Supporting Information for

Locating Fe dopants in catalytic PtPd nanoparticles on γ-alumina using x-ray absorption spectroscopy

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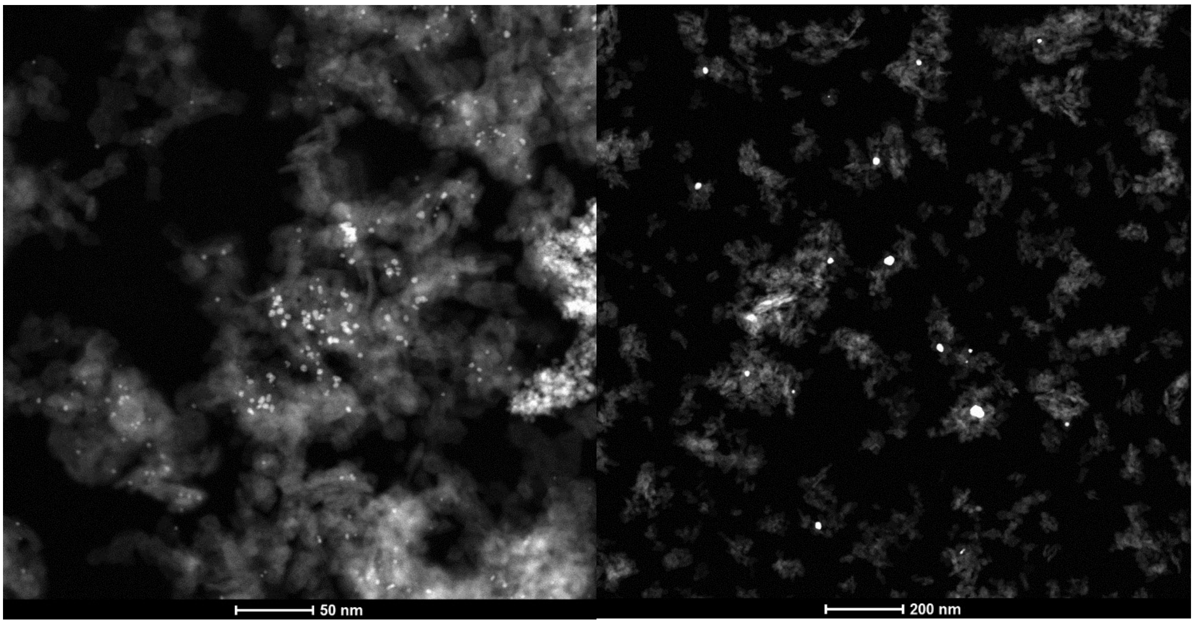
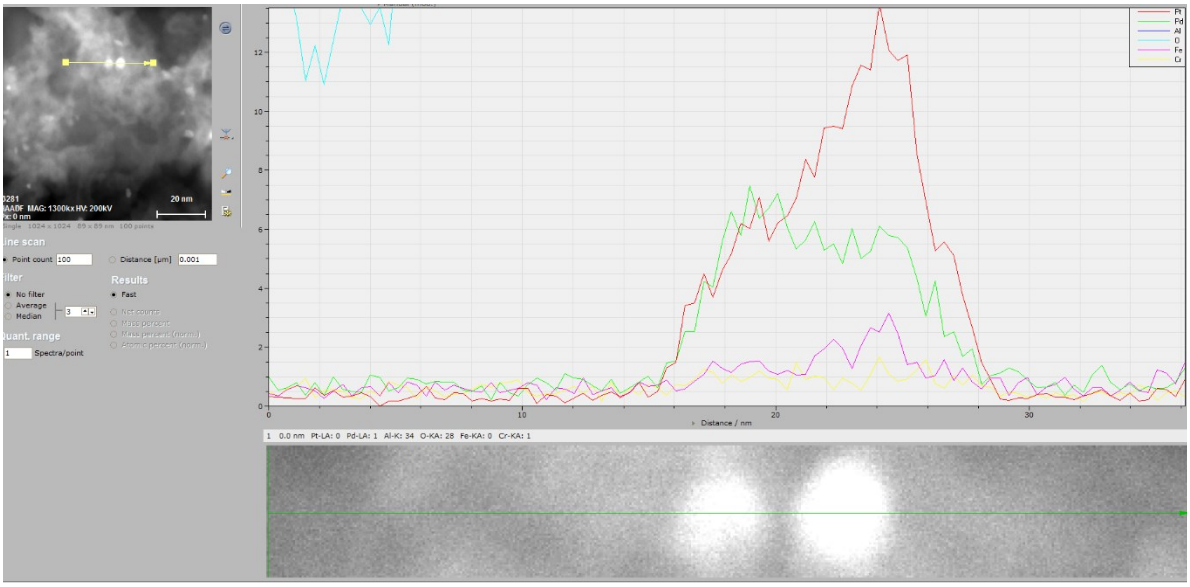
S1 – Nomenclature table. Silva *et al.* are labeling the samples using weight % summing Pt and Pd, while this work uses approximated atomic stoichiometry (or molar ratios). To avoid confusing the corresponding nomenclature are tabulated here, together with the specific nominal w% confirmed by EDX.[1] Note that the samples contain >99 w% alumina substrate.

