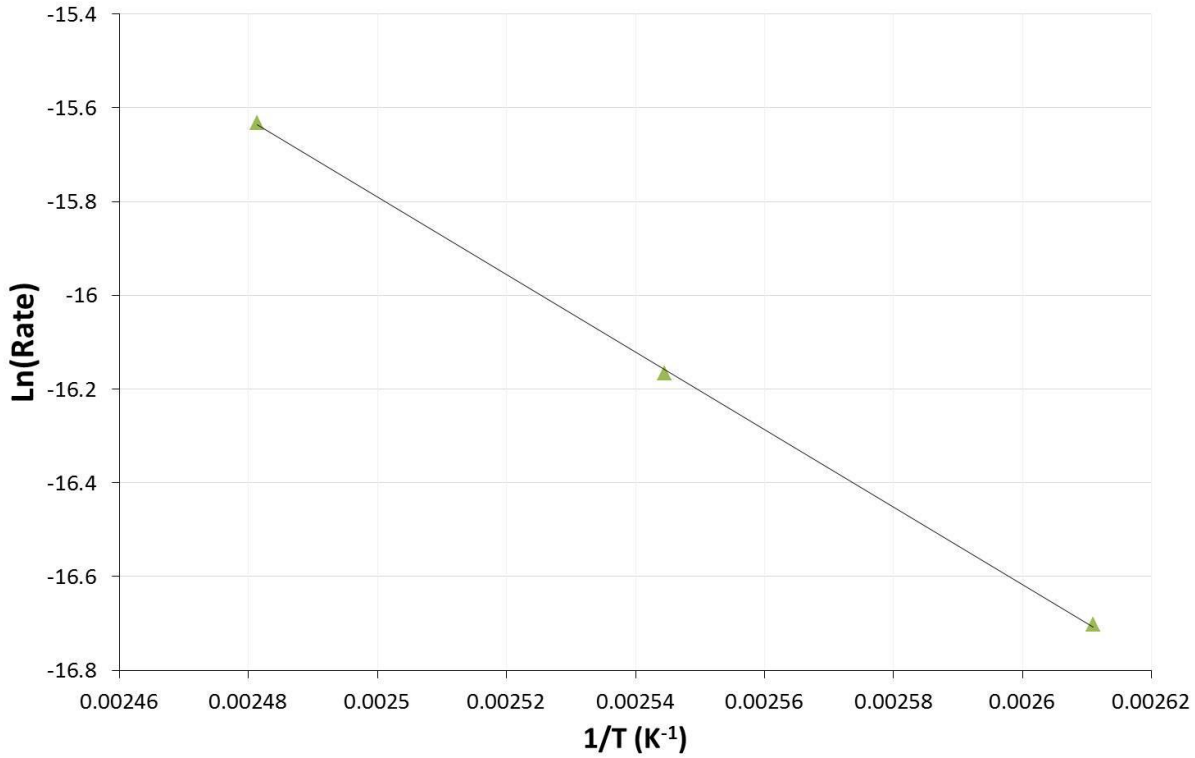
ESI Figure 3.3 - Kinetic plots for conversion of benzyl alcohol in aerobic oxidation with Pt catalyst at varying temperatures



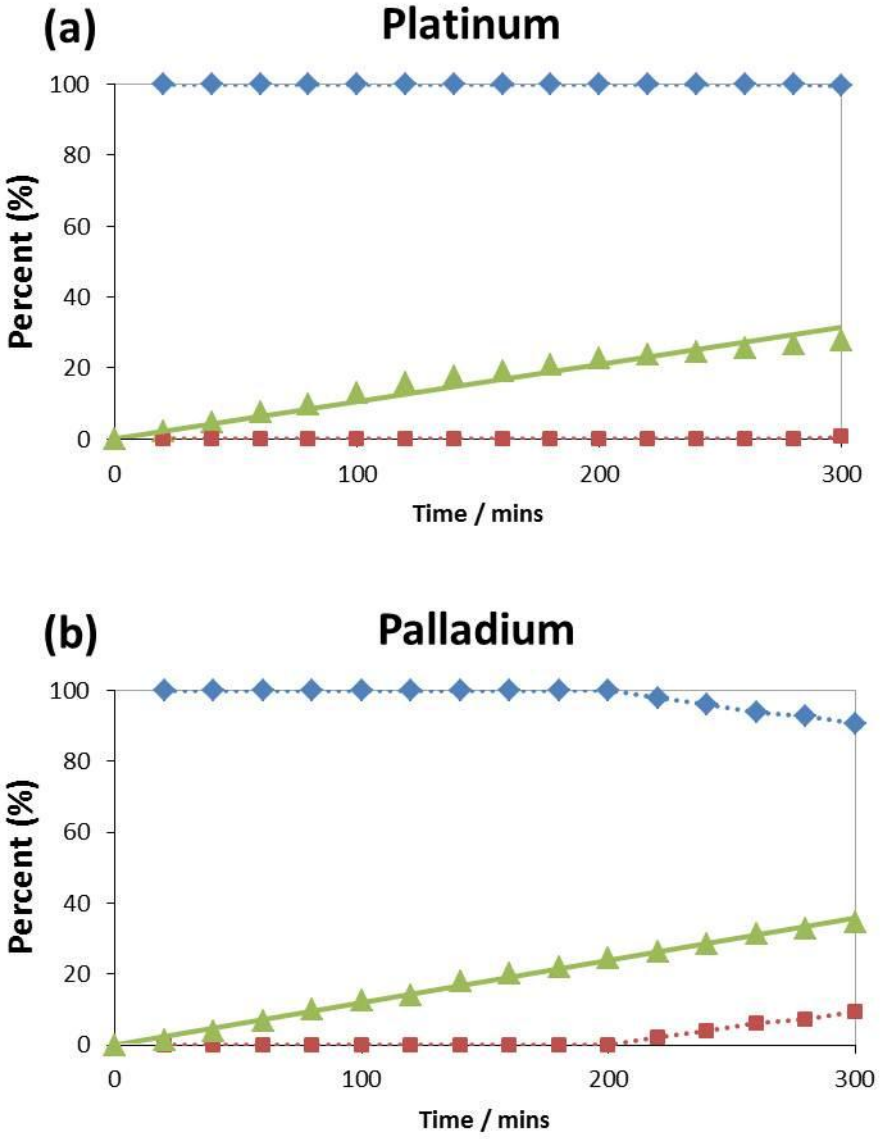
ESI Figure 3.4 - Arrhenius plot for the Pt catalyst



