Oxidation/reduction kinetics of supported Rh/Rh_2O_3 nanoparticles in plug flow conditions using dispersive EXAFS†

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The kinetics of oxidation and reduction of Al_2O_3 supported Rh nanoparticles have been determined on a 50 millisecond timescale using energy dispersive EXAFS (EDE).

Recent results regarding the behaviour of supported metal catalysts,[1–4] and even single crystal surfaces,[5,6] engaged in catalysis involving easily dissociable oxidants, such as O_2 and NO, have shown that changes of phase (from metallic to oxidic) of the active metal component have a very important role to play in determining the rates of catalytic oxidation, selectivity,[2] and even net performance in real situations.[4] A complete understanding and modelling of such systems requires that these processes be quantified

Measurement of the (relatively slow) oxidation of large ($\gg 1$ μm) metal particles,[7] foils,[8] or single crystals,[9] has been within the grasp of the experimentalist for some considerable time. However, the paucity of such detailed kinetic measurements on real, highly dispersed supported catalysts, bears testament to their difficulty. In the current, Rh based, case the only available data concern the reduction of 2–6 ML Rh_2O_3 films (electrochemically deposited from aqueous $RhCl_3$ onto roughened Au) using Surface Enhanced Raman Spectroscopy (SERS).[10] In that report however, "immeasurably fast reduction" was observed above 473 K within the 1 Hz sampling rate afforded by the SERS experiment.

EDE has provided a route to both structural and kinetic determinations in supported metal catalysts for reactions occurring on a time scale of a few seconds.[11] Here we show that EDE recorded in tens of milliseconds, *in situ*, on supported Rh catalysts held in a plug flow configuration, may be utilised to derive kinetic information regarding such rapid processes. 5 wt% Rh/γAl_2O_3 catalysts were made *via* wet impregnation of $RhCl_3 \cdot 3H_2O$. After overnight drying they were then calcined in flowing oxygen (673 K) and sieved to a *ca.* 100 μm fraction. These were then loaded into a previously described plug flow reactor.[1–3] The samples were then reduced *in situ* to 573 K under 20 ml min^{-1} 5% H_2/He.‡ Rh K EDE measurements were then made, during switching of gas flow from 20 ml min^{-1} (GHSV *ca.* 20000 h^{-1}) 5% H_2/He to 5% O_2/He. Detection of the XAFS was made using a phoshor masked FReLoN[12] CCD camera (readout time ~800 μs) using a typical total acquisition time of 50 ms. EDE measurements were made at the gas inlet end of the catalyst bed. The horizontal focus of the Si[311] was 500 μm (FWHM). As such the XAFS experiment is a highly local and specific probe as compared to the mass spectrometer that integrates over the whole 5000 × 3000 μm of the bed.

Figs. 1 and 2 depict the temporal variation in XANES derived from such experiments as a function of temperature: Fig. 1 showing that obtained for reduction of fully oxidised Rh nanoparticles; Fig. 2 that for the reverse process of oxidation of reduced Rh nanoparticles. Representative XAFS spectra along with a description of how these plots are derived is given as electronic supplementary information.† In Fig. 1, zero seconds refers to the time the switch is initiated. In the case of oxidation in Fig. 2, zero seconds refers to the start of a measurable reaction.

These results show that the characters of oxidation and reduction are significantly different. Reduction occurs in a single kinetically limiting step, following an induction period, and at 573 K is complete within 1 second. Oxidation occurs in two stages; a rapid first step, occurring again within one second, is followed by a much slower subsequent oxidation that is increasingly evident at lower temperatures. So the extent of the oxidation observed within the time frame of the experiment is very temperature dependent. An approximately linear correlation exists between the measured O_2 uptake and the changes observed in XANES (see ESI†) and indicates that at 373 K a net stoichiometry of RhO is observed at the end of the experiment; at 573 K this has increased to *ca.* $RhO_{1.85}$.

From these temperature dependent data Arrhenius plots may be constructed (Fig. 3) and from these estimates of the kinetics parameters defining these two processes.

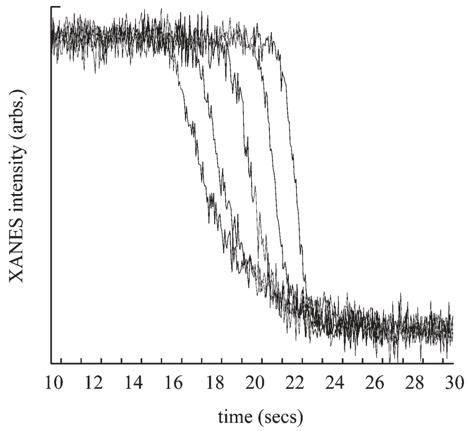

Fig. 1 Temporal variation in Rh K edge XANES during reduction in 20 ml min^{-1} 5% H_2/He at 373, 423, 473, 523 and 573 K. The H_2 was introduced at 0 seconds. A longer time for induction of reaction indexes increasing temperature.

