Supporting Information

Figure S01 shows the imaging results from HAADF-STEM of the fresh $(PtPd)_1/\gamma\text{-}Al_2O_3$ catalyst.

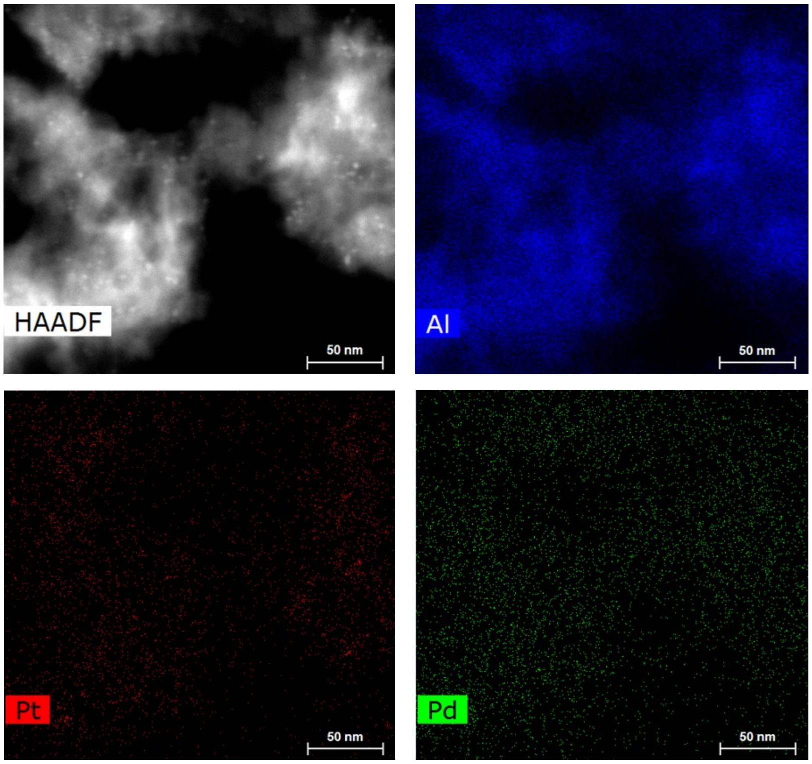

Figure S01 – EDX mapping of fresh $(PtPd)_1/\gamma\text{-}Al_2O_3$ catalyst.

SEM-EDX confirmed the incorporation of Fe in the $(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$ catalyst through supercritical synthesis, however to analyse the local composition of the supported nanoparticles, line-scans were performed through HAADF-STEM. Figure S02 a) shows a line-scan on the $\gamma\text{-}Al_2O_3$ support region and no Fe, Pt or Pd were detected, being Cr added as a standard element to stablish a level of noise. On the case of Figure S02 b) the nanoparticles composition is analysed, and the line-scan indicates the presence of Pt, Pd and Fe that is slightly above Cr signal.