ESI Figure 3.5 - Kinetic plots for conversion of benzyl alcohol in aerobic oxidation with Pd catalyst at varying temperatures



ESI Figure 3.6 - Arrhenius plot for the Pd catalyst



ESI Figure 3.7 - Benzyl alcohol conversion (green triangles), benzaldehyde selectivity (blue diamonds) and benzoic acid selectivity (red squares) for the platinum (a) and palladium (b) catalysts at 120 °C under 20 bar of air.

4. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

Leaching Studies

Leaching studies have been carried out to test the immobilisation of the nanoparticles to the surface of the parent framework host. ICP analysis was carried out by MEDAC Ltd on the reaction solutions extracted post-catalysis. It was calculated that with the given concentration, the maximum ppm value that would be observed if all the supported metal had leached would be 21,000 ppm. As can be seen, negligible amounts of Pt and Pd were detected, indicating no leaching of the metal to the reaction solution.

ESI Table 4.1 – Inductively-Coupled Plasma analysis of noble metal concentrations in reaction solutions post-catalysis

Metal	Concentration (ppm)
Gold	0.1
Platinum	2.0
Palladium	< 1.0

Metal Content Studies

To confirm the noble metal content of the framework material and accurately calculate turn-over numbers, ICP analysis was performed on the active calcined catalyst materials. The noble metal content is referenced against Rb and Cu, both of which are part of the parent host framework.

ESI Table 4.2 - Inductively-Coupled Plasma analysis of gold copper chloropyrophosphate catalyst material

Metal	Weight %	Atomic %
Au	6.43	3.26
Rb	29.49	34.50
Cu	17.77	27.95

ESI Table 4.3 - Inductively-Coupled Plasma analysis of platinum copper chloropyrophosphate catalyst material

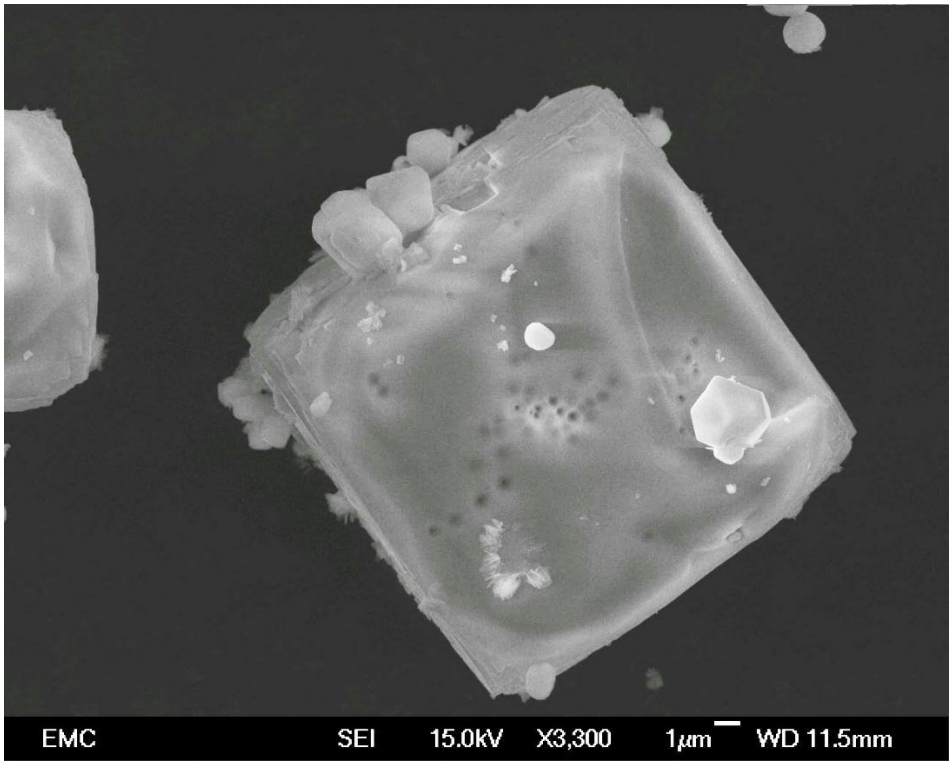
Metal	Weight %	Atomic %
Pt	2.72	1.39
Rb	31.90	37.32
Cu	18.32	28.83

ESI Table 4.4 - Inductively-Coupled Plasma analysis of palladium copper chloropyrophosphate catalyst material