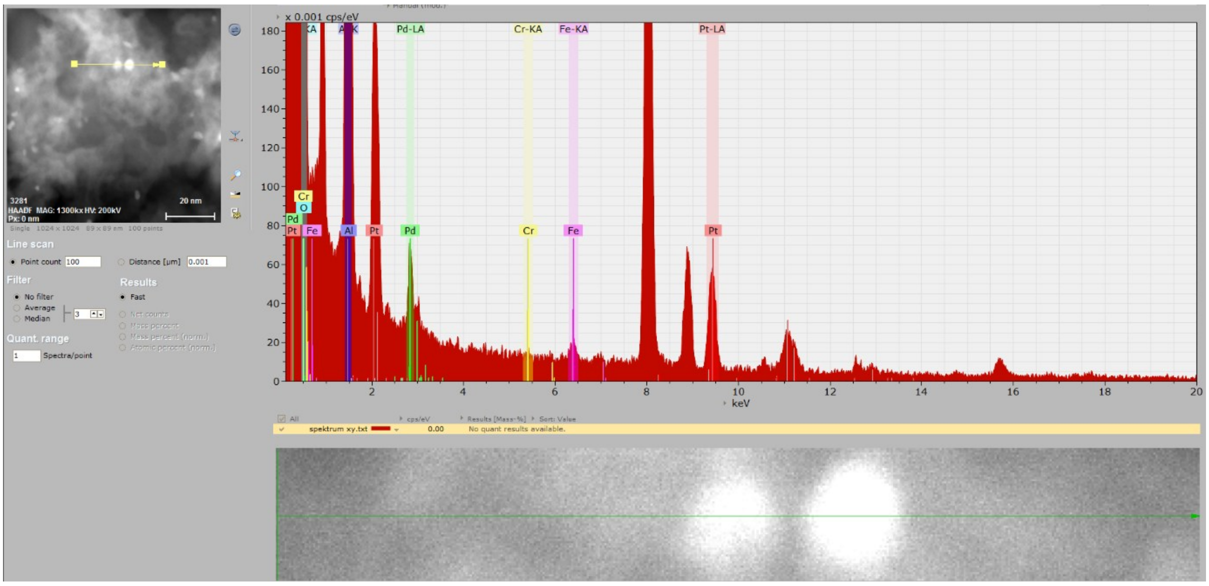
Silva et al.	Eikeland et al.	Pt / w%	Pd / w%	Fe / w%
$\mathbf{(PtPd)_{0.75}}$	$Pt_{0.8}Pd_{0.2}$	0.660	0.165	0
$\mathbf{(PtPd)_{0.70}Fe_{0.05}}$	$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	0.616	0.154	0.05
$\mathbf{(PtPd)_{0.65}Fe_{0.10}}$	$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	0.572	0.143	0.10
$\mathbf{(PtPd)_{0.55}Fe_{0.20}}$	$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	0.484	0.121	0.20
$\mathbf{(PtPd)_{0.70}Fe_{0.05}}$	$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	0.440	0.110	0.25

S2 – STEM picture of the fresh $Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$ sample (left) and annealed sample (right).

