

Supplementary Information.

Table S1. Structural parameters obtained from EXAFS analysis of Pd/Al₂O₃ sample. Refined values for the threshold energy (ΔE), coordination number (N), interatomic distance (R) and Debye-Waller factors ($2\sigma^2$) are tabulated. Fitting results of Pd foil and PdO reference materials are shown for comparison.

(Ref material)	1 st shell PdO			2 nd shell PdO			1 st shell Pd metal			R_{fit} (%)
	N	R_{Pd-O} (Å)	$2\sigma^2$ (Å ²)	N	R_{Pd-Pd} (Å)	$2\sigma^2$ (Å ²)	N	R_{Pd-Pd} (Å)	$2\sigma^2$ (Å ²)	
(PdO)	4.0	2.02	0.007	1.8	3.03	0.010				12.19
(Pd foil)							12	2.74	0.011	29.28
212	4.0	2.02	0.007	2.7	3.03	0.011				19.71
290	4.1	2.02	0.008	2.7	3.04	0.016				17.09
417	4.0	2.02	0.009	2.2	3.04	0.015				15.47
504	4.1	2.02	0.011	1.8	3.03	0.015				16.89
602	3.9	2.02	0.011	1.4	3.03	0.014				17.58
700	3.8	2.02	0.011	1.0	3.04	0.014				18.39
831	3.5	2.03	0.014	0.9	3.03	0.013				19.22
900	1.2	2.01	0.015	2.0	2.99	0.036	7	2.75	0.023	30.49
881	0.9	2.01	0.024	3.2	2.91	0.037	8.4	2.71	0.036	39.43
784	0.9	2.00	0.017	3.1	2.99	0.026	8.8	2.75	0.026	33.56
682	1.2	2.01	0.006	3.0	3.00	0.022	8.2	2.76	0.022	35.50
580	3.2	2.02	0.006	1.7	3.03	0.012				20.62
478	3.2	2.02	0.005	1.7	3.03	0.008				19.16
376	3.4	2.02	0.005	1.7	3.03	0.005				18.79
274	3.4	2.02	0.004	1.7	3.03	0.004				20.96
173	3.5	2.02	0.004	2.1	3.04	0.003				19.92
71	3.5	2.02	0.003	2.5	3.04	0.003				20.46
55	3.4	2.02	0.003	2.5	3.05	0.003				20.30
42	3.4	2.02	0.002	2.6	3.04	0.002				21.17
32	3.5	2.02	0.002	2.6	3.04	0.003				20.87

XRD:

A powder sample was measured using Cu radiation on a Bruker D8 Advance Diffractometer with Göbel mirrors and a Vantec PSD detector over a range 20–70° 2 θ . In situ data was collected in an Anton Paar XRK900 Environmental Cell. Data were analysed using Bruker EVA 2007 and TOPAS V4.2 software.