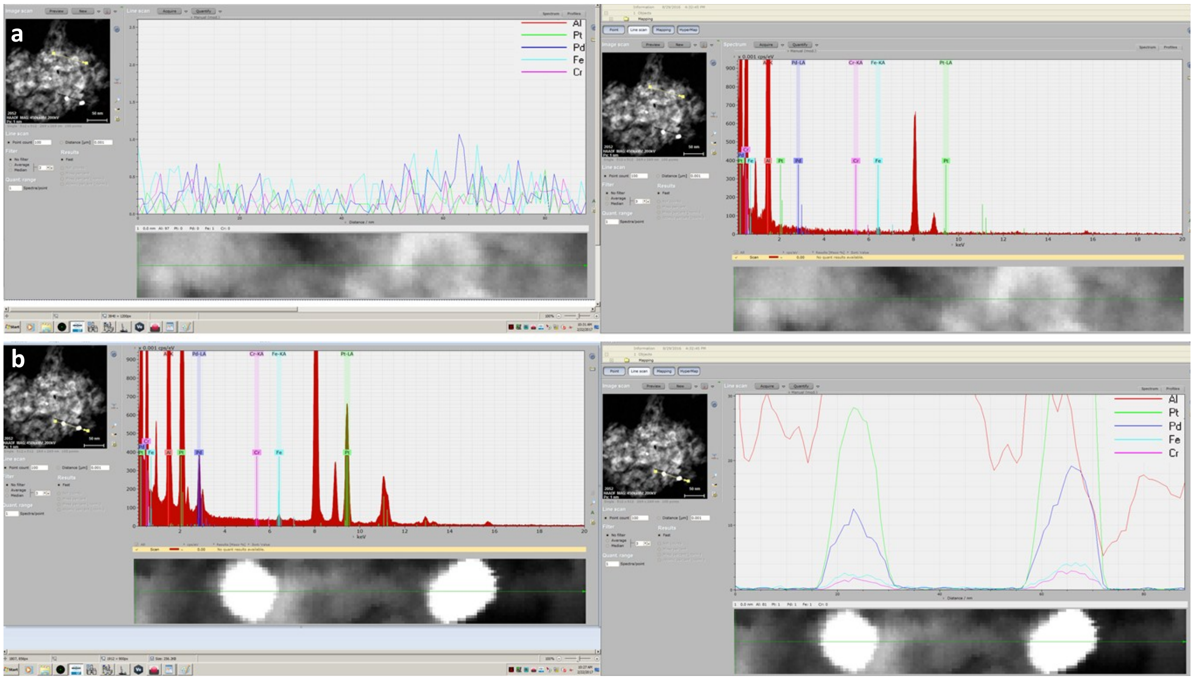

Figure S02 – a) EDX line-scan of the support region of the $(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$ fresh catalyst b) EDX line-scan of the $(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$ fresh catalyst nanoparticles.

Figure S03, shows the elemental mapping of the aged $(PtPd)_1/\gamma\text{-}Al_2O_3$ catalyst, were the O mapping is matching with the $\gamma\text{-}Al_2O_3$ support and the nanoparticle region indicates the presence of Pt and Pd.

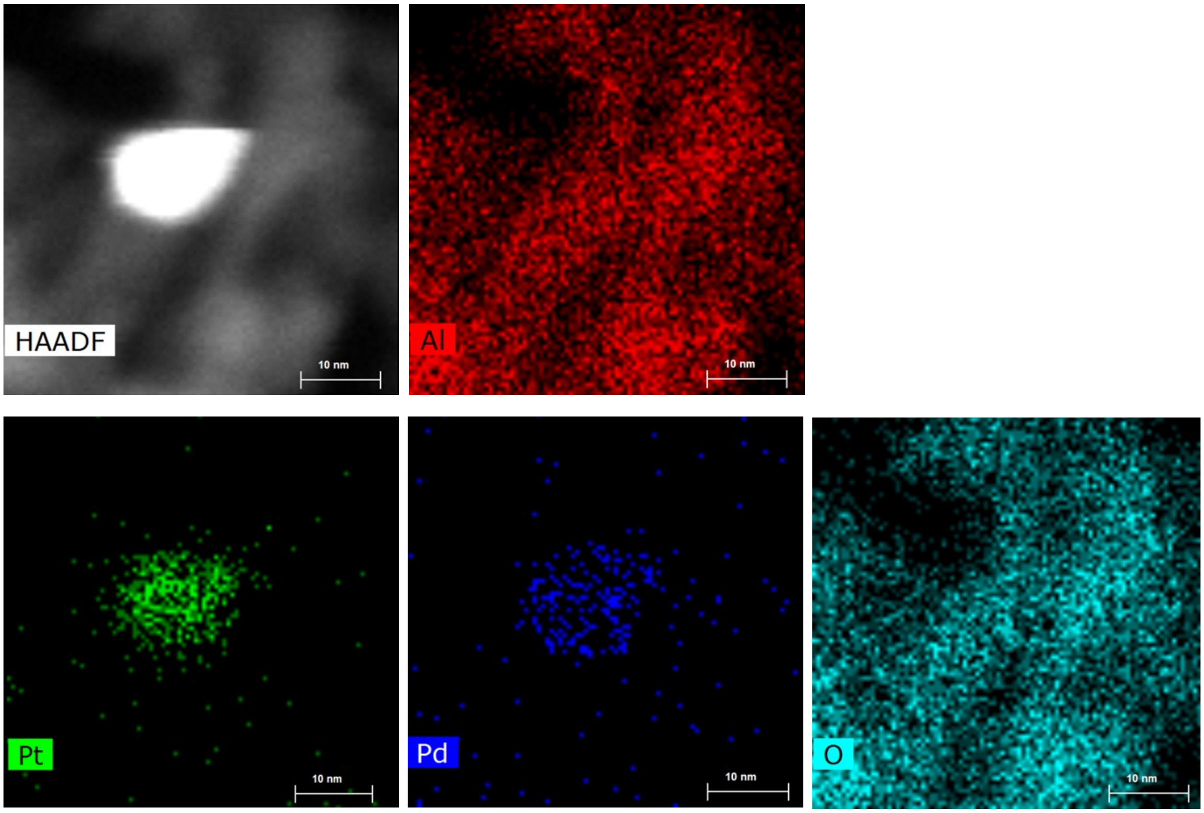

Figure S03 – EDX mapping of the aged $(PtPd)_1/\gamma\text{-}Al_2O_3$ catalyst nanoparticles.