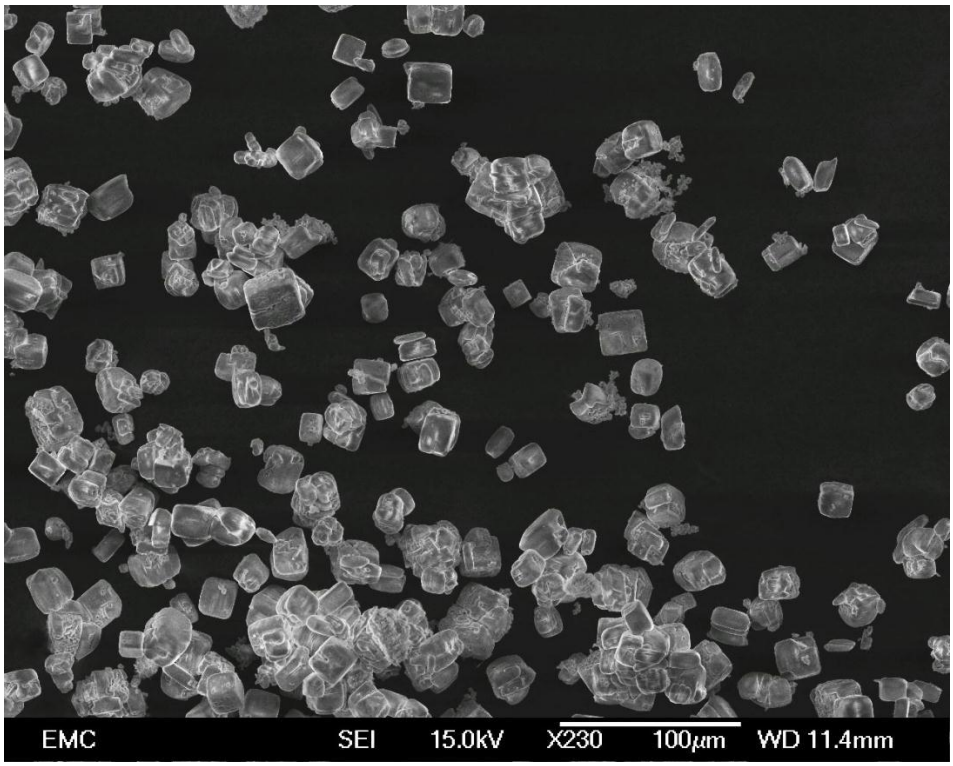
Metal	Weight %	Atomic %
Pd	3.34	3.14
Rb	31.32	36.64
Cu	18.51	28.83

5. SEM Images

As-synthesised Platinum Catalyst

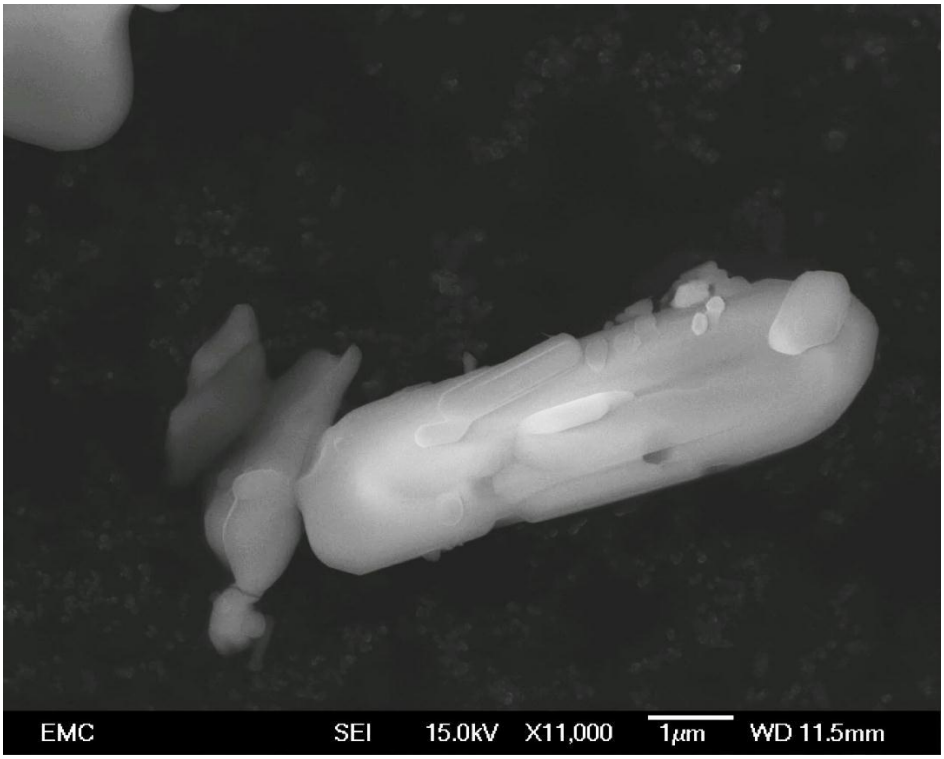


ESI Figure 5.1 – SEM depicting a single crystal of the as-synthesised platinum catalyst