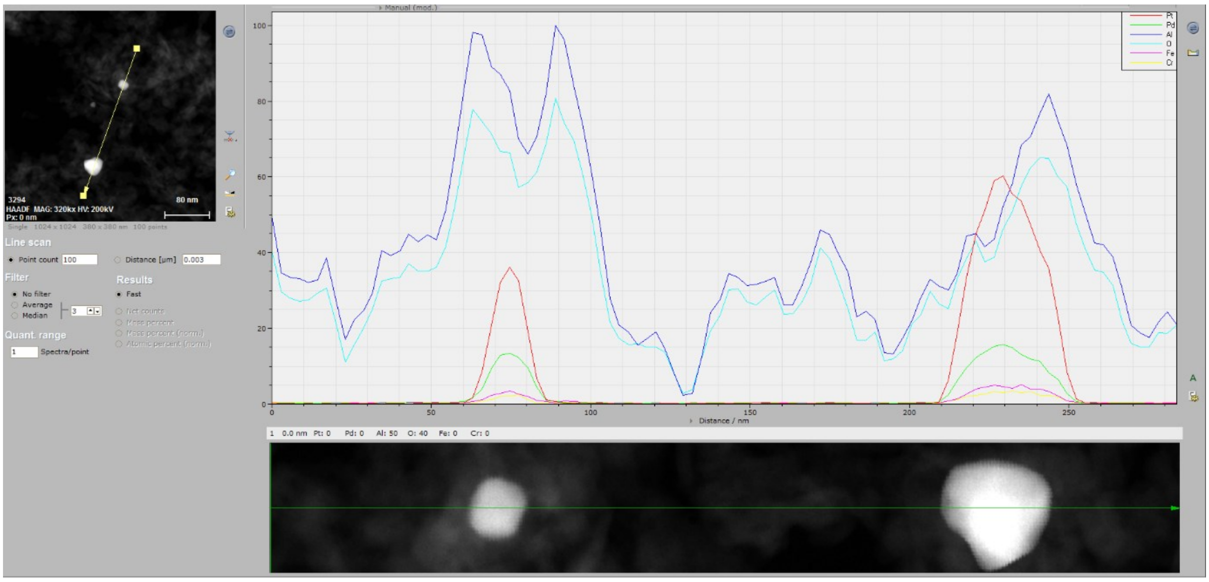


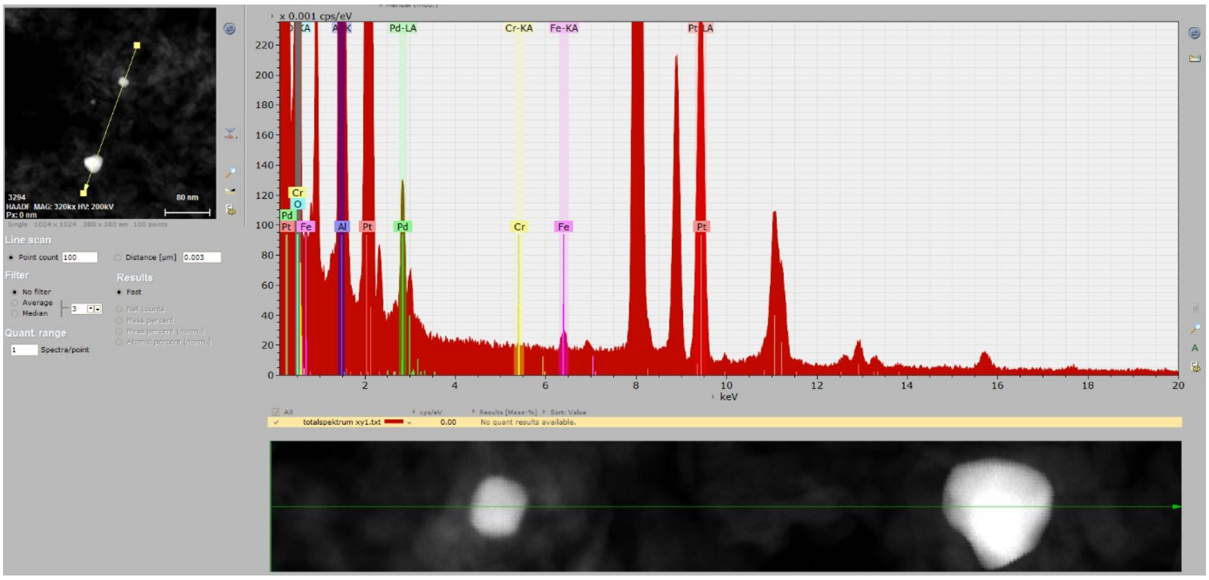
S2. STEM-EDX linescans for the fresh $Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$ sample, showing that the nanoparticles do contain some amount of Fe. Cr is included as an indication of the background signal.





S3. STEM-EDX linescans for the aged $Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$ sample, showing that the nanoparticles do contain some amount of Fe. Cr is included as an indication of the background signal.





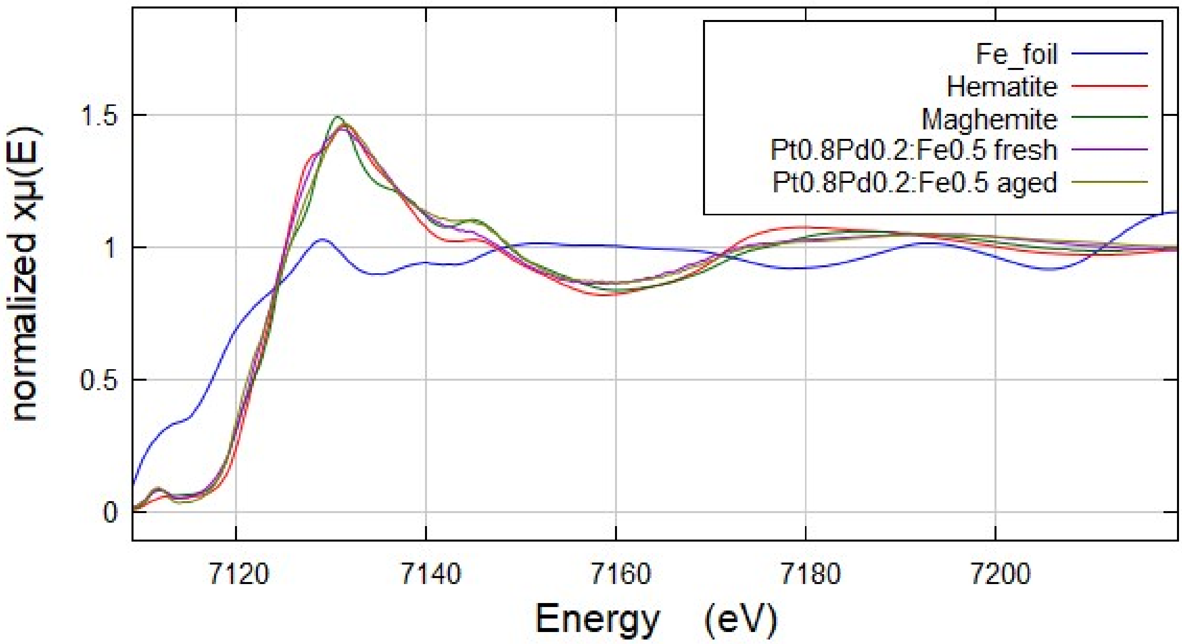
Scanning transmission electron microscopy (STEM) was carried out using a FEI TALOS F220A including energy dispersive X-ray spectroscopy (EDX) and high angle annular dark field (HAADF) at 200kV.

