Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2023

Supporting Information

A Comparative Study of Palladium-Gold and Palladium-Tin Catalysts in the Direct Synthesis of H_2O_2.

Dávid Kovačič [a†], Richard J. Lewis[a†*], Caitlin M. Crombie[a], David J. Morgan[a,b] Thomas E. Davies[a], Ángeles López-Martín[a], Tian Qin[c] Christopher S. Allen[f,g] Jennifer. K. Edwards[d], Liwei Chen[c] Martin Skov-Skjøth Rasmussen[e] Xi Liu[c*] and Graham J. Hutchings[a*]

[a]Max Planck–Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF24 4HQ, UK.

[b]Harwell XPS, Research Complex at Harwell (RCaH) Didcot, OX11 0FA, UK

[c]In-situ Centre for Physical Sciences, School of Chemistry and Chemical, Frontiers Science Centre for Transformative Molecules, Shanghai 200240, P. R. China

[d]Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK.

[e]Haldor Topsøe A/S, Haldor Topsøes Allé 1, DK-2800 Kongens Lyngby, Denmark

[f]Electron Physical Sciences Imaging Centre, Diamond Light Source ltd, Didcot, OX11 0DE, United Kingdom

[g]Department of Materials, University of Oxford, Oxford. OX1 3PH. UK

[†]These authors contributed equally to this work.

*LewisR27@cardiff.ac.uk, LiuXi@sjtu.edu.cn, Hutch@cardiff.ac.uk

Table S.1. Surface area measurements of Pd-based TiO_2 supported catalysts, as determined by BET.

Catalyst	Surface Area / m^2g^{-1} *
TiO_2	59
0.5%Pd/TiO_2	57
0.25%Pd/TiO_2	56
0.25%Pd-0.25%Au/TiO_2	55
0.25%Pd-0.50%Au/TiO_2	55
0.25%Pd-0.75%Au/TiO_2	52
0.25%Pd-1.5%Au/TiO_2	48
0.25%Pd-2.25%Au/TiO_2	48
0.25%Pd-0.25%Sn/TiO_2	57
0.25%Pd-0.50%Sn/TiO_2	53
0.25%Pd-0.75%Sn/TiO_2	51
0.25%Pd-1.5%Sn/TiO_2	51
0.25%Pd-2.25%Sn/TiO_2	50

Note: All catalysts were exposed to an oxidative reductive heat treatment prior to use (static air, 400 °C, 3 h, 10 °Cmin^{-1}). The TiO_2 support was analysed as received from suppliers. *Surface area determined from nitrogen adsorption measurements using the BET equation.

Table S.2. A comparison of catalytic performance at iso-conversion.

Catalyst	Reaction time / min	H_2 Conversion / %	H_2O_2 Selectivity / %	H_2O_2 Conc. / wt. %
0.5%Pd/TiO_2	5	16	78	0.07
0.25%Pd-0.25%Au/TiO_2	5	14	83	0.07
0.25%Pd-0.25%Sn/TiO_2	10	16	91	0.08
0.5%Pd/TiO_2	15	42	47	0.11
0.25%Pd-0.25%Au/TiO_2	20	47	65	0.17
0.25%Pd-0.25%Sn/TiO_2	60	47	57	0.12

H_2O_2 direct synthesis reaction conditions: Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 20 ˚C 1200 rpm. **Note**: Reaction rates are based on theoretical metal loading.

