Electronic Supplementary Information: **An *in situ* XAS study of the activation of precursor-dependent Pd nanoparticles**

Christian W. Lopes[ab], Jose L. Cerrillo[a], Antonio E. Palomares[a], Fernando Rey[a], Giovanni Agostini[c]*

[a]Instituto de Tecnología Química (Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas), Avda. de Los Naranjos s/n, Valencia 46022, Spain.

[b]CAPES Foundation, Ministry of Education of Brazil, Brasília 70040-020, Brazil.

[c]Leibniz-Institut für Katalyse, Albert-Einstein-Straβe 29a, Rostock 18059, Germany.

Contents

Table S1. Summary of EXAFS fit of the Pd standards.

Table S2. Summary of optimized parameters by fitting EXAFS data of catalysts after reduction in H_2 at 25 ºC.

Figures

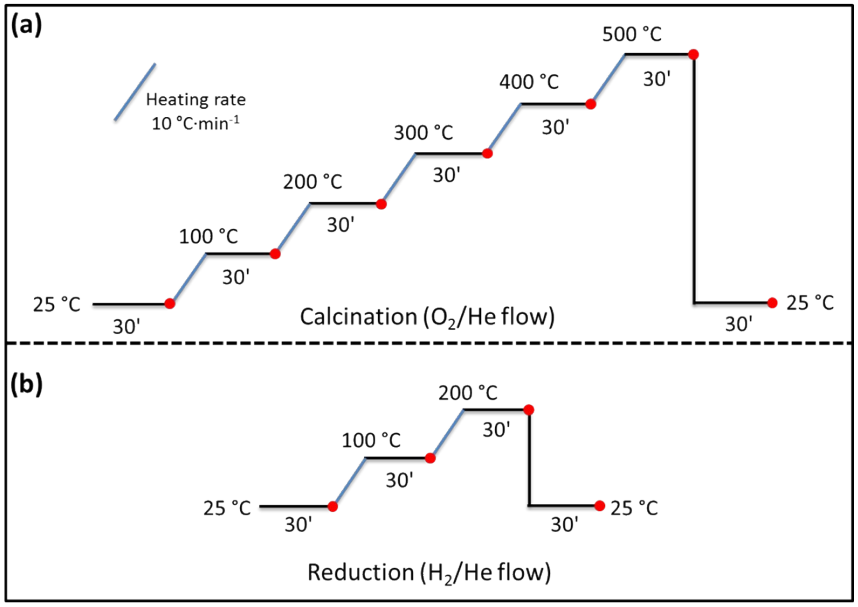

Fig. S1. Experimental steps used in the XAS study of Pd-based catalysts: (a) calcination under O_2/He flow and (b) reduction under H_2/He flow. Every red dot represents a set of 3 measurements.

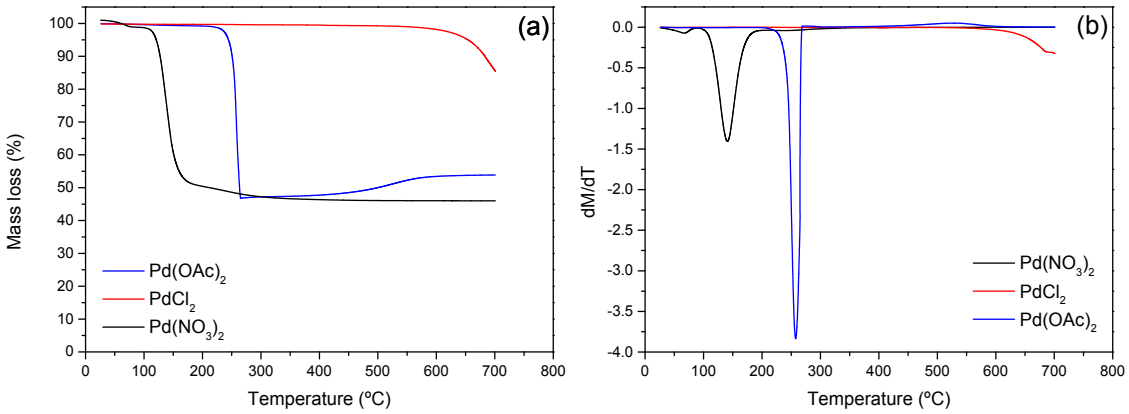

Fig. S2. Thermogravimetric analysis (a) and respective derivative (b) of $Pd(OAc)_2$, $PdCl_2$ and $Pd(NO_3)_2$ precursors.