S4. Amount of (PtPd)O_x as result of the temperature programmed reduction experiments (TPR) on the fresh Fe:$Pt_{0.8}Fe_{0.2}$ samples.

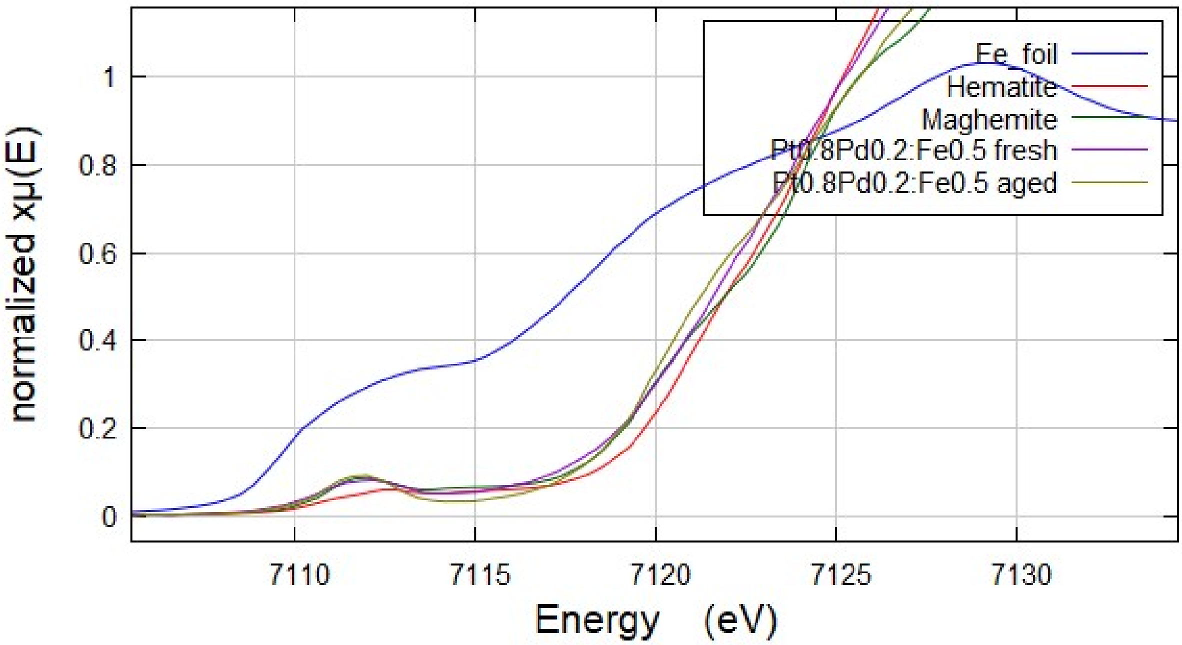
The reduction profiles for the different samples was obtained when using dynamic H_2 chemisorption conditions in a surface characterization apparatus (i.e. 3-Flex from Micromeritics). For this ca. 100 mg of sample were loaded into a quartz reactor that was placed inside an oven and while under a H_2 flow (i.e. 50 ml/min) a temperature ramp of 10 °C/min was applied until 600 °C. The consumption of H_2 obtained from reduction profile area was related with the amount of $(PtPd)O_x$ on the catalyst samples. Since the amount of Pt and Pd oxide on the aged samples was low, it was not possible to use to solve the same technique on the former samples. The TPR results are normalized using a fully oxidized Cu_2O sample and corrected by subtracting the value for the pure substrate. The TPR values are generally higher than the values derived from EXAFS, although it looks as though the addition of Fe reduce amount of oxidized $PtPdO_x$.

Eikeland et al.	**EXAFS / %mol $PtPdO_x$**	**TPR / %mol $PtPdO_x$**
$Pt_{0.8}Pd_{0.2}$	36.5	51(3)
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	37.5	46(3)
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	22.4	44(3)
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	28.8	44(3)
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	31.4	45(3)

S.5 Fe K-edge absorption spectra of all 10 samples and hematite, maghemite and metallic Iron standards. Pd K-edge spectra of all 10 samples including metallic Pd and PdO. Pt L_{III}-edge spectra for all 10 samples including metallic Pt and PtO_2 standards.

