

Tuning the properties of PdAu bimetallic nanocatalysts for selective hydrogenation reactions.

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Supporting information

XRD: Powder X-ray diffraction patterns were measured at ambient temperature using a scan range from 10 to 130° 2 θ with 0.02° step size, on a Bruker AXS D8 diffractometer equipped with a Cu K α (Ni filtered) radiation source and a Lynxeye Position Sensitive Detector.

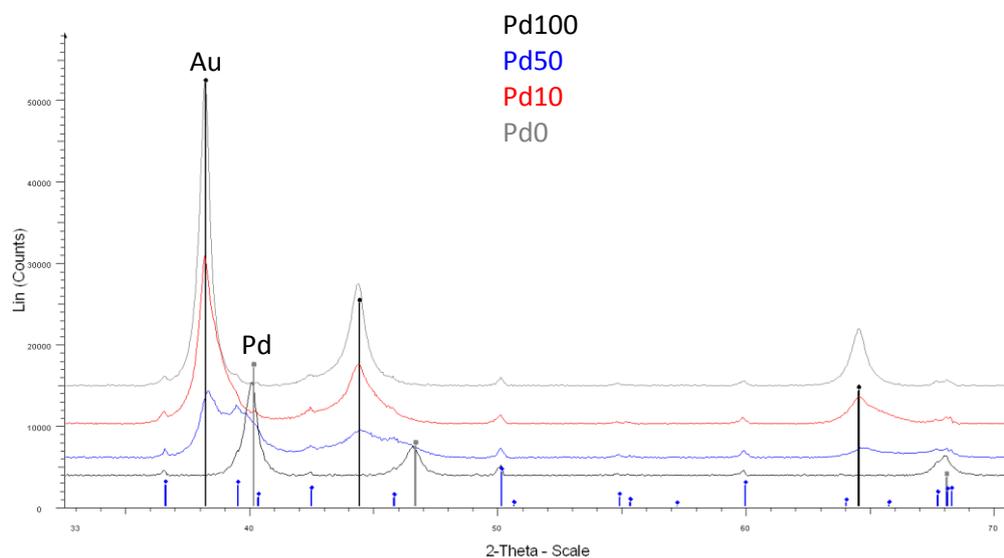


Figure S1: XRD diffractograms of Pd100, Pd50, Pd10 and Pd0 materials

EXAFS: Spectra were recorded at Pd-K edge (24 350 eV) and at the Au-L₃ edge (11 919 eV) with measurements made in transmission mode using a Si(311) channel-cut monochromator and a Si(111) ones, respectively. The data were normalized and analysed according to standard procedures using IFEFFIT package (Athena and Artemis).