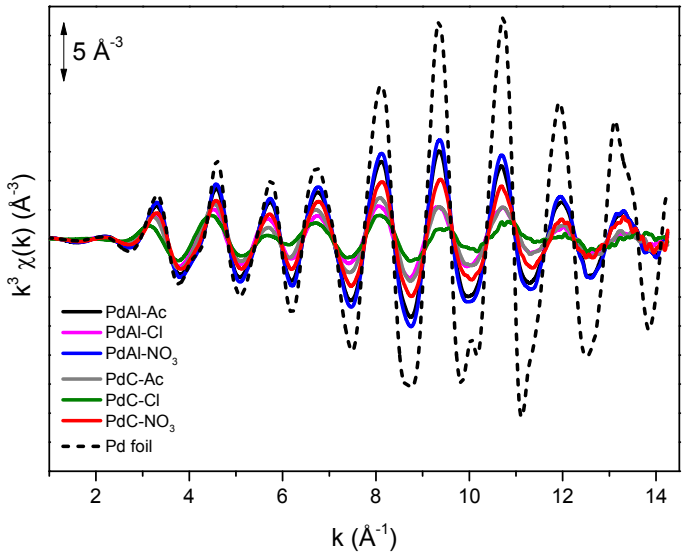

Fig. S3. k^3-weighted, phase-uncorrected $\chi(k)$ functions of Pd-based catalysts during reduction in H_2 at 200 ºC.