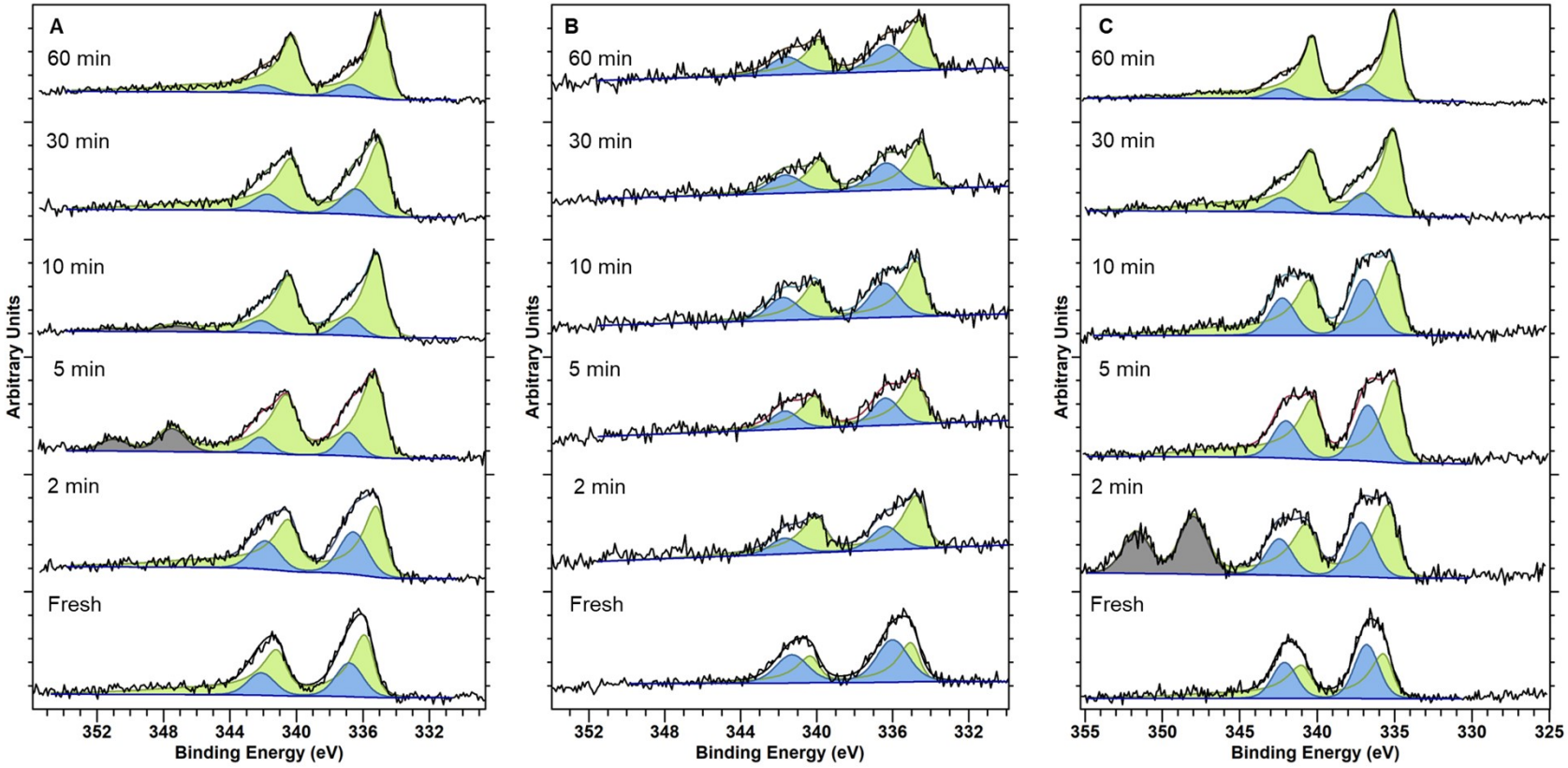

Figure S.1. XPS spectra of Pd(3d) regions of the **(A)** 0.5%Pd/TiO_2, **(B)** 0.25%Pd-0.25%Au/TiO_2 and **(C)** 0.25%Pd-0.25%Sn/TiO_2 catalysts, as a function of reaction time. ***Key:*** Pd^0 (*green*) Pd^{2+} (*blue*), Ca^{2+} (*grey*). **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 20 °C 1200 rpm. **Note:** Used catalysts are dried under vacuum (30 °C, 16 h) prior to subsequent XPS analysis.