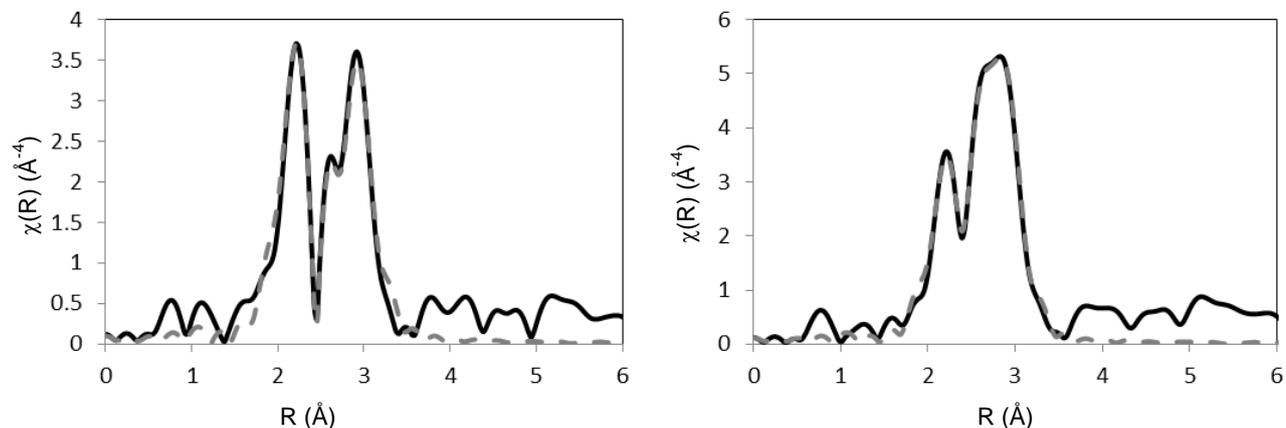
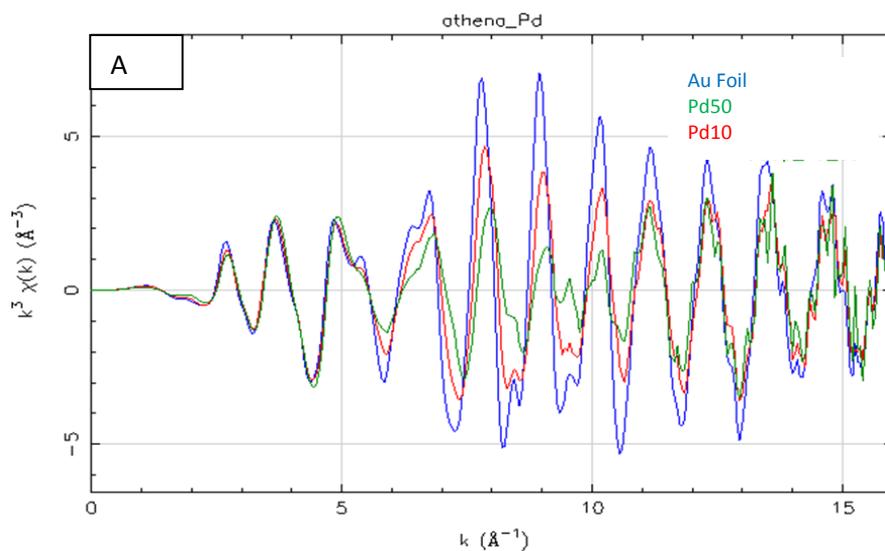


Figure S2: Fourier transform (k^3 weighted, $\Delta k = 3.5\text{--}14 \text{ \AA}^{-1}$) of Au L₃ edge EXAFS data for Pd100, Pd50 and Pd10. Continuous lines: experimental, broken lines: fit.



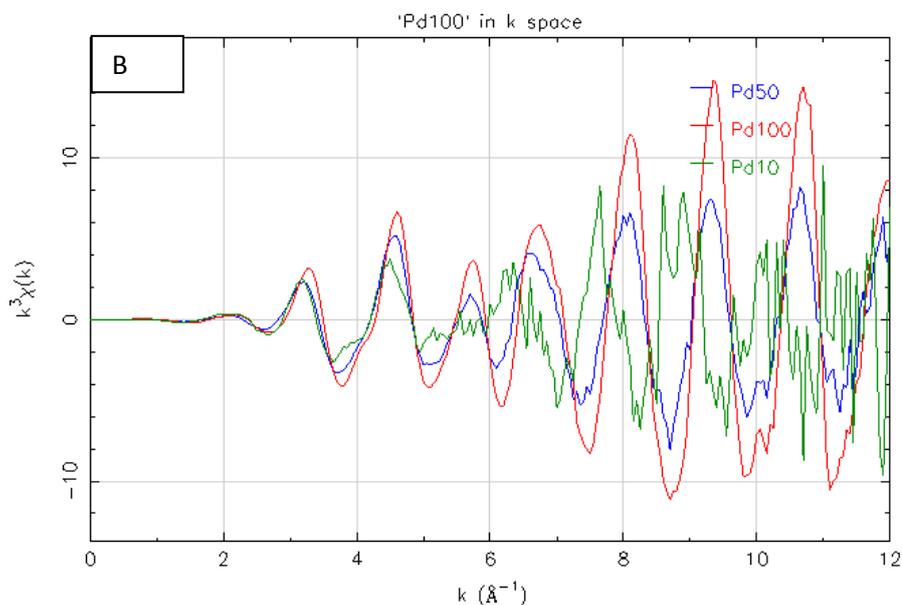


Figure S3: Experimental k^3 -weighted (a) Au L_3 edge and (b) Pd K edge EXAFS spectra of the materials.