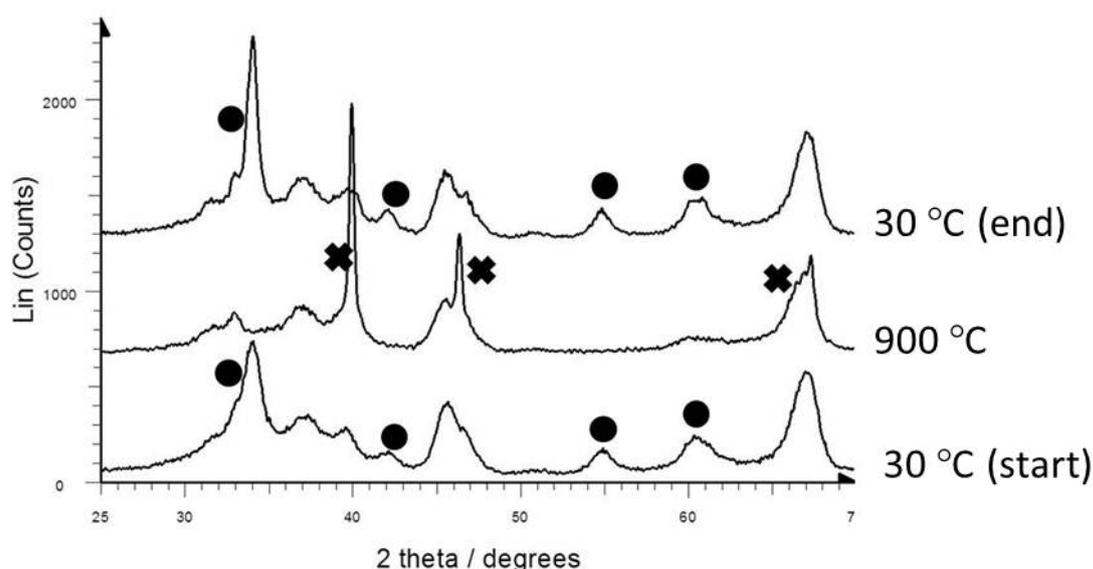


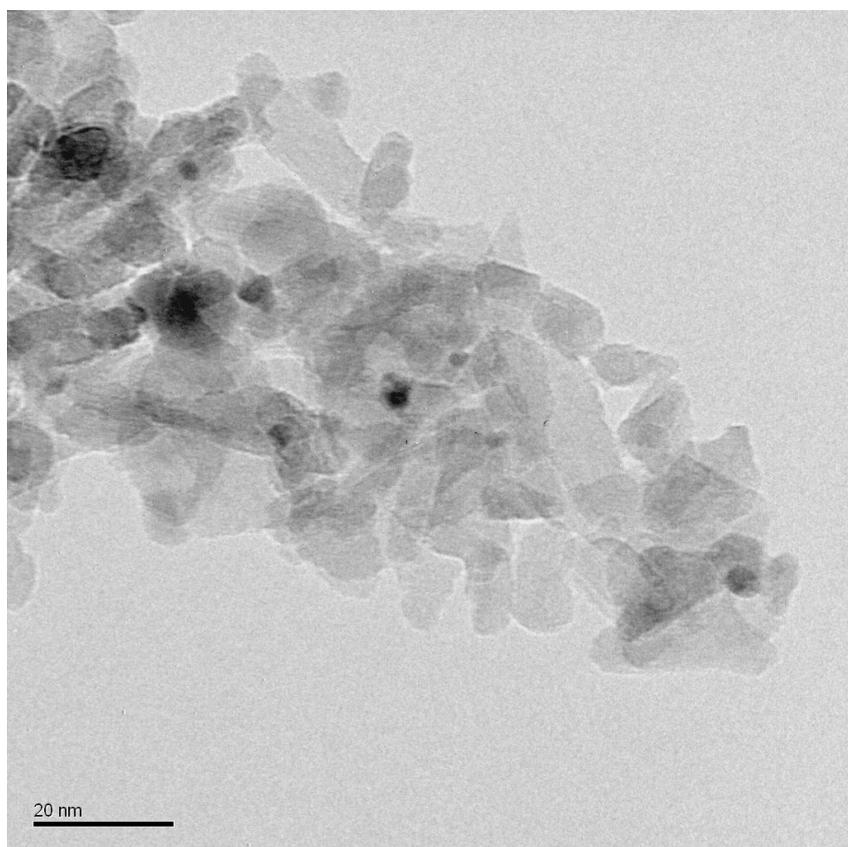
Figure S1. *In situ* laboratory XRD of 4 wt.% Pd/Al₂O₃ sample measured at room temperature (bottom), 900 °C (middle) and room temperature after cooling (top). Circles represent reflections belonging to PdO and crosses represent reflections belonging to metallic Pd. All other broad features originate from the Al₂O₃ support phase.

Table S2. Average crystallite size of Pd/PdO phases for 4wt% Pd/Al₂O₃ as determined by Rietveld analysis (LVol-IB, Bruker TOPAS V4.2) of laboratory *in situ* XRD data.

Conditions	Crystalline Phase, LVol-IB ,nm	
	PdO	Pd
30 °C (start)	4.6	-
900 °C	-	23.3
30 °C (end)	11.2	-

TEM:

The sample was examined in an FEI Tecnai F20 Transmission Electron Microscope using an accelerating voltage of 200 kV and C2 aperture of 30 & 50 m in Bright Field (BF) and STEM high annular dark field (HAADF) mode. A small portion of the powdered sample was dusted onto a holey carbon film coated Cu TEM grid. EDX (Energy dispersive X-ray spectroscopy) was also undertaken for elemental characterisation.



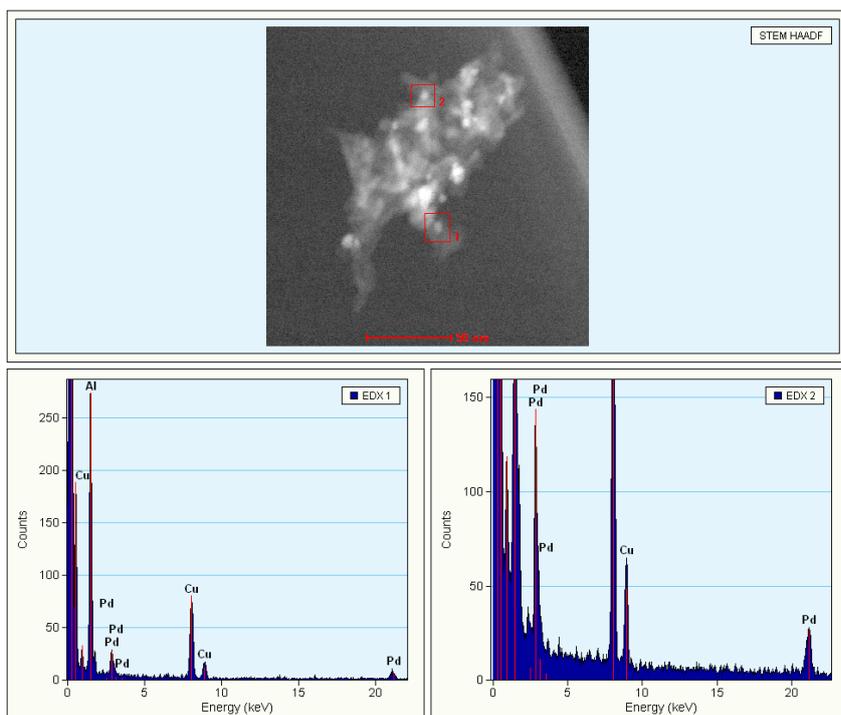


Figure S2. TEM micrographs of 4 wt.% Pd/Al₂O₃: top: Bright Field, and bottom: EDX analysis modes. EDX data are given for area scans which demonstrate that the nanoparticles contain Pd, manifested by peaks of intensity in the EDX scan. The large Cu peaks are caused by the TEM grid used in these experiments. The detection limit of EDX is considered 1 wt% from the interaction volume of the area analysed. The scale bar is 20nm (top) and 50 nm (bottom).