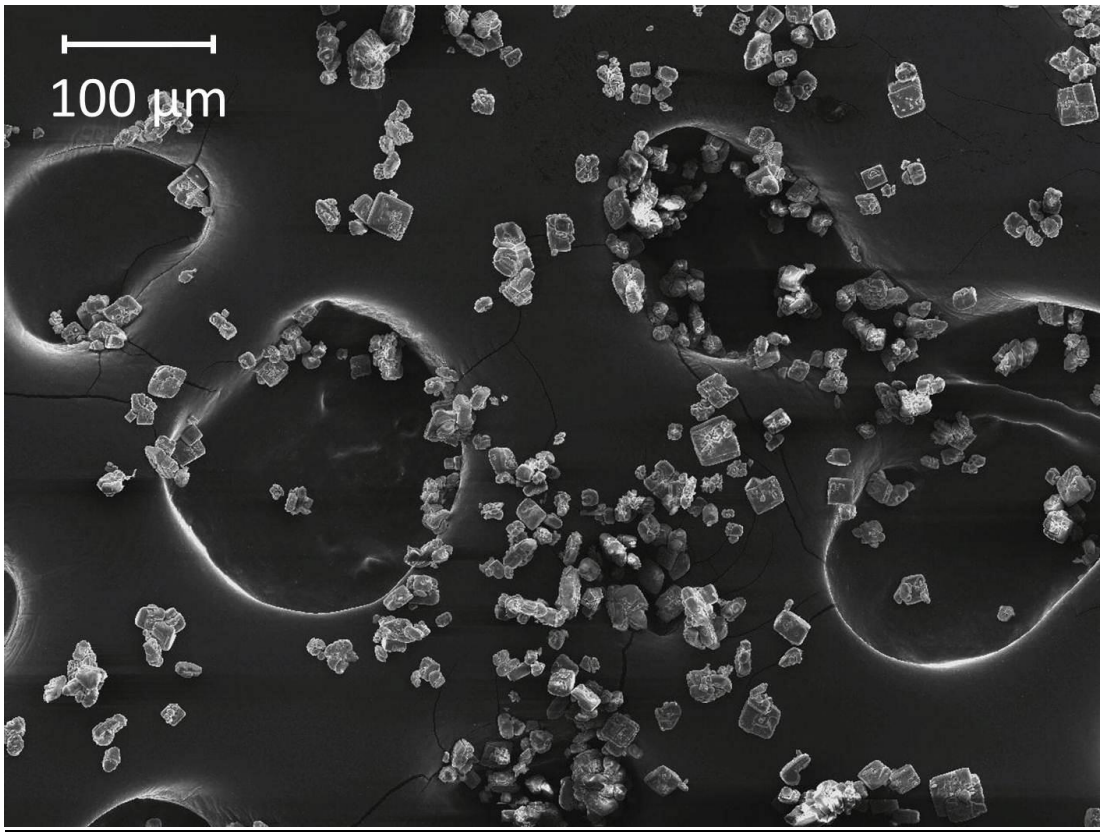
ESI Figure 5.2 – SEM Micrograph depicting the homogeneous morphology of crystals across a sample

Calcined Platinum Catalyst

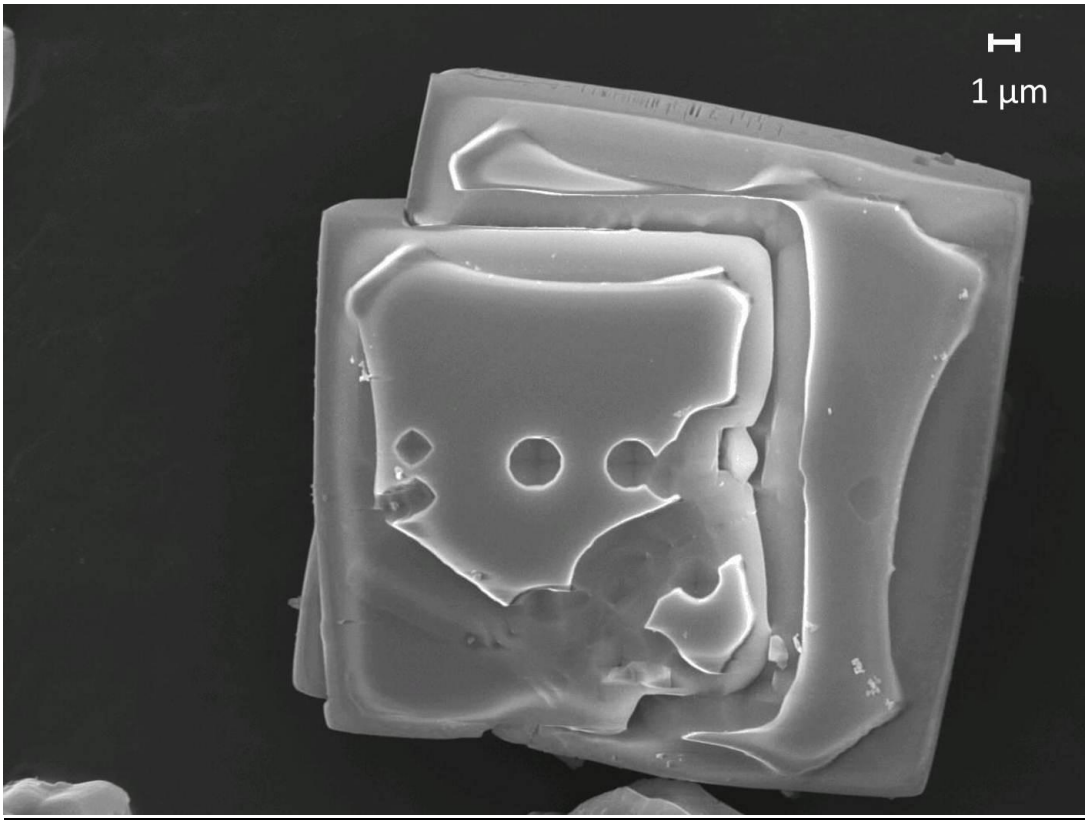


ESI Figure 5.3 – SEM Micrograph of platinum catalyst post-calcination with platinum particles visible on the surface