XPS analyses were performed using a Thermo V. G. Scientific ESCALAB 250. Powders of the supported nanoparticles were dusted onto carbon tape and thereby mounted on a sample stub. The exciting radiation used in the studies was monochromatised aluminium $K\alpha$ radiation in a 650 μm spot at 200 W power. Charge compensation was activated, provided by the in-lens flood gun at a 2 eV setting and the 401 argon ion flood source at a "zero energy" setting.

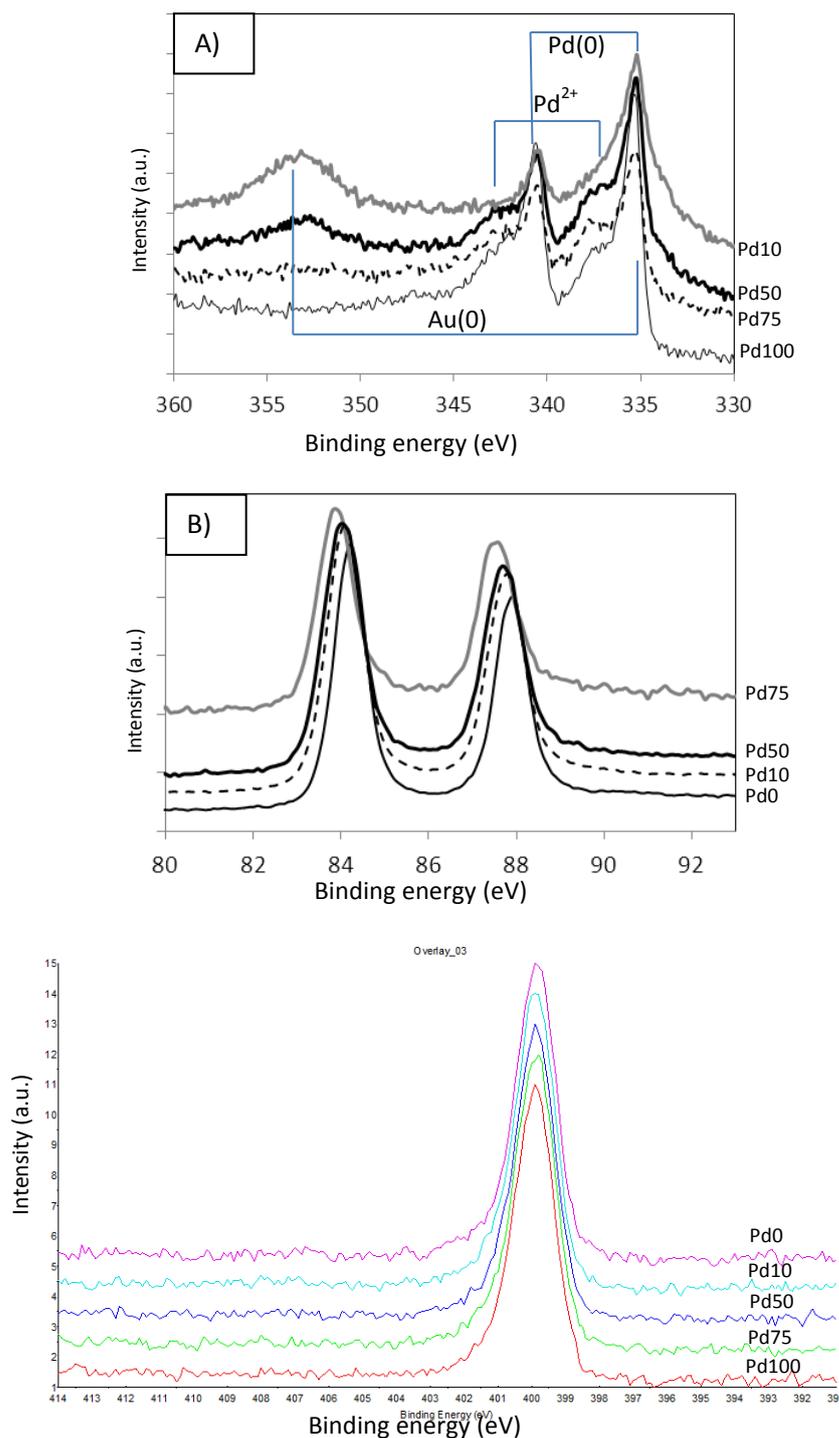


Figure S4: (a) Pd 3d and Au 4d XPS signal of various materials. Pd²⁺ was observed for all the catalysts studied except for Pd10. (b) Au 4f XPS signal of various materials showing a shift towards lower BE as the amount of Pd increases. (c) N 1s signal of the materials showing the presence of PVP on the catalyst surface.

Table S1: Pd and Au binding energies for the materials studied. N/C XPS atomic ratio for the various materials.

Catalyst	Pd3d5	Au4f	N/C XPS atomic ratio
Pd100	335.39		0.072
Pd75	335.37	83.88	0.072
Pd50	335.32	84.03	0.069
Pd10	335.27	84.08	0.067
Pd0	n/a	84.21	0.060

TEM analysis: A small portion of the sample was crushed and then dusted onto a holey carbon film on a TEM grid (Cu). The samples were examined in the Tecnai F20 Transmission Electron Microscope using a voltage of 200 kV, and C2 aperture of 30 & 50 m, in bright field (BF) STEM (HAADF) mode, and performing in situ EDX analysis. EDX data are given for line scans which demonstrate that the two metals are co-located in the same NPs, manifested by correlated peaks in intensity for both metals along the line scan. The large Cu peak is caused by the TEM grid used in these experiments.