Figure S04 and Figure S05, shows the results of HAADF-STEM mapping and line-scan, respectively, for the aged $(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$ catalyst. As a result, even after aging, Fe is confirmed to be part of the nanoparticles composition, along with Pt and Pd.

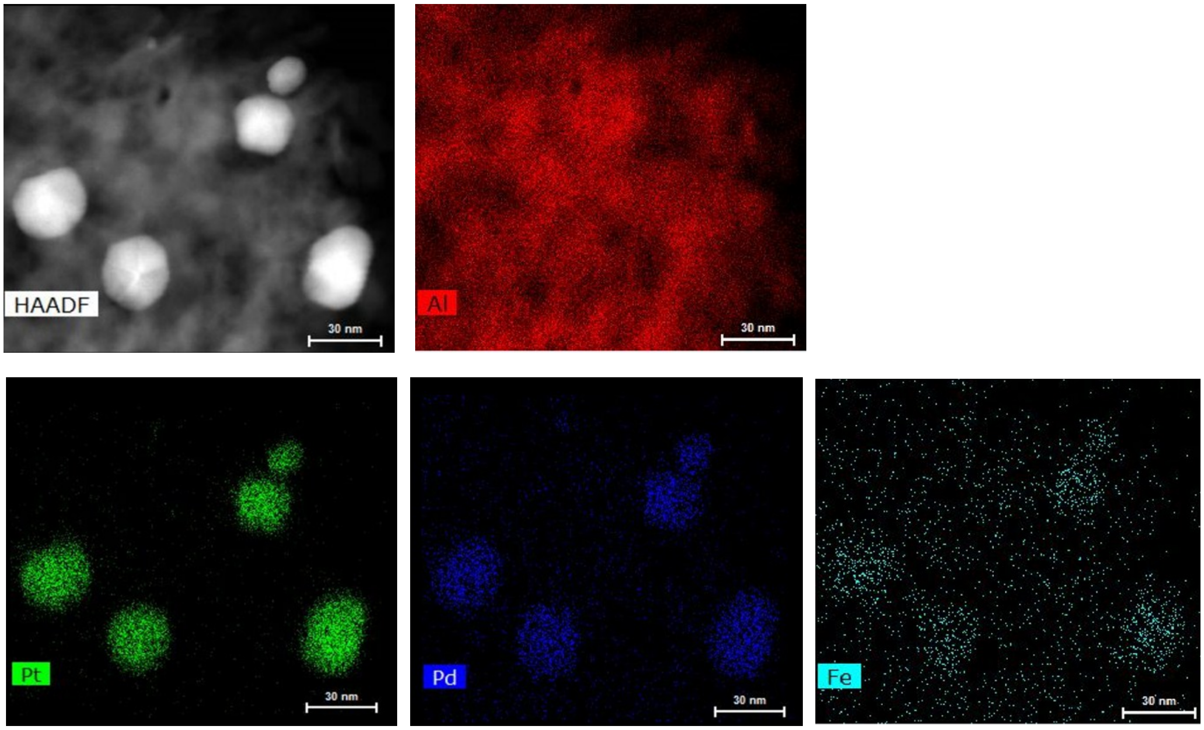

Figure S04 – EDX mapping of the aged $(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$ catalyst nanoparticles.

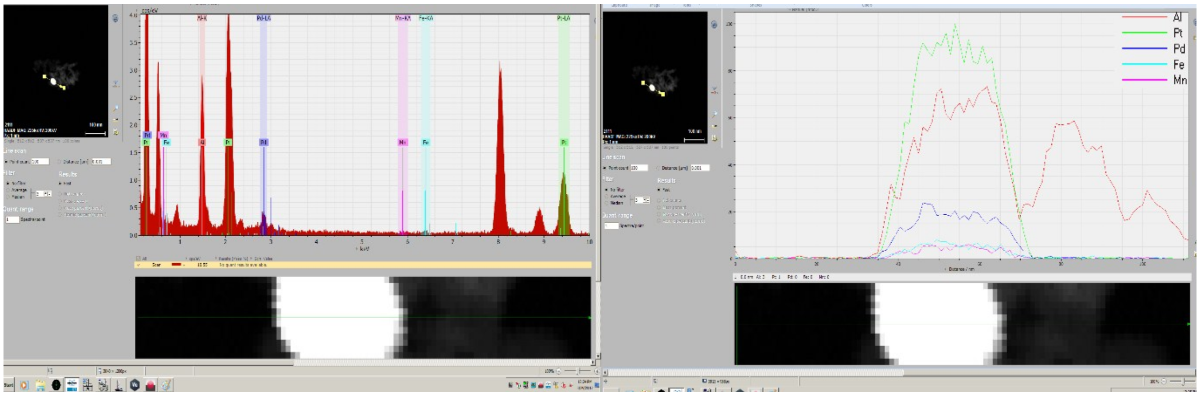

Figure S05 - EDX line scan of the aged $(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$ catalyst nanoparticles.