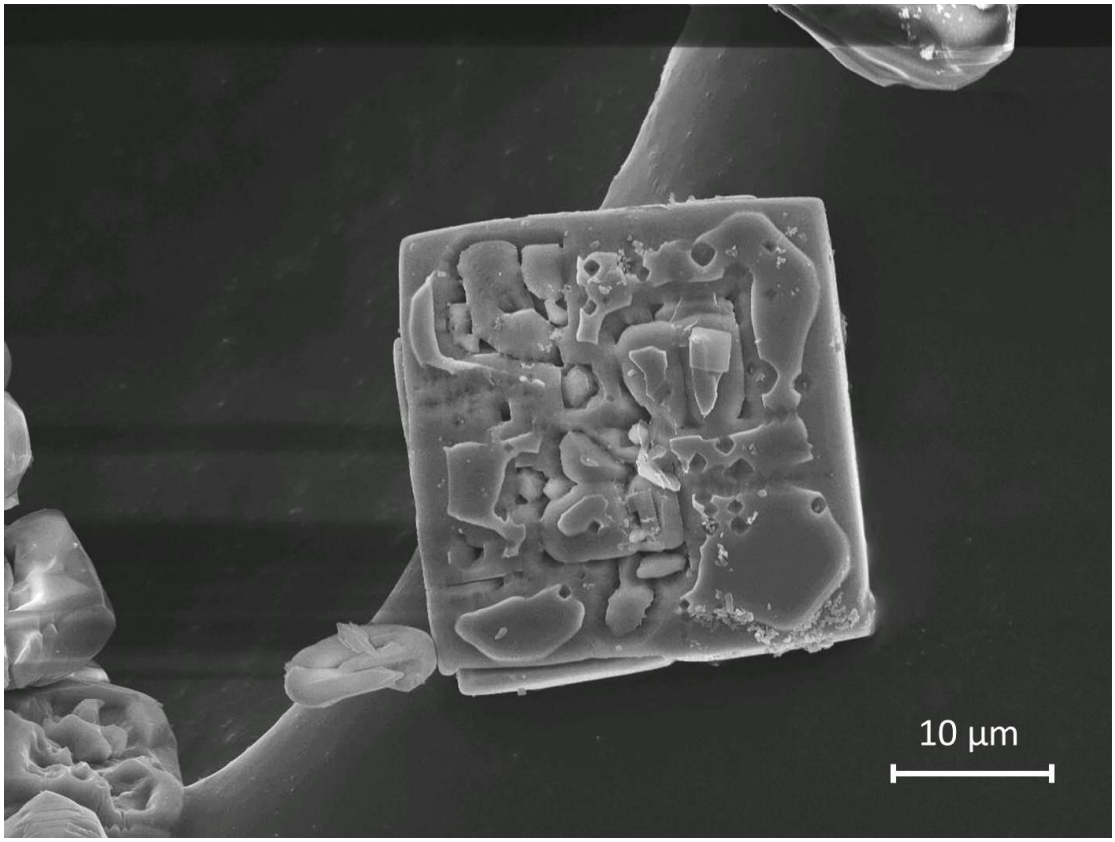
As-synthesised Palladium Catalyst



ESI Figure 5.4 – SEM Micrograph depicting the homogeneous morphology of crystals across a sample

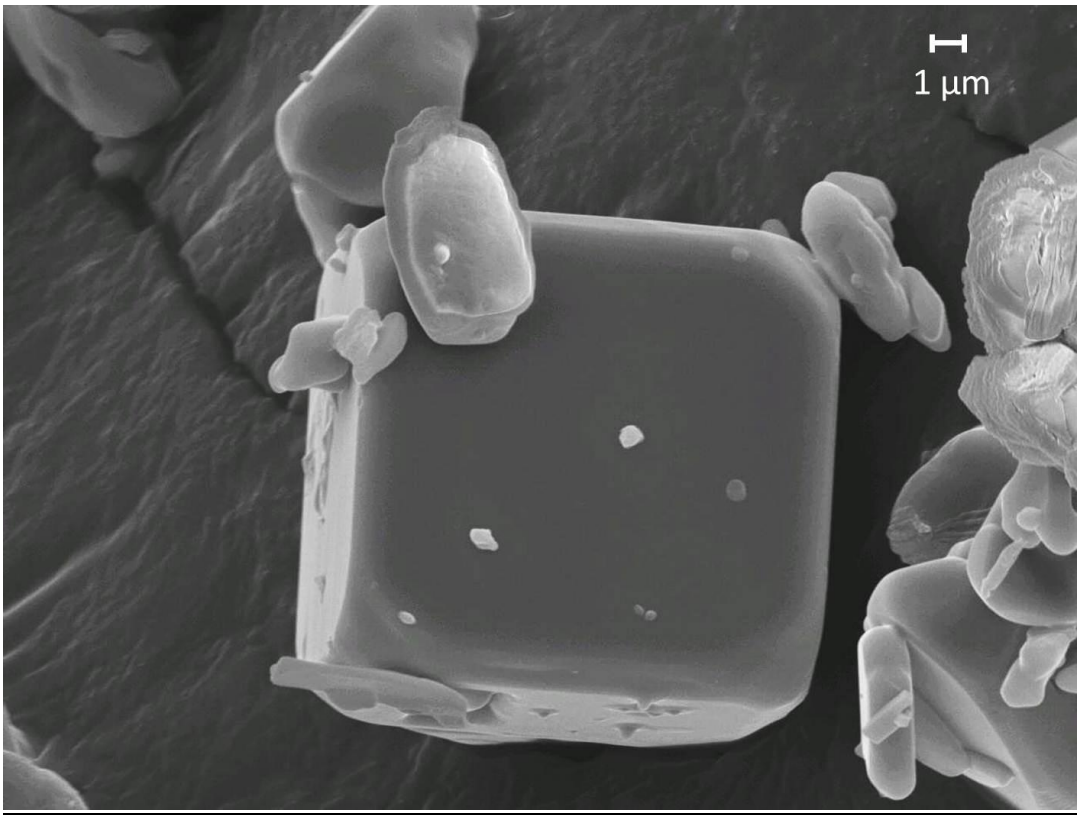


ESI Figure 5.5 - SEM depicting a single crystal of the as-synthesised palladium catalyst