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† Electronic supplementary information (ESI) available: Representative XAFS spectra and a description of how the plots are derived. See http://www.rsc.org/suppdata/cc/b4/b411493k/

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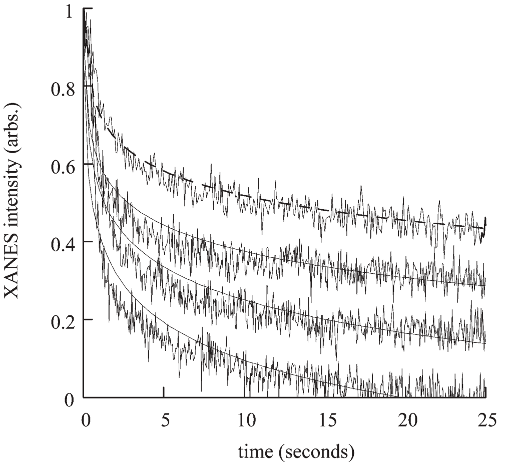

Fig. 2 Temporal variation in Rh K edge XANES (at 23.31 keV) during oxidation at 373, 458, and 573 K. Progressively larger changes index increasing temperature. Smooth lines show logarithmic fits to the data. The increasing spectral intensity in the XANES during this process has been inverted for display.

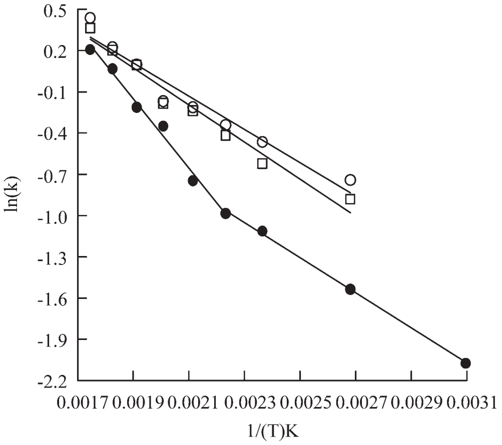

Fig. 3 Arrhenius plots for Rh reduction (solid circles) and oxidation (open circles) . Results from two modes of analysis for the initial oxidation are shown. Open squares are those derived from logarithmic fitting.

Rh reduction follows a pseudo first order rate expression across the temperature range investigated. In the case of the oxidation two methods of analysis were employed. The first was to evaluate the initial rate within the first second of observable reaction; the second to fit the entire oxidation using logarithmic rate law.[8,9] Table 1 summarises the kinetic parameters derived from these approaches and also give those for reduction of rhodium oxide films[10] and oxidation of Rh surfaces.[9]

Table 1 Kinetic parameters derived for oxidation and reduction of supported Rh nanoparticles and those derived for oxidation (of Rh surfaces) in ref. 9 and reduction of Rh_2O_3 particles in ref. 10

Process	E_{act}/kJ mol^{-1}	v/s^{-1}
Reduction (<450 K)	11	7
Reduction (>450 K)	21	100
Reduction (average all T)	14	20
Reduction (ref. 10)	13	30
Initial oxidation (initial rate)	9	10
Oxidation (logarithmic)	12	40
Rh(100)/Rh foil (ref. 9)	4 to 9	

The analysis of the reduction hints at a change in the kinetics of the reduction process above 450 K. Above this temperature there is evidence that E_{act} almost doubles (from 10.6 to 21 kJ mol^{-1}), though this is compensated for by an increase in v by an order of magnitude. The lower temperature (<450 K) value is consistent with that derived from previous SERS experiments[10] *i.e.* 12.5 ($\pm$4) kJ mol^{-1}, as is the average E_{act}, derived by fitting a single line across the data range (14.1 kJ mol^{-1}).

As can be seen from Fig. 1 the oxidation process can be reasonably fitted using a logarithmic rate law, though the quality of fit decreases with increasing temperature. This is consistent with models derived for the oxidation of Rh foil[8] ($873 \text{ K} < T < 973$ K), and Rh[100][9] ($400 < T < 600$ K). The apparent activation energy for this process in nanoparticulate Rh lies in the range $9.2 < E_{act} < 11.8$ kJ mol^{-1}.

Reduction, using H_2, and the initial oxidation by O_2 are therefore facile processes and, as such, the structure of the supported nanoparticles may be highly fluxional (bistable) in environments where the feedstock is prone to fluctuation between oxidising and reducing conditions. The kinetic determinations made (at $T < 450$ K) for the reduction of oxidised Rh nanoparticles are consistent with data derived from SERS[10] though the increased sampling speed attained here leads to a considerably larger dataset for such determinations. Moreover, the rapidity of the EDE experiment allows us to investigate this process at temperatures where it became too fast for SERS (at $T > 473$ K); and it is above this temperature that we find evidence for a change in the kinetics of the reduction process.

An induction time is observed both here and in reference 10 suggesting a nucleation–growth mechanism. Where our results differ from those of ref. 10 is in the induction time for reduction decreasing with increasing temperature; we observe the opposite behaviour suggesting that, in the oxide supported catalyst, the probability of nucleation decreases with increasing temperature.

As with extended Rh surfaces[9] oxidation of these supported Rh nanoparticles is self poisoning and a logarithmic dependence upon time results: the rapid formation of an oxide layer decreases O_2 dissociation, and subsequent oxidation becomes rate limited by diffusion of atomic oxygen into, or Rh atoms out of, the remaining metallic core. The activation energies for this process for extended Rh surfaces,[9] and the catalysts used in the current study, are remarkably similar given the opposite extremes of Rh dispersion they represent.

In summary we have shown that EDE made on a time scale of tens of milliseconds may be used as an effective and quantitative *in situ* probe of the dynamics of rapid phase change in supported nanoparticulate metal catalysts under realistic conditions.

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Notes and references

‡ After reduction the Rh nanoparticles are characterised by a Rh–Rh co-ordination number of *ca.* 7 (average particle diameter of *ca.* 11 Å).

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