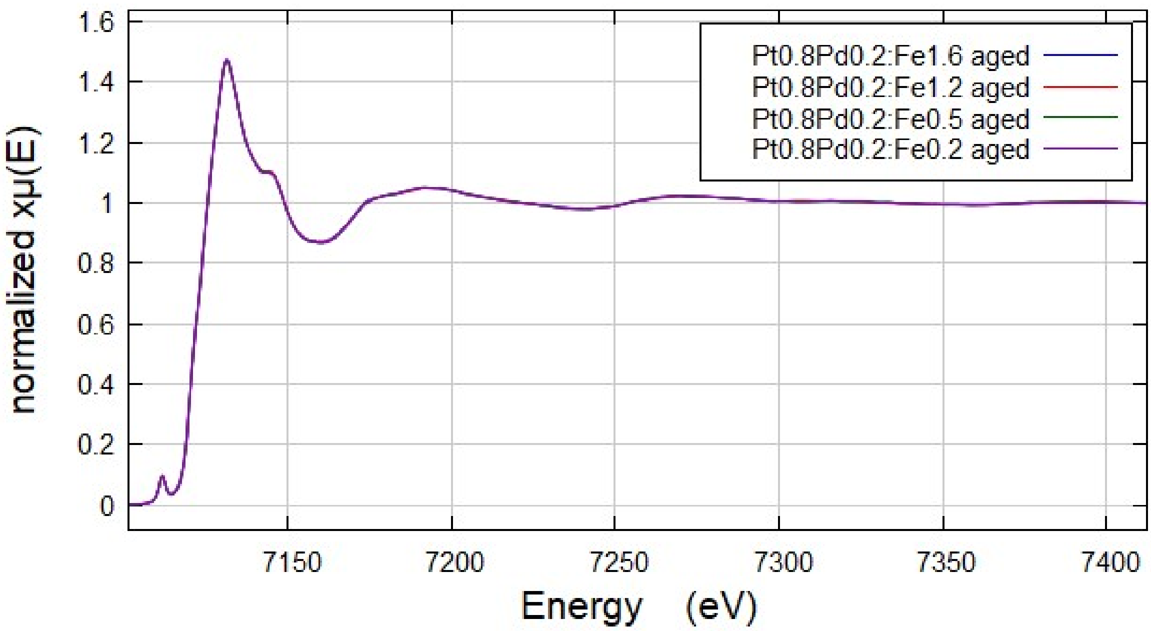


S.5 a) Fe K-edge absorption spectra for $Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$ (fresh & aged) and the metallic Fe, hematite and Meghemite standard. It can be seen that the spectra for the aged and fresh sample is very similar to the hematite and maghemite

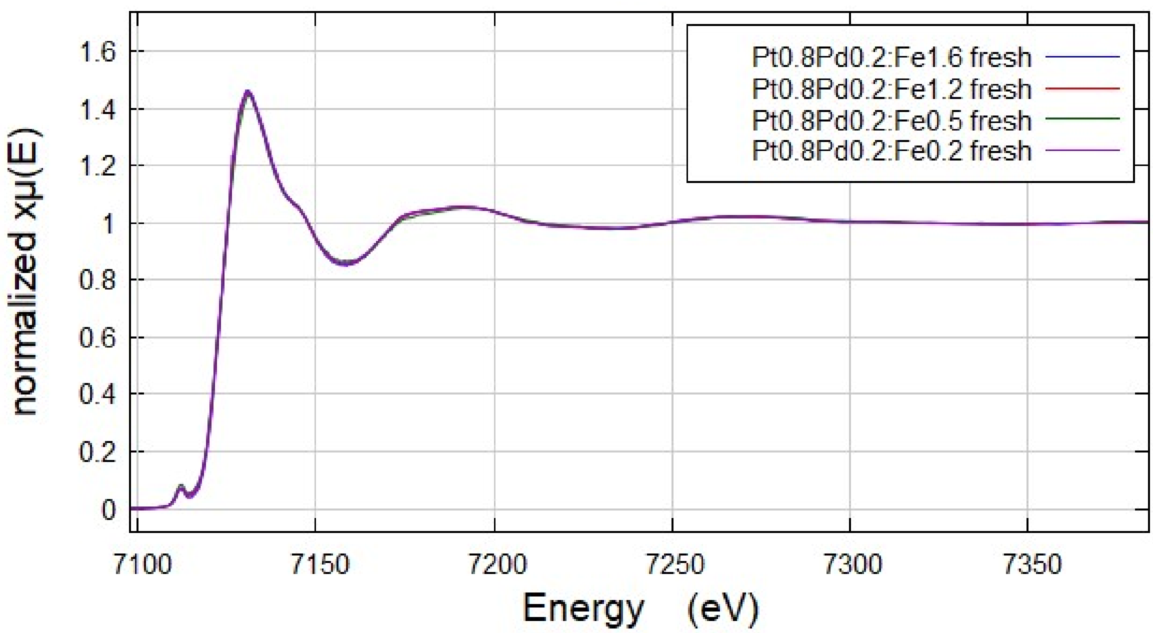


S.5 b) Zoom of figure a, showing that the $Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$ fresh spectrum is shifted slightly to the left towards the Fe standard, indicating that the sample contains some metallic Fe.

standard.