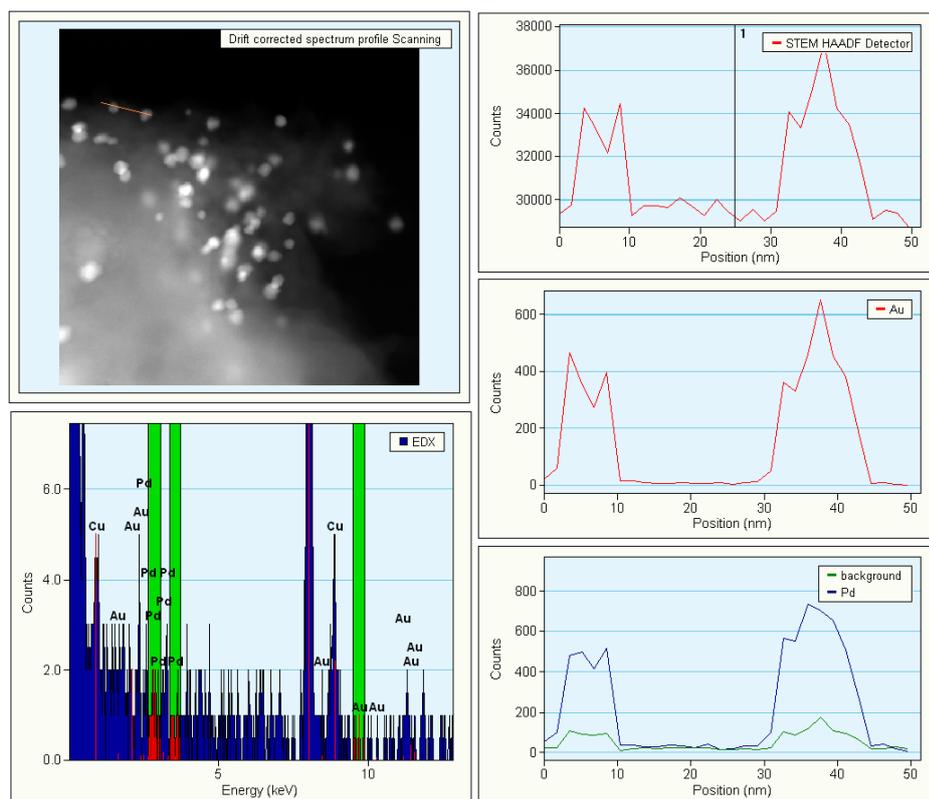


Figure S5- TEM and EDX data for Pd75

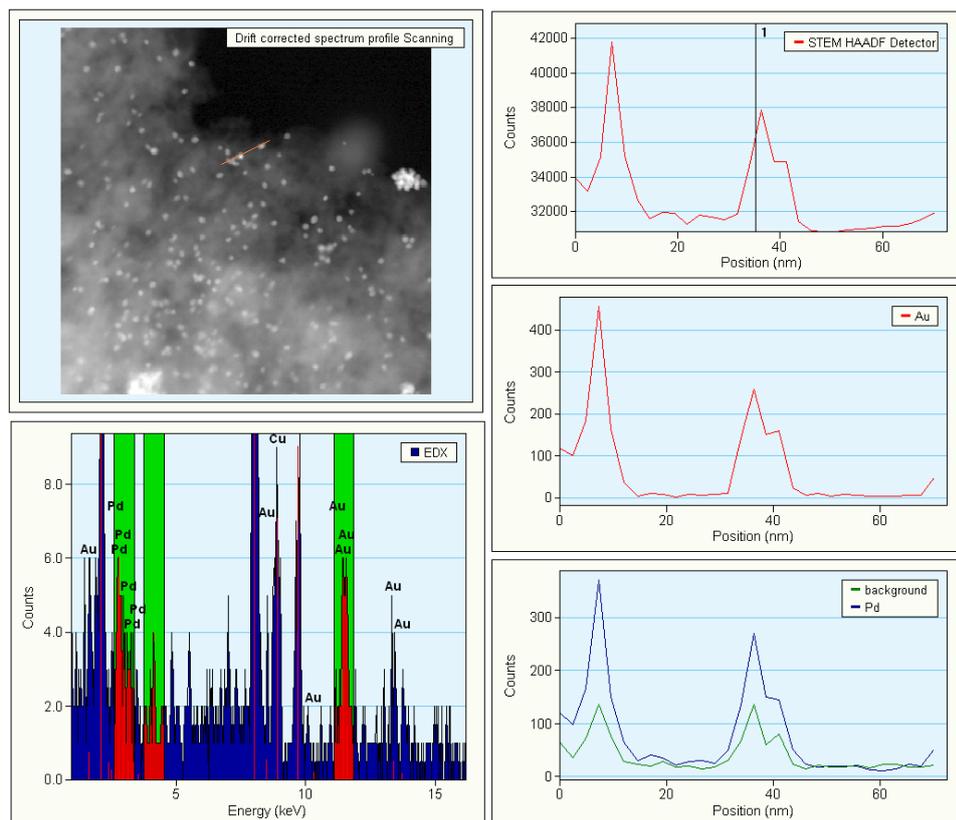


Figure S6- TEM and EDX data for Pd50

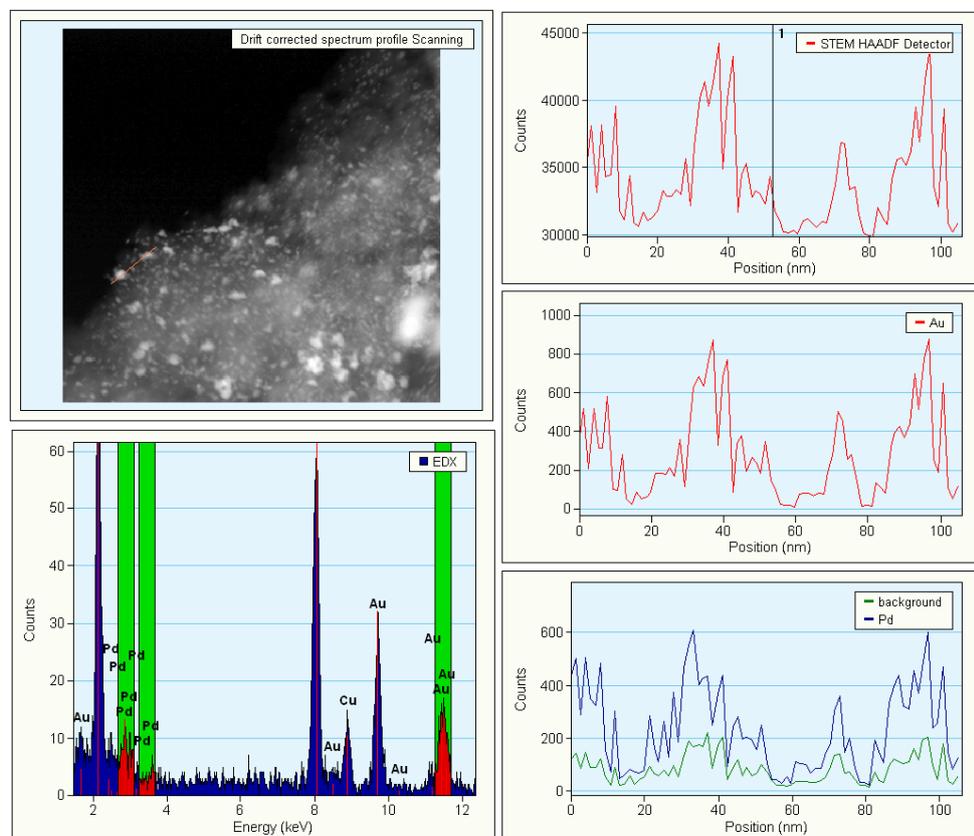


Figure S7- TEM and EDX data for Pd10

H₂ – TPR was carried out under 10 % H₂Ar gas mixture from RT to 500 °C.

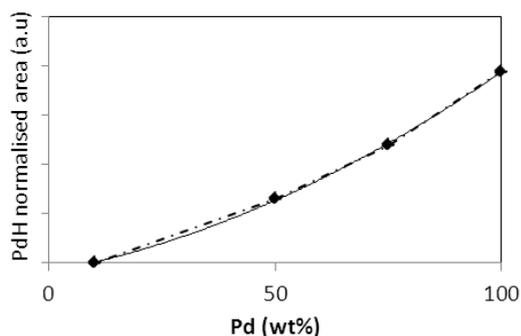


Figure S8: Evolution of the β -PdH peak area normalised to Pd content with the Pd/Au ratio (wt%)

