Supporting Information

1. Catalyst synthesis

Catalysts were synthesised using wet impregnation of $Pd(NO_3)_2$ solutions (15.05wt% Pd, Johnson Matthey) diluted as appropriate. This solution was then added to γ-Al_2O_3 (Alfa Aesar; pellets pre-ground/sieved to between a 90 and 75 micron mesh fraction) in a dropwise manner until incipiently wet. The resulting solid was then dried overnight in air at 373 K, washed in H_2O, and then dried again overnight. The samples were then calcined in flowing air (1 $K \cdot min^{-1}$ ramp to 773K and then held at temperature for 4 hours before cooling at 1 $K \cdot min^{-1}$). Once cooled the samples were then sieved again to a 90 and 75 micron mesh fraction before use.

2. Operando EXAFS measurements

Quick scanning EXAFS measurements were made at B18 at the Diamond Light Source and the Swiss-Norwegian Beamline at the European Synchrotron radiation facility using a Si (111) double crystal monochromators and Ion chambers for detection of X-ray absorption, normalisation, and energy scale (Pd foil) calibration. The dimensions of the X-ray beam were 0.5 mm (V) x 2 mm (h) (B18) and 0.35 mm (v) x 3 mm (h) (SNBL) to sample through the 4mm i.d. sample bed. Bi-directional Quick scanning EXAFS was employed with a time per (uni-directional) spectrum (24 to 25.5 keV) of between 6 to 20 seconds.

During experimentation QuEXAFS spectra were sequentially collected along the catalyst bed at intervals of between 0.35 and 0.5mm, starting at the inlet and ending at the outlet. This process was then repeated throughout the remainder of the experiment. Data reduction was made using “Prestopronto” XAFS [S1] software or PAXAS[S2] prior to EXAFS analysis using EXCURV.[S3]

The continuous flow reactor and the overall experimental protocols followed in this study have been fully described elsewhere. Briefly, the solvent used comprised 50:50 mix of H_2O/EtOH. The solvent components were individually degassed using nitrogen gas bubbled through the liquids followed by sonication after mixing. The sample was packed into a quartz tube – to yield beds of ca. 5 mm in length – and secured on either side using γ-Al_2O_3 of a smaller particle size and then quartz sand. Once loaded in the reactor the sample was located and mapped in a dry state prior to the solvent being pumped through at 0.1 $mL \cdot min^{-1}$ flow and the bed mapped again “wet”. The sample was then heated at 1 $K \cdot min^{-1}$ under the flowing solvent to 353 K whereupon it was held at this temperature for the remainder of the experiment. Pd K-edge EXAFS maps of the bed were continually collected throughout with a single complete axial map of the bed being obtained every 5–7 minutes.

3. Linear combination analyses

Spectra were processed using the Demeter open source software suite incorporating IFEFFIT version 1.2.11d and Athena version 0.9.12 for normalisation, background subtraction and linear combination fitting of XANES.[S4] Spectra were fit using PdO and a Pd foil reference spectra over the range –20 eV to 50 eV relative to the Pd K-edge.

4. Transmission Electron Microscopy.

TEM measurements were carried out at Imperial College London. The Pd/Al_2O_3 catalysts were dispersed in isopropanol and ground prior to being applied to a TEM grid. Images were collected using a Jeol 2100F microscope. Figure S1 gives the particle size distributions for the 0.5, 1, 2, and 5wt% catalysts.

Average Pd particle sizes for these catalysts range from around 3.5- 4 nm (5 and 10wt%) to ca. 2-3 nm (1 and 2wt%). Only in the case of the catalysts displaying an average particle size of > ca. 3.5 nanometres (5wt% and above) is facile reduction of the Pd is observed.

In cases where the particle size distribution is dominated by particles of < ca. 3 nm in diameter the reduction for the starting PdO phase is greatly retarded. Indeed it seems likely that the values for N_1^{Pd} returned from the EXAFS in the cases are not purely reflecting the average size of the reduced Pd particles present, as it does for the most part in the 5 and 10wt% systems when ostensibly reduced, but rather reflecting that part of the overall PSD that exists above ca. 3 nm that is greatly diminished in the lower loaded catalysts.