Figure S06, shows the PtPdFe nanoparticles size-distribution on the $(PtPd)_{0.65}Fe_{0.10}/\gamma\text{-}Al_2O_3$ catalyst, being the average nanoparticle size estimated to be 2.7 ± 0.6 nm.

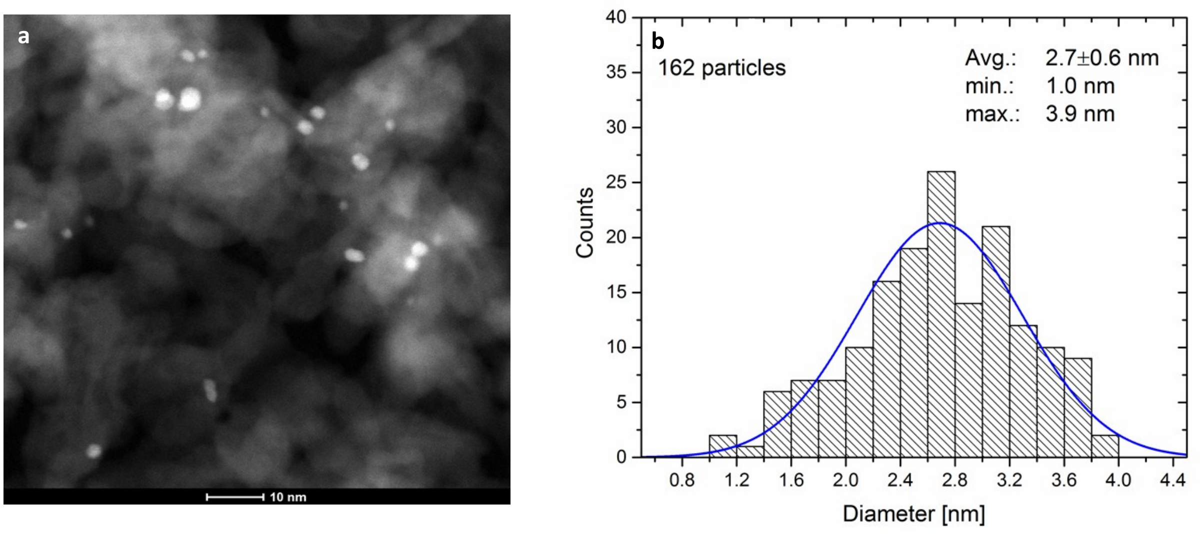

Figure S06 – a) HAADF-STEM images and b) particle size distribution with fitted normal distribution curve of the $(PtPd)_{0.65}Fe_{0.10}/\gamma\text{-}Al_2O_3$ catalyst.

Figure S07 shows the average crystallite sizes of the supercritical synthesized $PtPd/\gamma\text{-}Al_2O_3$ and $PtPdFe/\gamma\text{-}Al_2O_3$ catalysts, as a result of synchrotron x-ray powder diffraction measurements.