Table S2: H₂O₂ productivity, H₂ Conversion and H₂O₂ Selectivity of PdAu catalysts using 20 ml 2.5 wt% H₂SO₄-methanol solution and 2.5 μ molPd. Reaction conditions: 32 bar, 90 min, room temperature, 2.2 % H₂ - 40 % O₂ /N₂ gas mixture.

Catalyst	H ₂ Conversion (%)	Selectivity (%)	Productivity (mol _{H₂O₂} .mol _{Pd} .h ⁻¹)
Pd100	32	95	272
Pd75	46	95	420
Pd50	44	97	403
Pd10	5	48	20

H₂O₂ decomposition / hydrogenation measurements were performed at RT and 20 bars. 0.00027 g Pd, and a 2.2 wt% H₂O₂ 1.6M H₃PO₄ aqueous solution were charged in the autoclave, purged one time before filling with H₂ gas at 20 bar. Stirring (1100 rpm) was commenced on reaching the desired pressure and experiments were carried out for 60 minutes. The H₂O₂ decomposition/hydrogenation was determined by titration of aliquots of the reaction solution after 5, 30 and 60 min with KMnO₄. The KMnO₄ was standardised against Fe(NH₄)₂(SO₄)₂.6H₂O.

Table S3: H₂O₂ hydrogenation/decomposition rate

Catalyst	H ₂ O ₂ decomposition / hydrogenation rate	
	mol _{H₂O₂} .h ⁻¹ .mol _{Pd} ⁻¹	mol _{H₂O₂} .h ⁻¹ .mol _{metal} ⁻¹
Pd100	97	97
Pd75	143	121
Pd50	132	85
Pd10	164	28