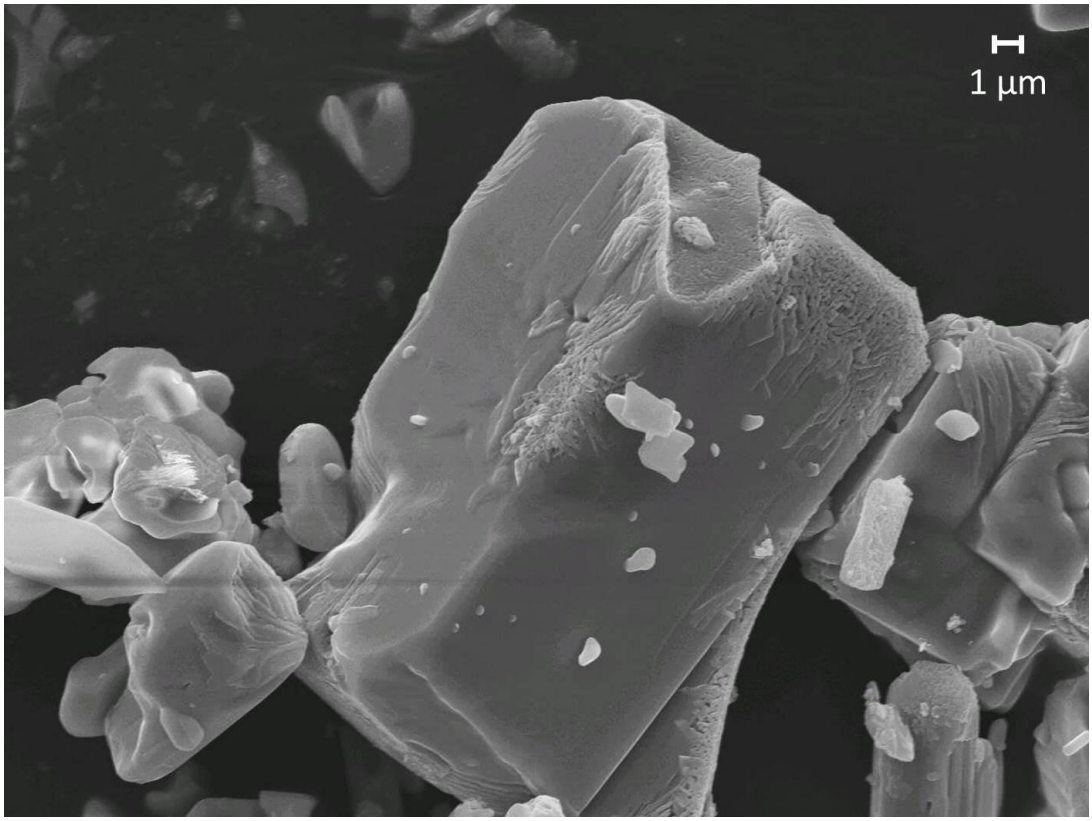


ESI Figure 5.6 - SEM depicting a single crystal of the as-synthesised palladium catalyst

Calcined Palladium Catalyst

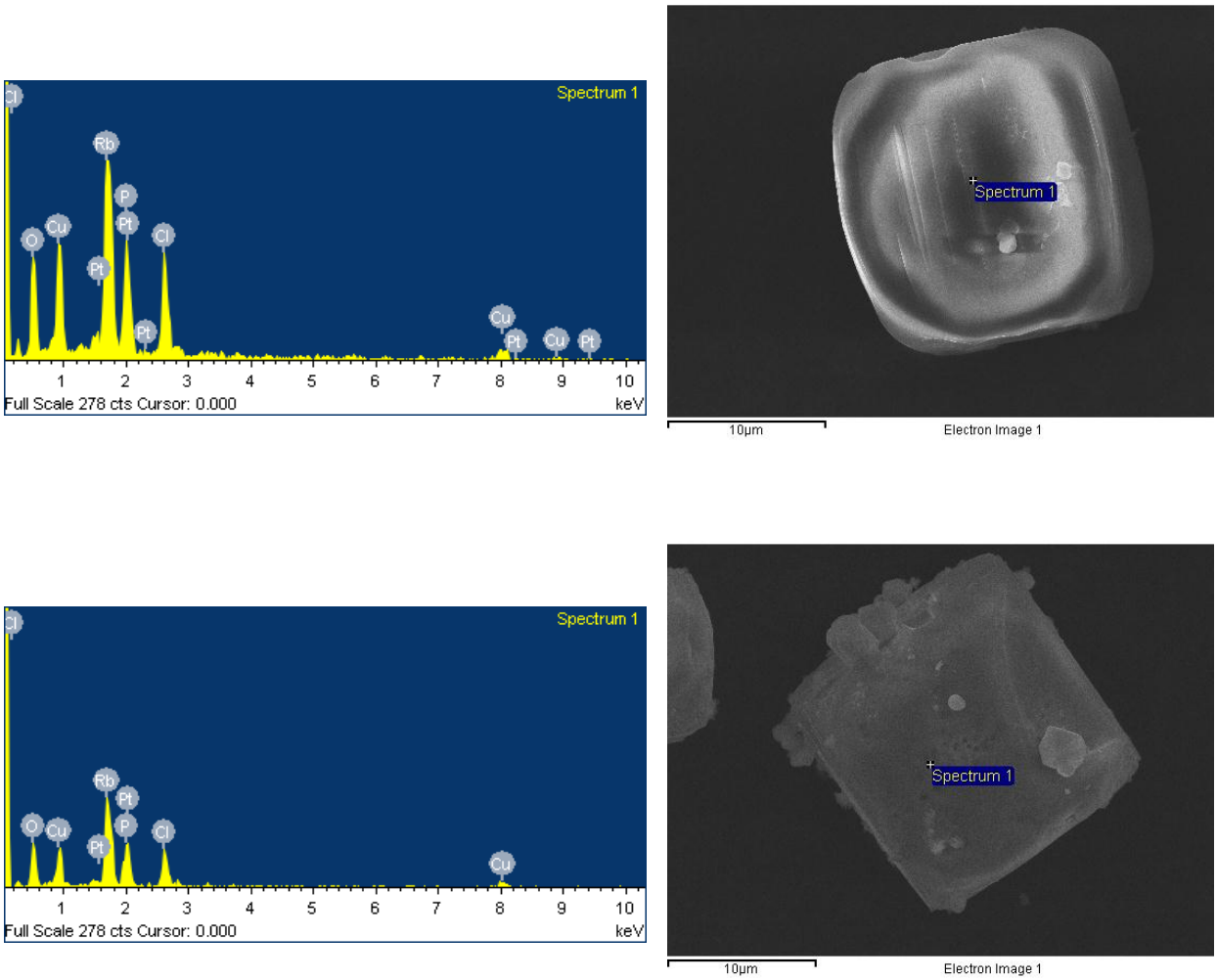


ESI Figure 5.7 – SEM depicting a single crystal of the calcined palladium catalyst