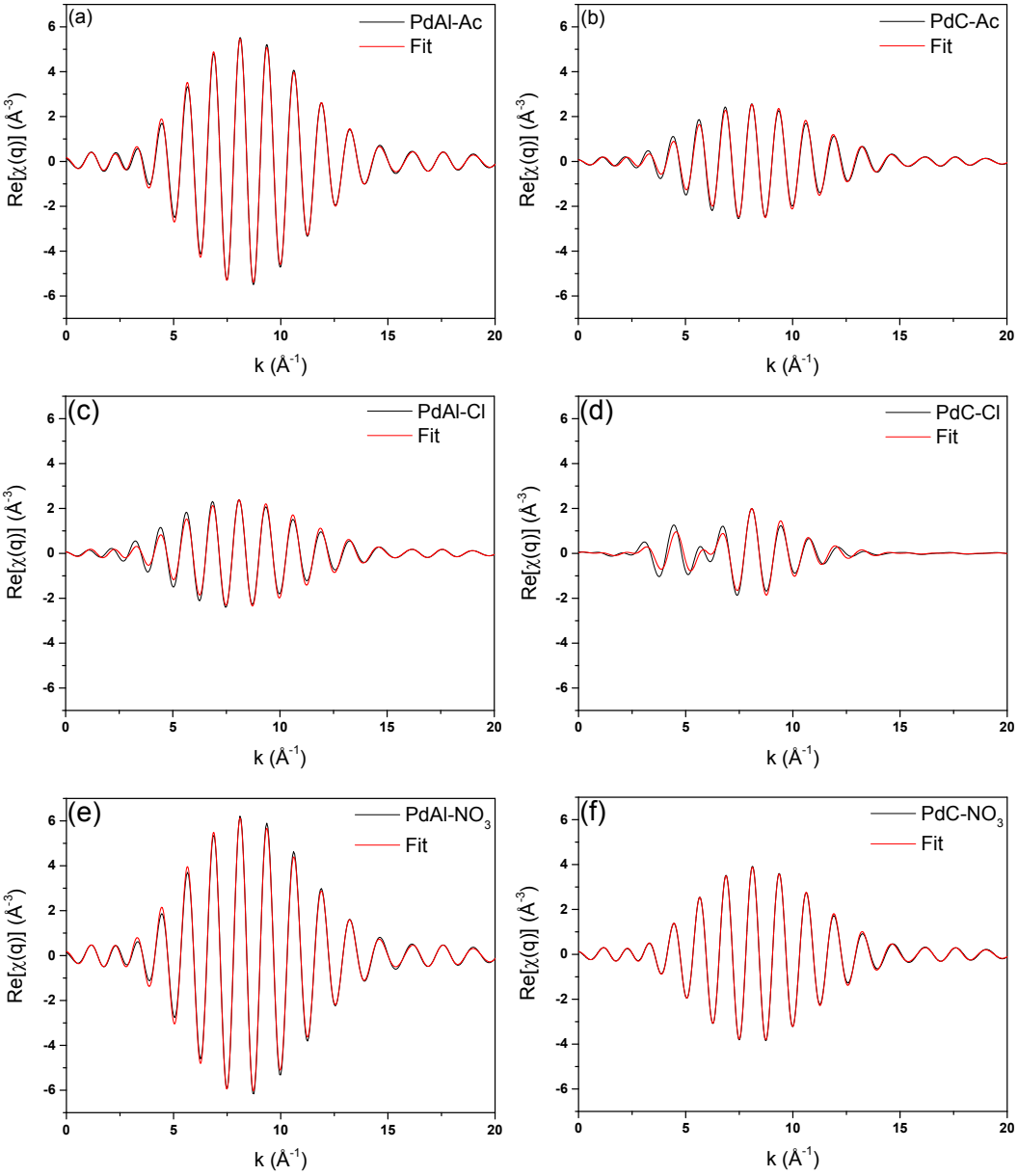

Fig. S4. k^3-weighted, $\chi(q)$ functions (q-range = 2.2-3.0 Å) of Pd-based catalysts during reduction in H_2 at 200 ºC: (a) PdAl-Ac (b) PdC-Ac (c) PdAl-Cl (d) PdC-Cl (q-range = 1.4-3.0 Å) (e) PdAl-NO_3 (f) PdC-NO_3.