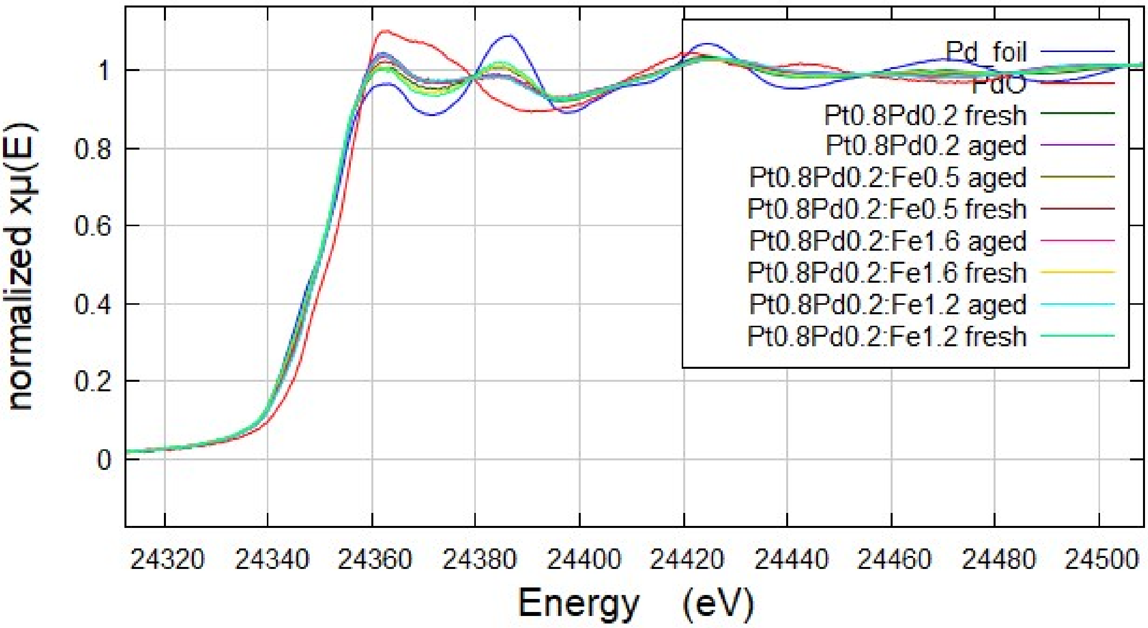


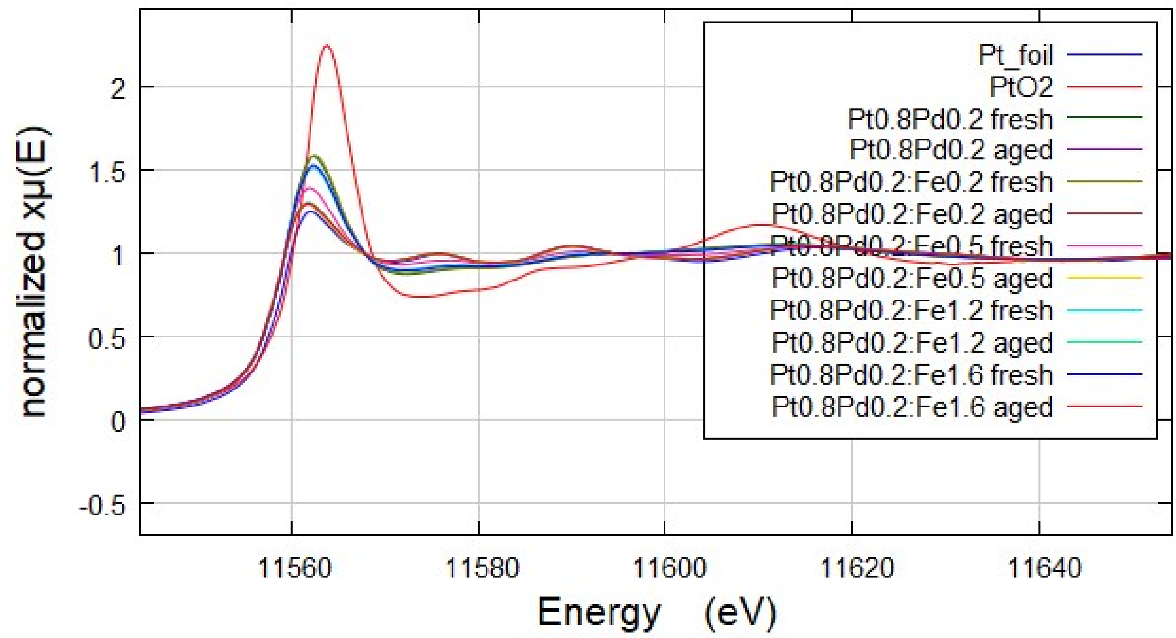
S.5 c) Fe K-edge absorption spectra for the 5 aged samples. The spectra are all very similar.