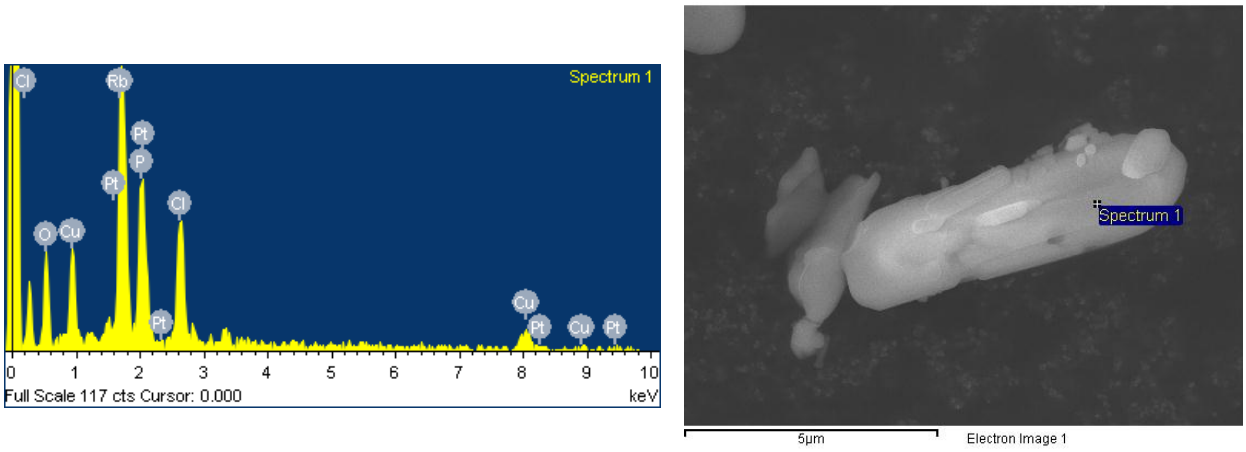


ESI Figure 5.8 - SEM depicting a single crystal of the calcined palladium catalyst