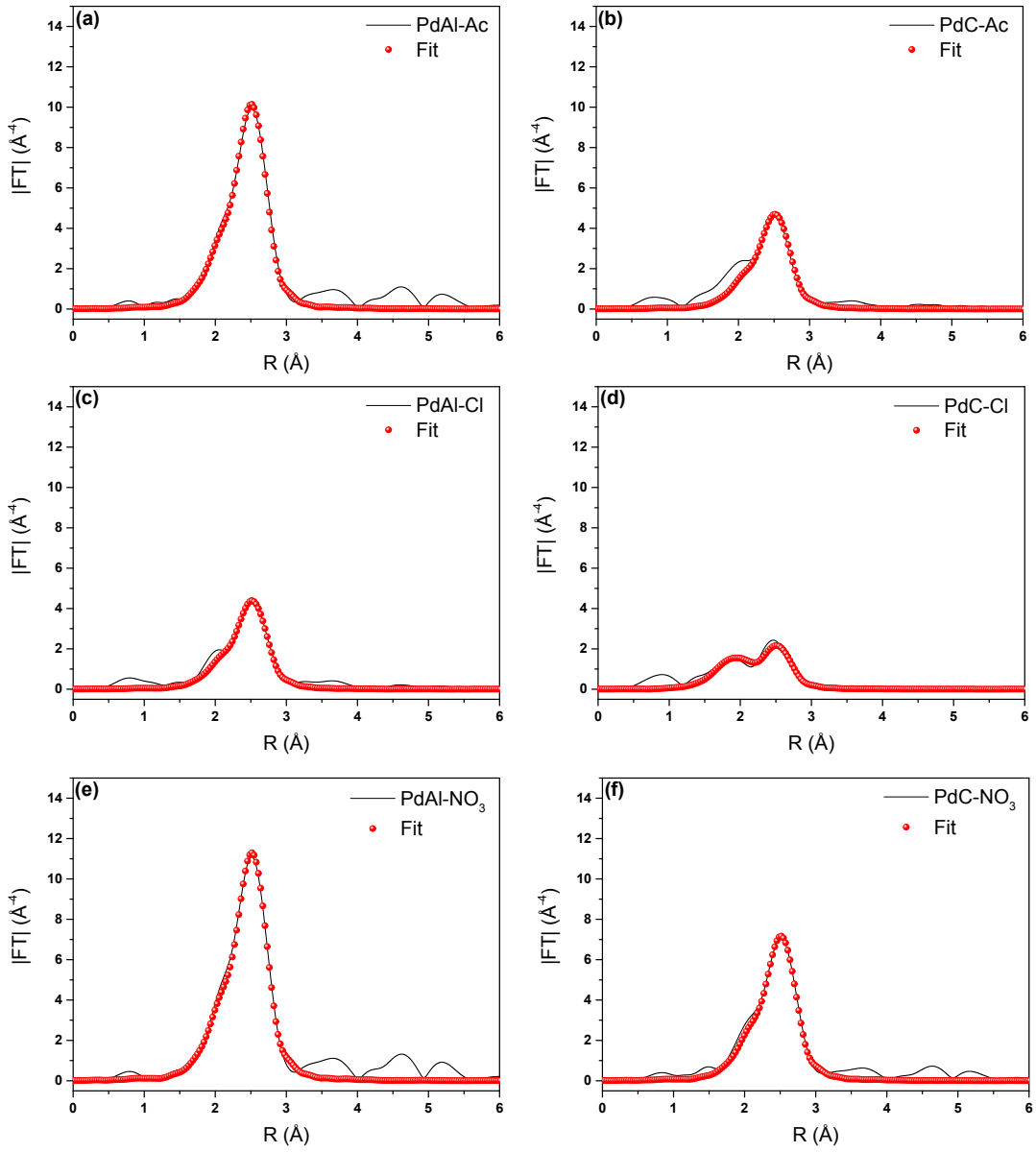

Fig. S5. |FT| of the k^3-weighted $\chi(k)$ functions of catalysts during reduction in H_2 at 200 ºC: (a) PdAl-Ac (b) PdC-Ac (c) PdAl-Cl (d) PdC-Cl (e) PdAl-NO_3 (f) PdC-NO_3.

