Supplementary material (ESI) for Chemical Communications  
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**Supplementary information.**

Supplementary figure 1 shows raw Rh K edge XAFS data obtained at 473K for fully reduced (red) and oxidised Rh nanoparticles (black) obtained in 50 msecs using the FReLoN camera and Si [311] polychromator in Bragg configuration. The inset shows an expanded view of the near edge region and the arrow indicates the major changes in XANES used to follow the oxidation/reduction cycles. Such changes in this part of the XAFS spectrum are indicative of Rh in +3 (black) and 0 (red) oxidation states.

**Figure S1.**

Supplementary figure 2 shows $k^2$ weighted spectra derived from those shown in figure S1, along with theoretical fits derived from analysis in EXCURV98. Structural and statistical information derived from such theoretical fitting is given in table S1.

The data shown in these figures/table may be compared, and found comparable to, previous XAFS data from similar systems $^{1-3}$ taken with the Princeton CCD camera $^4$ and asymmetrically cut Si [111] monochromator in a Laue configuration.$^5$

**Figure S2**
The FReLoN camera, with its greatly superior readout time per spectrum (ca. 800 µsecs compared to ca. 300 msec), compared to the Princeton camera, permits the current experiments to be made with little apparent degradation in data quality. Similarly, the use of a Si [311] in a Bragg configuration, with its greater stability under the heat load of the beam on ID24, has not significantly affected the resolution obtainable at the Rh K edge. The horizontal focus of the beam is however ca 5-10 time greater, than that obtained from the Si[111] in Laue configuration and the band pass the Bragg polychromator provides is ca. 1/2 of that given by a Laue (ca. 2.5KeV) in this energy range.6

Supplementary figure 3 shows the correlation between the extent of oxidation (as measured by changes in the near edge structure of the Rh K edge XAFS) versus atomic oxygen uptake (per Rh present in the sample), as determined by downstream mass spectrometric analysis of the gas phase during oxidation.

**Figure S3.**

At the lowest temperatures investigated a stoichiometry of RhO is indicated after 60 seconds exposure to the oxidising feed; by ca 473K this has reached that expected for the formation of nanosize Rh₂O₃. Above 473K the stoichiometry of the oxidised product at T> 450K is in excess of that expected for the formation of nanosize Rh₂O₃ (reaching a maximum at 573K of ca. RhO₁.₈₅). We have no reason to believe that Rh in excess of an
oxidation state of +3 is being formed at these higher temperatures. Instead mass spectrometry indicates that this apparent “super stoichiometry” is the result of the oxidation of carbon containing residues present on the surface of the support contributing to the apparent oxygen uptake above 473K.

**Supplementary references.**