Supplementary Data

Redox Behaviour of Pd-based TWCs under Dynamic Conditions: Analysis using dispersive XAS and Mass Spectrometry

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Fig. S1. Experimental spectra for PdA, PdCA and PdZCA samples. The spectrum for the calcined sample is followed by those acquired through the step experiment.
Table S1 Principal Component Analysis of Pd K-edge XANES Results. To determine the number of individual components, an F-test based on the variance associated with factor k and the summed variance associated with the pool of noise factors was performed. A factor was accepted as a "pure" chemical species (i.e. a factor associated with signal and not noise) when the percentage of significance level of the F-test, %SL, was lower than a test level set in previous studies at 5%. The latter means that the null hypothesis of the F test, e.g. that factor k is associated with noise, is rejected for %SL values below such limiting value. The ratio between the reduced eigenvalues, R(r), which describes the ratio between the mathematical norm of factors, was also used in determining the number of chemical species present in the sample. This ratio should approach one (e.g. equal statistical “weight”) for noise-only factors. These tests are fully described in M. Fernández-García, et al., *J. Phys. Chem.*, 99, 12565 (1995).

| Factor | Eigenvalue | %SL | R(r) | Variance
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The variance is a measure of the weight of the eigenvalue norm in the series. Variances lower than 10^-3 are not reported.
The gas mixture and its redox properties are defined by using the Air to Fuel (A/F) and lambda (λ) parameters, both calculated for the inlet gas stream. In our case:

\[
\frac{A}{F} = \frac{14.63}{1 + 0.0255\{[CO] + 9[C_3H_6] - 2[O_2] - [NO]\}}
\]

\[
\lambda = \frac{(A/F)_{ACTUAL}}{(A/F)_{STOI}}
\]

where “actual” stands for the λ value corresponding to the gas mixture under study and “stoi.” for the stoichiometric gas mixture (A/F = 14.63).