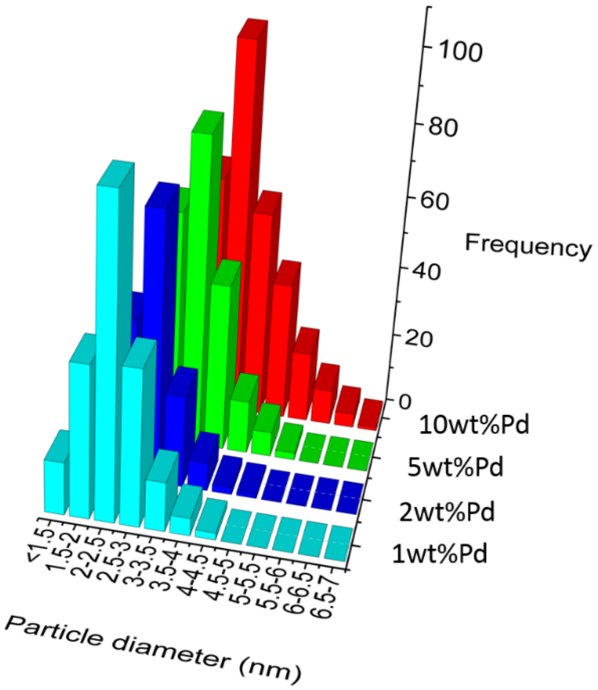

Figure S1 TEM Particle size distributions for the 1, 2, 5, and 10 wt% Pd/Al_2O_3 catalysts

5. XANES Comparison of the 1, 2wt% and 5wt% Pd systems:

Figure S2 shows normalised Pd K-edge white line intensities (24.367 keV) as a function of loop number and comparing 1 wt%Pd/Al_2O_3 (open circles), 2wt% Pd/Al_2O_3 (solid black circles) and 5wt% Pd/Al_2O_3 (solid red circles). The behaviour of the 2wt% Pd sample is more akin to the 1wt% than 5wt% case reinforcing the idea that there appears to be an intrinsic step change in the redox behaviour of Pd between ca. 3 to 4 nm average particle diameter.

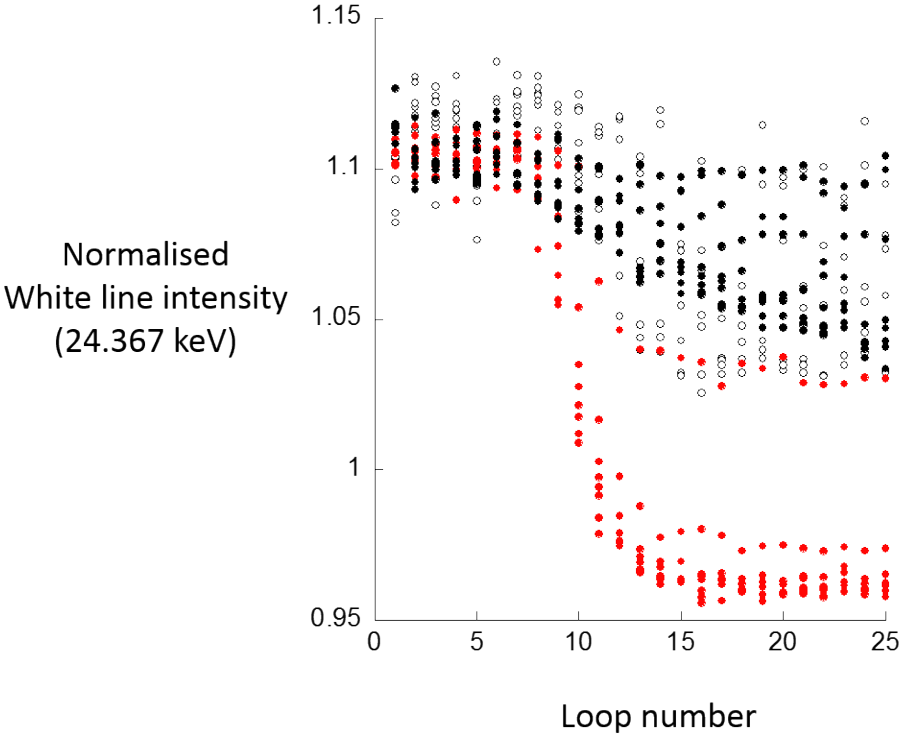

Figure S2 Comparison of normalised Pd K edge white line intensity for 1 wt% Pd (open circles), 2 wt% Pd, (black circles), and 5wt% Pd (solid red) versus loop number. The temperature ramp to 353 K takes place between loop 1 and 13. Beyond loop 13 each sample experiences isothermal operation at 353 K.

Supplementary references

S1 C. Prestipino, "Software for analysis of Quick Exafs and Dispersive XAFS data", https://code.google.com/p/prestopronto/

S2 N. Binsted, PAXAS: Programme for the analysis of X-ray adsorption spectra, University of Southampton, 1988.

S3 N. Binsted, EXCURV98 CCLRC Daresbury Laboratory computer program, 1998.

S4 "*Athena, Artemis, Hephaestus: data analysis for X-ray absorption spectroscopy using IFEFFIT*" B. Ravel and M. Newville, *J. Synchrotron Rad.*, (2005), ***12***, 537–541