Supplementary Data

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

A. Iglesias-Juez,[a] A. Martínez-Arias,[a] M. A. Newton,[b] S. G. Fiddy,[b] and M. Fernández-García[a,*]

a) Instituto de Catálisis y Petroleoquímica, CSIC, Campus Cantoblanco, 28049-Madrid, Spain; b)The European Synchrotron Radiation Facility, BP220, 38043-Grenoble, Cedex 9, France

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.
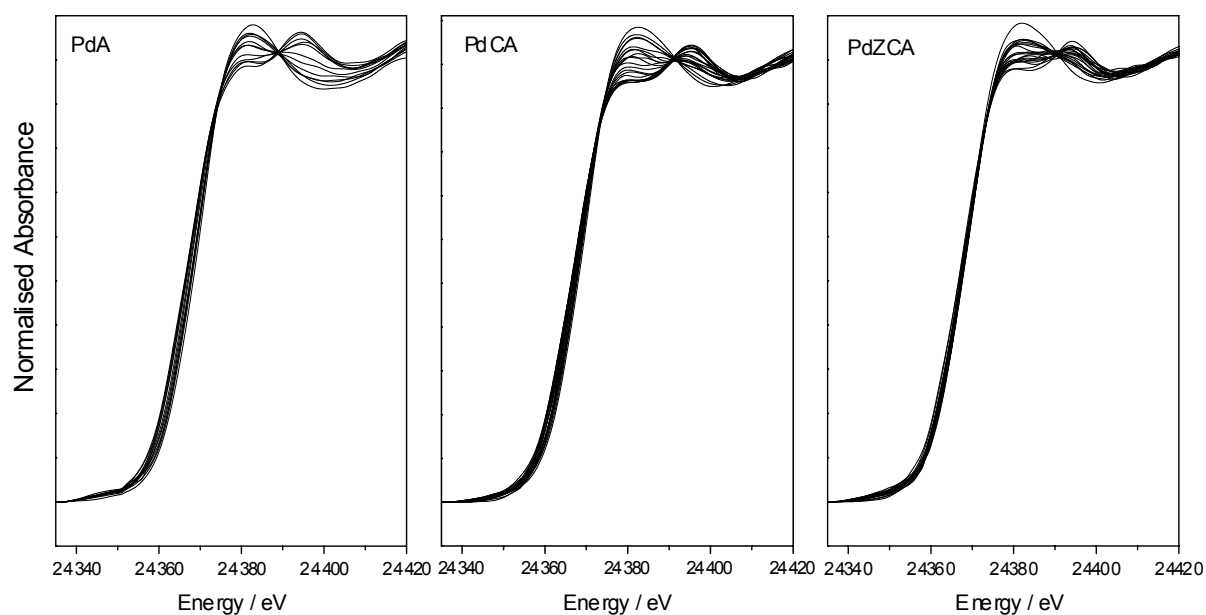
Table S1 Principal Component Analysis of Pd K-edge XANES Results. To determine the number of individual components, an F-test based on the variance associated with factor k and the summed variance associated with the pool of noise factors was performed. A factor was accepted as a "pure" chemical species (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[a]
A. PdA				
1	435.80	0.00	1410.15	99.935
2	0.27575	0.00	63.21	0.063
3	0.00383	12.80	1.63	0.001
4	0.00204	16.05	2.45	0.001
5	0.00070	34.85	1.05	
6	0.00055	36.74	0.86	
7	0.00051	32.61	1.14	
8	0.00033	34.35	1.67	
B. PdCA				
1	644.90	0.00	1793.5	99.946
2	0.33223	0.00	56.04	0.052
3	0.00543	9.03	1.85	0.001
4	0.00268	16.66	1.40	
5	0.00173	21.17	1.06	
6	0.00146	19.02	1.49	
7	0.00087	25.78	1.08	
8	0.00071	25.22	1.14	
C. PdCZA				
1	773.10	0.00	6633.7	99.984
2	0.10882	0.00	21.23	0.014
3	0.0476	11.76	1.73	0.001
4	0.00255	20.61	1.03	
5	0.00228	18.80	1.21	
6	0.00172	20.64	1.17	
7	0.00134	21.90	1.30	
8	0.00093	26.40	1.05	

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:

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

$$\lambda = \frac{\left(A/F\right)_{ACTUAL}}{\left(A/F\right)_{STOI.}}$$

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).