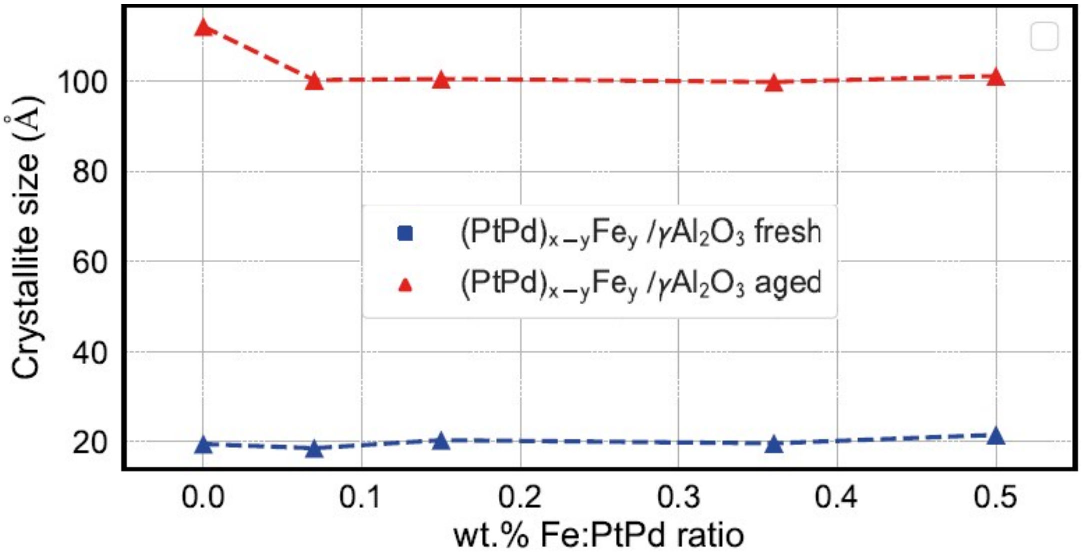

Figure S07 – Average crystallite sizes of the supercritical synthesized PtPd/γ-Al_2O_3 and PtPdFe/γ-Al_2O_3 catalysts measured by synchrotron x-ray powder diffraction.

Table S01 shows the wt.% composition of the supercritical synthesized catalysts, named as $(PtPd)_xFe_y$/γ-Al_2O_3, where x stands for the combined PtPd nominal metal loading and y represents Fe nominal metal loading in wt.%. Moreover, the EDX metallic loadings are provided for comparison with the nominal amounts. It should be noted that elemental quantification of Fe and Pd through SEM-EDX is challenging since the nominal amounts are close to the detection limit of the technique.

Table S01 – Compilation of the supercritical synthesized catalyst samples with their respective nominal and EDX determined metallic composition in wt.%.

Catalyst name	**Nominal Composition (wt%)**			**EDX Composition (wt%)**		
	(Pt)	**(Pd)**	**(Fe)**	**(Pt)**	**(Pd)**	**(Fe)**
$(PtPd)_1/\gamma\text{-}Al_2O_3$	0.89	0.20	-	0.78	0.17	-
$(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$	0.89	0.20	0.30	0.73	0.13	0.12
$(PtPd)_{0.75}/\gamma\text{-}Al_2O_3$	0.66	0.15	-	0.65	0.10	-
$(PtPd)_{0.70}Fe_{0.05}/\gamma\text{-}Al_2O_3$	0.62	0.14	0.05	0.58	0.13	0.06
$(PtPd)_{0.65}Fe_{0.10}/\gamma\text{-}Al_2O_3$	0.58	0.13	0.10	0.51	0.13	0.11
$(PtPd)_{0.55}Fe_{0.20}/\gamma\text{-}Al_2O_3$	0.49	0.11	0.20	0.45	0.11	0.18
$(PtPd)_{0.50}Fe_{0.25}/\gamma\text{-}Al_2O_3$	0.44	0.10	0.25	0.40	0.07	0.19

The turn over frequency (TOF) was calculated for $(PtPd)_1/\gamma\text{-}Al_2O_3$ and $(PtPd)_1Fe_{0.3}/\gamma\text{-}Al_2O_3$ catalysts, using the following equation:

$$TOF = \frac{Atomic\ Rate}{Dispersion \cdot Total\ number\ of\ atoms}$$

where the atomic rate expresses the number of propene molecules converted per unit of time, and the dispersion factor that is multiplying by the total number of atoms, represents the number of surface atoms available for the propene oxidation reaction. Overall, the TOF quantifies the specific activity of a catalytic site under defined reaction conditions per unit of time [1]. The atomic rate, can be simply determined by multiplying the measured reaction conversion by the total flow rate of propene molecules that is supplied to the reactor. The dispersion factor is the fraction of surface atoms, and assuming spherical nanoparticles the following equation can be used for calculations:

$$Dispersion = \frac{6 \cdot \left({}^{av}/_{as} \right)}{dp}$$

where av is the volume occupied by an atom in bulk of the metal, as is the area occupied by a surface atom and dp the nanoparticles average diameter. To facilitate the calculations, the av and as were obtained from tabled values that are derived from XRD analysis, and for simplification was assumed the data of face-centered cubic Pt metal [2]. The nanoparticles average diameter, *dp*, is a result of the HAADF-STEM nanoparticle size-distribution analysis, shown in Figure 5.

References

[1] M. Boudart, Turnover Rates in Heterogeneous Catalysis, Chem. Rev. 95 (1995) 661–666. doi:10.1021/cr00035a009.

[2] G. Bergeret, P. Gallezot, Particle size and dispersion measurements, Handb. Heterog. Catal. Online. (2008) 738–765.