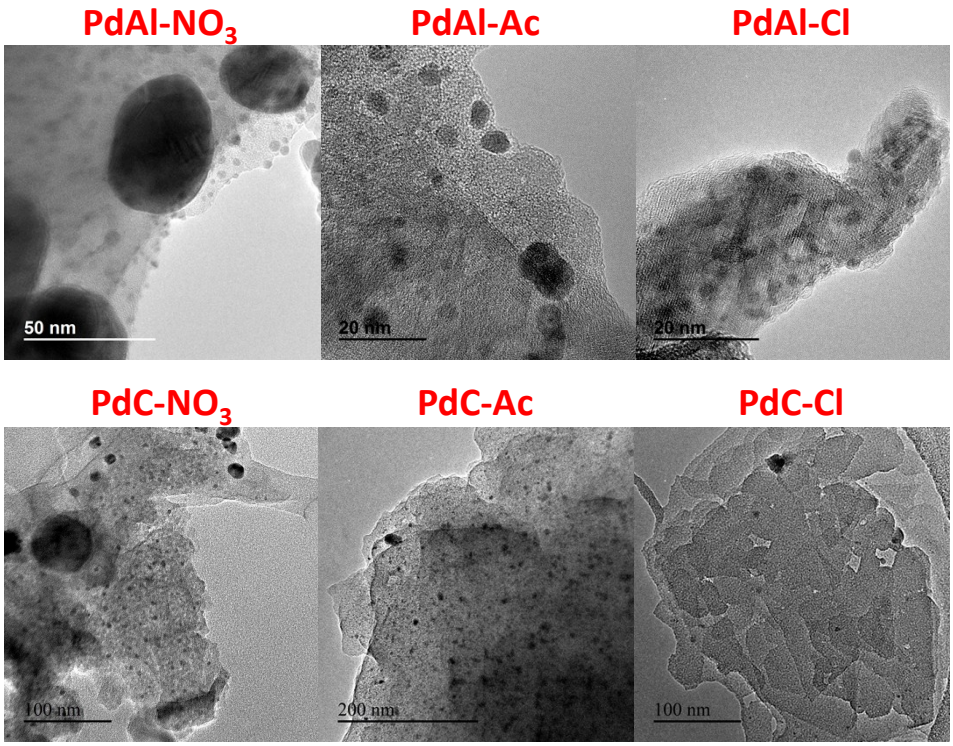

Fig. S6. TEM images of as-reduced Pd/Al_2O_3 (top) and Pd/C (bottom) catalysts according the scheme reported in Fig.S1b.

Tables

Table S1 Summary of EXAFS fit of the Pd standards[a]

Standard	CN	S_0^2	Path	R (Å)	σ^2 (Å^2)	E_0 (eV)	r-factor
Pd foil[b]	12	0.75 ± 0.07	Pd-Pd	2.743 ± 0.003	0.0053 ± 0.0005	4.3 ± 0.8	0.0013
$PdCl_2$[c]	4	1.07 ± 0.05	Pd-Cl	2.314 ± 0.002	0.0033 ± 0.0003	4.2 ± 0.6	0.0013
PdO[d]	4	0.77 ± 0.08	Pd-O	2.022 ± 0.007	0.0016 ± 0.0010	-0.2 ± 1.4	0.0088
$Pd(OAc)_2$[d]	4	0.84 ± 0.13	Pd-O	2.001 ± 0.010	0.0021 ± 0.0008	1.0 ± 1.9	0.0184

[a]The fits were performed on the first coordination shell (at different ΔR) over FT of the k^3-weighted χ(k) functions performed in the Δk = 2.3-13.7 Å^{-1} interval, resulting into a number of independent parameters of $2\Delta R\Delta k/\pi$ = 7.0 (6.8 for Pd foil). Non optimized parameters are recognizable by the absence of the corresponding error bar. [b]ΔR = 2.0-3.0 Å; [c]ΔR = 1.4-2.4 Å; [d]ΔR = 1.0-2.0 Å.

Table S2 Summary of optimized parameters by fitting EXAFS data of catalysts after reduction in H_2 at 25 ºC[a]

Sample	CN	Path	R (Å)	σ^2 (Å^2)	E_0 (eV)	r-factor
PdAl-Ac	-		-			-
PdAl-Cl	6.4 ± 0.3	Pd-Pd	2.792 ± 0.003			0.0027
PdAl-NO_3	12.0 ± 0.6		2.823 ± 0.003	0.0082 ± 0.0003	2.9 ± 0.5	0.0041
PdC-Ac	5.6 ± 0.3		2.783 ± 0.003			0.0126
PdC-Cl[b]	3.1 ± 0.2	Pd-Pd	2.775 ± 0.006			0.0559
PdC-NO_3	7.6 ± 0.4		2.806 ± 0.004			0.0029

[a]A simultaneous fit of the spectra was adopted, fixing the σ^2 and E_0 values; the fits were performed on the first coordination shell (ΔR = 2.2-3.0 Å) over FT of the k^3-weighted χ(k) functions performed in the Δk = 2.3-13.7 Å^{-1} interval, resulting into a number of independent parameters of $2\Delta R\Delta k/\pi$ = 33.3. Non optimized parameters are recognizable by the absence of the corresponding error bar. [b]ΔR = 1.4-3.0 Å.