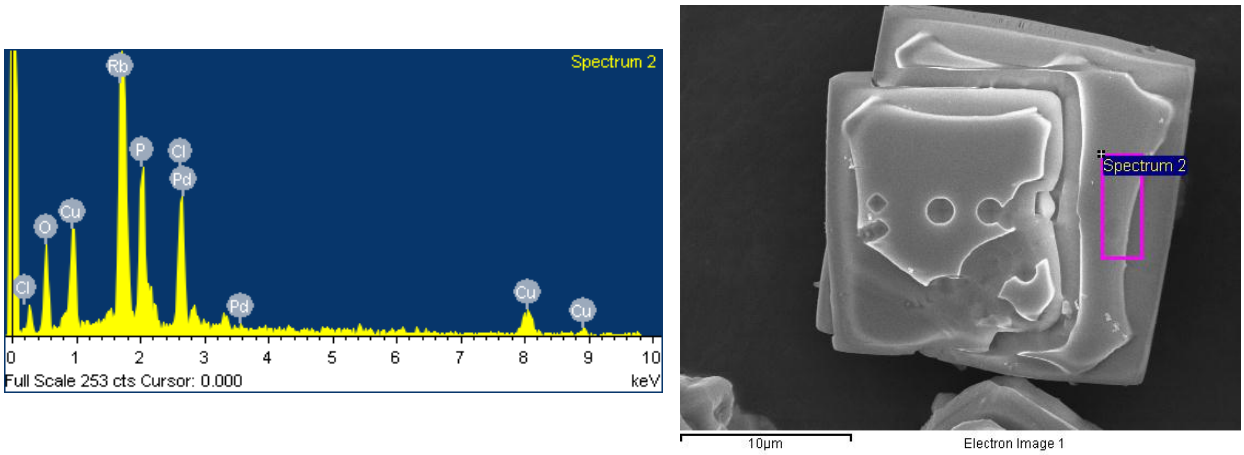
6. EDX Analysis from SEM



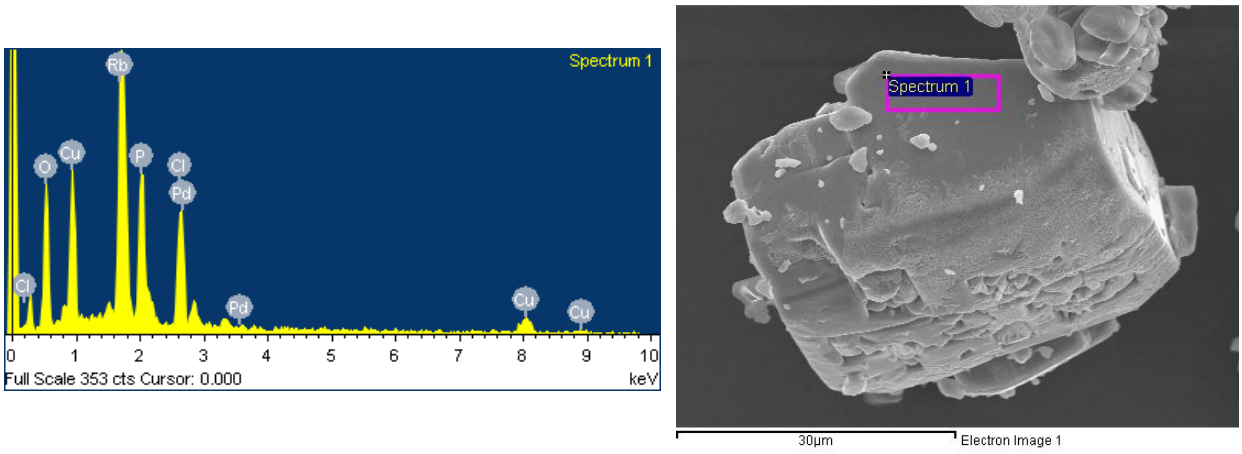
ESI Figure 6.1 - EDX Spectra of as-synthesised platinum catalyst

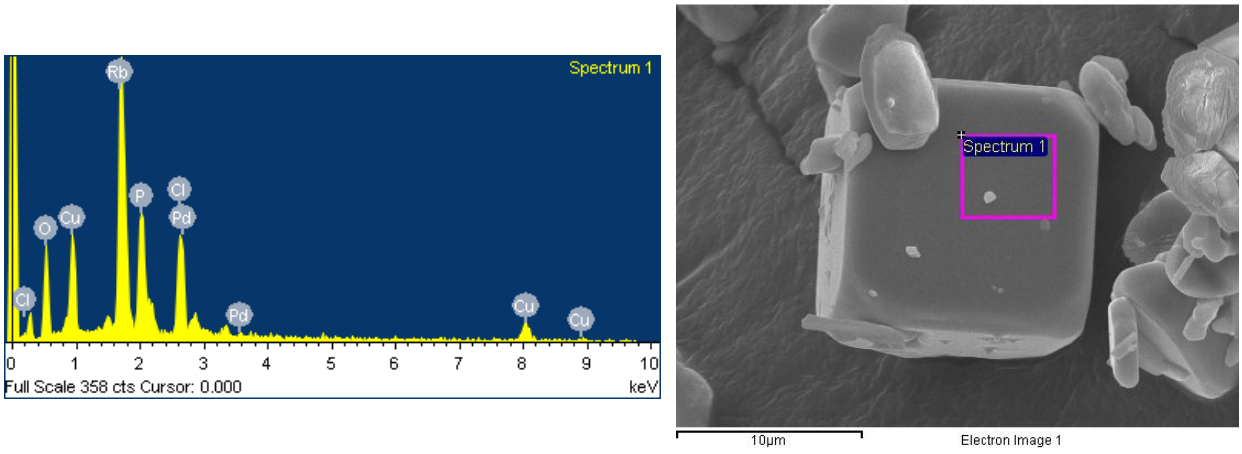


ESI Figure 6.2 – EDX spectra of calcined platinum catalyst



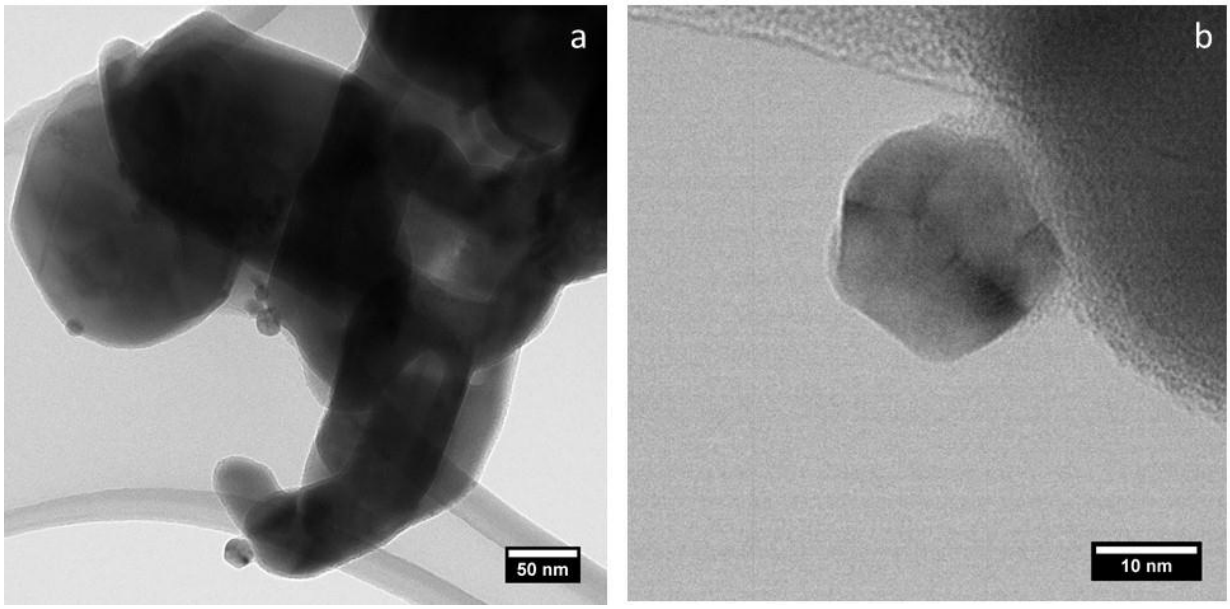
ESI Figure 6.3 - EDX Spectra of as-synthesised palladium catalyst





ESI Figure 6.4 – EDX Spectra of calcined palladium catalyst

7. TEM Images



ESI Figure 7.1 - TEM image of the calcined Pd catalyst showing the presence of faceted nanocrystals.