S.5 d) Fe K-edge absorption spectra for the 5 fresh samples. The spectra are all very similar

S.5 e) Pd K-edge absorption spectra for the 10 samples together with the metallic Pd and PdO standards. All 10 samples can be described as a linear combination of the two standards.





S.5 f) Pt L_{III}-edge absorption spectra for the 10 samples together with the metallic Pt and PtO_2 standards. All 10 samples can be described as a linear combination of the two standards.

Phase fractions from the XANES analysis

					g-Fe2O3		Fe		a-Fe2O3	
Data		**rfactor**	**chinu**	**chisqr**	**weight**	**error**	**weight**	**error**	**weight**	**error**
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	Fresh	0.002459	0.000634	0.10526	0.224466	0.044784	1.05E-09	0.008579	0.775534	0.045598
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	Aged	0.003345	0.000844	0.13919	0.797447	0.051598	5.9E-09	0.009912	0.202553	0.052542
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	Fresh	0.002421	0.000618	0.10199	0.241077	0.044077	5.36E-11	0.008475	0.758923	0.044884
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	Aged	0.003595	0.000894	0.14749	0.805119	0.053016	4.04E-10	0.010198	0.194881	0.053988
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	Fresh	0.00216	0.000531	0.08763	0.349751	0.040961	0.019726	0.007864	0.630523	0.041709
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	Aged	0.003557	0.000894	0.14747	0.766748	0.053117	0.000459	0.010194	0.232792	0.054086
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	Fresh	0.00274	0.000695	0.11528	0.23287	0.046869	3.39E-08	0.008983	0.76713	0.047723
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	Aged	0.003671	0.000913	0.15064	0.759054	0.053622	1.97E-08	0.010308	0.240946	0.054604
$Pt_{0.8}Pd_{0.2}$	Fresh	0.002771	0.000723	0.12	0.270352	0.04777	2.44E-09	0.009167	0.729648	0.048642
$Pt_{0.8}Pd_{0.2}$	Aged	0.00353	0.000881	0.14616	0.844492	0.052624	4.43E-09	0.010115	0.155508	0.053588

					Pd				PdO			
Data		rfactor	chinu	chisqr	weight	error	e0	error	weight	error	e0	error
$Pt_{0.8}Pd_{0.2}$	Fresh	0.000447	6.28E-05	0.0098	0.597958	0.006164	-0.74092	0.063622	0.402042	0.006164	-0.90291	0.079771
$Pt_{0.8}Pd_{0.2}$	Aged	0.000439	6.51E-05	0.01008	0.453926	0.006335	-0.50956	0.087428	0.546074	0.006335	-1.07831	0.062518
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	Fresh	0.000578	8.11E-05	0.01258	0.567031	0.007075	-0.77182	0.077298	0.432969	0.007075	-1.15059	0.086272
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	Aged	0.000823	0.000118	0.01833	0.53676	0.008541	-0.34157	0.104509	0.46324	0.008541	-1.42838	0.10509
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	Aged	0.000749	0.000108	0.0169	0.462858	0.008103	-0.57206	0.109458	0.537142	0.008103	-1.09518	0.08165
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	Fresh	0.000784	0.000111	0.01735	0.476197	0.008171	-0.89871	0.103598	0.523803	0.008171	-1.04177	0.080876
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	Aged	0.000738	0.000109	0.01687	0.470301	0.008165	-0.46732	0.113089	0.529699	0.008165	-1.22392	0.087128
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	Fresh	0.000523	7.36E-05	0.0114	0.627493	0.006696	-0.58275	0.067962	0.372507	0.006696	-1.37027	0.099511
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	Aged	0.000829	0.000123	0.01904	0.445506	0.008685	-0.6093	0.120641	0.554494	0.008685	-0.99818	0.082562
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	Fresh	0.000424	5.91E-05	0.00917	0.674952	0.006011	-0.61014	0.056971	0.325048	0.006011	-1.46952	0.102974

					Pt_foil				PtO2			
	Data	rfactor	chinu	chisqr	weight	error	e0	error	weight	error	e0	error
$Pt_{0.8}Pd_{0.2}$	Fresh	0.000871	0.000184	0.02976	0.643047	0.004435	-0.49749	0.039115	0.360138	0.004031	-1.03184	0.030521
$Pt_{0.8}Pd_{0.2}$	Aged	0.000238	0.000046	0.00746	0.954106	0.002242	-0.60837	0.012063	0.056695	0.002042	-0.67171	0.086194
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	Fresh	0.00083	0.000174	0.02842	0.638925	0.004333	-0.56372	0.037072	0.367369	0.003942	-0.92045	0.027981
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$	Aged	0.000322	0.000062	0.01011	0.964584	0.002596	-0.61259	0.014004	0.046085	0.002365	-0.7422	0.125502
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	Fresh	0.000795	0.000155	0.02503	0.850738	0.004056	-0.60411	0.027324	0.155955	0.003685	-1.13984	0.065328
$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$	Aged	0.00047	8.97E-05	0.01454	0.958168	0.003128	-0.63687	0.016985	0.051491	0.00285	-0.72961	0.133696
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	Fresh	0.000878	0.00018	0.02908	0.720838	0.00439	-0.53601	0.034114	0.287432	0.003991	-0.98403	0.037164
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$	Aged	0.000547	0.000105	0.01696	0.950382	0.003394	-0.62308	0.017922	0.061593	0.003097	-0.4982	0.114597
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	Fresh	0.001004	0.000204	0.03312	0.700443	0.004689	-0.5416	0.037246	0.304814	0.004262	-0.96433	0.037119
$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$	Aged	0.000519	9.93E-05	0.01608	0.9558	0.003306	-0.58999	0.017311	0.055715	0.003017	-0.45623	0.122912

The XANES analysis of the PtPd1.0Fe0.30 samples gave the following metallic phase fractions, similar to figure 1 in the main text.

Fresh			**Aged**		
Pt	Pd	Fe	Pt	Pd	Fe
0.728(4)	0.564(8)	0.043(9)	0.964(2)	0.503(9)	0.011(8)

S.6 EXAFS refinement parameters using Artemis (Demeter software package v.0.9.26)

Amplitude dampening factor, Pt-Pt cluster (so)
Amplitude dampening factor, Pt-Pd cluster (so2)
Energy shift, Pt-Pt cluster (ee)
Energy shift, Pt-Pd cluster (ee2)
Scattering length (d)
Debye-Waller dampening (ss)
k-range = 3.0 – 14.0 $Å^{-1}$
R-range = 1.7 – 3.3 Å
so & so2 are normalized to give the number of Pt-Pt and Pt-Pd neighbors, respectively. The normalization factor is found by refining the Amplitude dampening factor using data collected on a Pd bulk standard.

$Pt_{0.8}Pd_{0.2}$ aged

guess parameters:

```
 so     =  10.76668350   # +/-   1.16859794
 ee     =  10.52655319   # +/-   0.96485734
 d      =   0.04674709   # +/-   0.00570227
 ss     =   0.00554384   # +/-   0.00057387
 so2    =   0.77993462   # +/-   0.48837628
 ee2    =   4.43612473   # +/-   5.45151973
```

Reduced chi-square : 2556.8595539

R-factor : 0.0306801

$Pt_{0.8}Pd_{0.2}$:$Fe_{0.2}$ aged

```
 so     =  10.36796229   # +/-   1.03737037
 ee     =  10.53639517   # +/-   0.90944151
 d      =   0.04447622   # +/-   0.00551790
 ss     =   0.00568304   # +/-   0.00055487
 so2    =   0.08901803   # +/-   0.03023334
 ee2    =   6.02053159   # +/-   3.03373108
```

Reduced chi-square : 1224.9504310

R-factor : 0.0266678

$Pt_{0.8}Pd_{0.2}$:$Fe_{0.5}$ aged

```
 so     =   9.26817957   # +/-   0.95557021
 ee     =  10.45738678   # +/-   0.96678268
 d      =   0.04121301   # +/-   0.00604678
 ss     =   0.00558257   # +/-   0.00060706
 so2    =   1.85951131   # +/-   0.37451284
 ee2    =   7.50426323   # +/-   1.87886648
```

Reduced chi-square : 664.0829065

R-factor : 0.0309945

$Pt_{0.8}Pd_{0.2}$:$Fe_{1.2}$ aged

```
 so     =  10.01633870   # +/-   1.07692304
 ee     =  10.45523796   # +/-   0.98856221
 d      =   0.04308736   # +/-   0.00627751
 ss     =   0.00577232   # +/-   0.00063013
 so2    =   1.47953940   # +/-   0.43371099
 ee2    =   6.64134320   # +/-   2.62096732
```

Reduced chi-square : 637.7214395

R-factor : 0.0330918

$Pt_{0.8}Pd_{0.2}$:$Fe_{1.6}$ aged

```
 so     =  10.41969875   # +/-   1.12787956
 ee     =  10.60899722   # +/-   0.97751045
```

d = 0.04536011 # +/- 0.00597983
ss = 0.00567520 # +/- 0.00060165
so2 = 1.20372612 # +/- 0.45986020
ee2 = 5.82506988 # +/- 3.37424933

Reduced chi-square : 655.2328385
R-factor : 0.0314529

PtPd1.0Fe0.30* [a sample containing 0.3 w% Fe and 1.0 w% Pt+Pd (4:1 molar ratio). The results are not included in the main paper, since the metal load is much higher]
so = 10.48248032 # +/- 1.11325263
ee = 10.38904653 # +/- 0.96841676
d = 0.04350763 # +/- 0.00574403
ss = 0.00569379 # +/- 0.00057736
so2 = 1.10771570 # +/- 0.45201357
ee2 = 5.77859854 # +/- 3.66718980
Reduced chi-square : 1670.2470602
R-factor : 0.0289680

Reference

1. H. Silva, P. Hernandez-Fernandez, A. K. Baden, H. L. Hellstern, A. Kovyakh, E. Wisaeus, T. Smitshuysen, I. Chorkendorff, L. H. Christensen, D. Chakraborty and C. Kallesøe, *Catalysis Science & Technology*, 2019, **9**, 6691-6699.