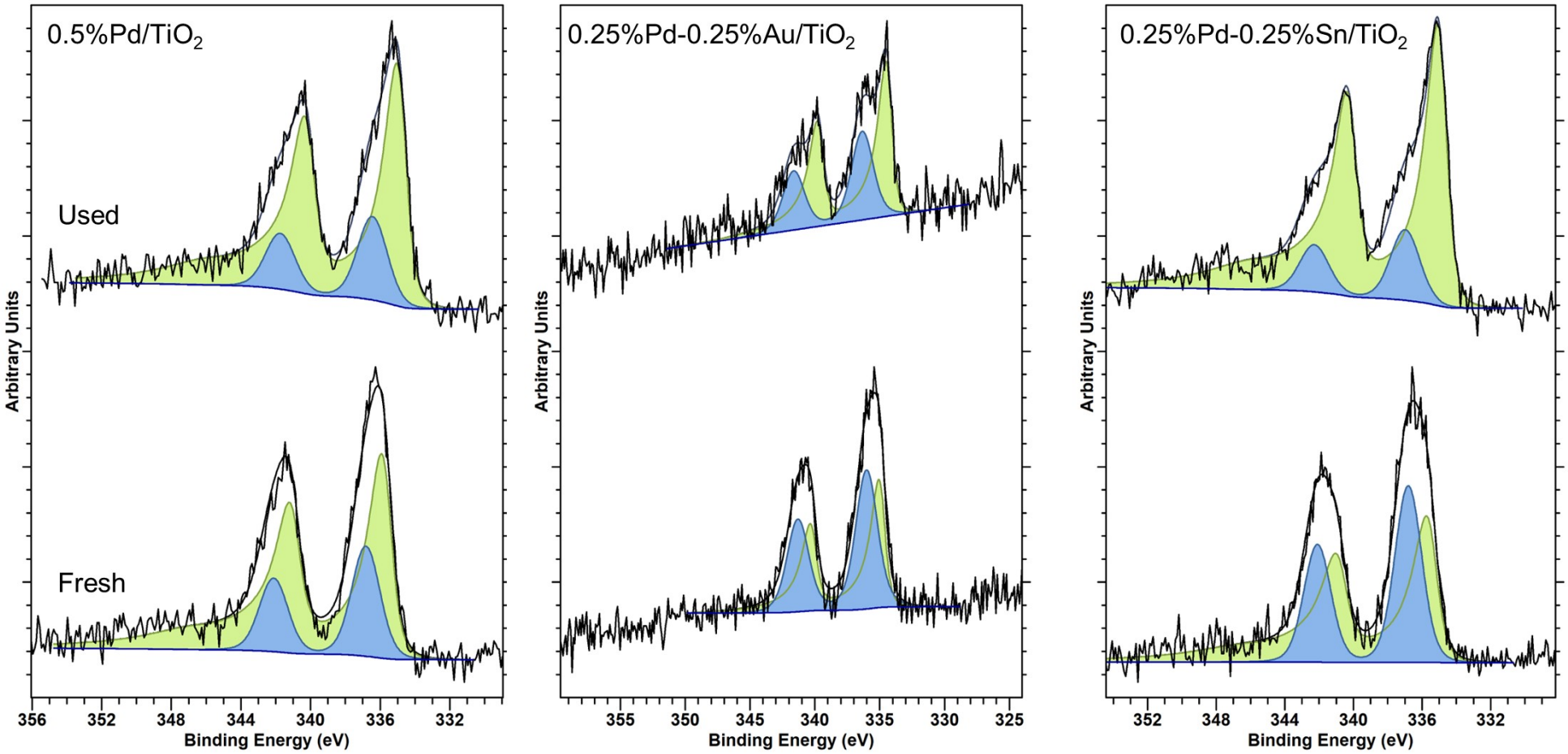

Figure S.2. XPS spectra of Pd(3d) regions of the as-prepared 0.5%Pd/TiO_2, 0.25%Pd-0.25%Au/TiO_2 and 0.25%Pd-0.25%Sn/TiO_2 catalysts, in addition to analysis of the catalysts after use in the direct synthesis of H_2O_2. ***Key:*** Pd^0 (*green*) Pd^{2+} (*blue*), Ca^{2+} (*grey*). **H_2O_2 direct synthesis reaction conditions:** Catalyst (0.01g), H_2O (2.9g), MeOH (5.6g), 5% H_2 / CO_2 (420 psi), 25% O_2 / CO_2 (160 psi), 0.5 h, 20 °C 1200 rpm. **Note:** Used catalysts are dried under vacuum (30 °C, 16 h) prior to subsequent XPS analysis.

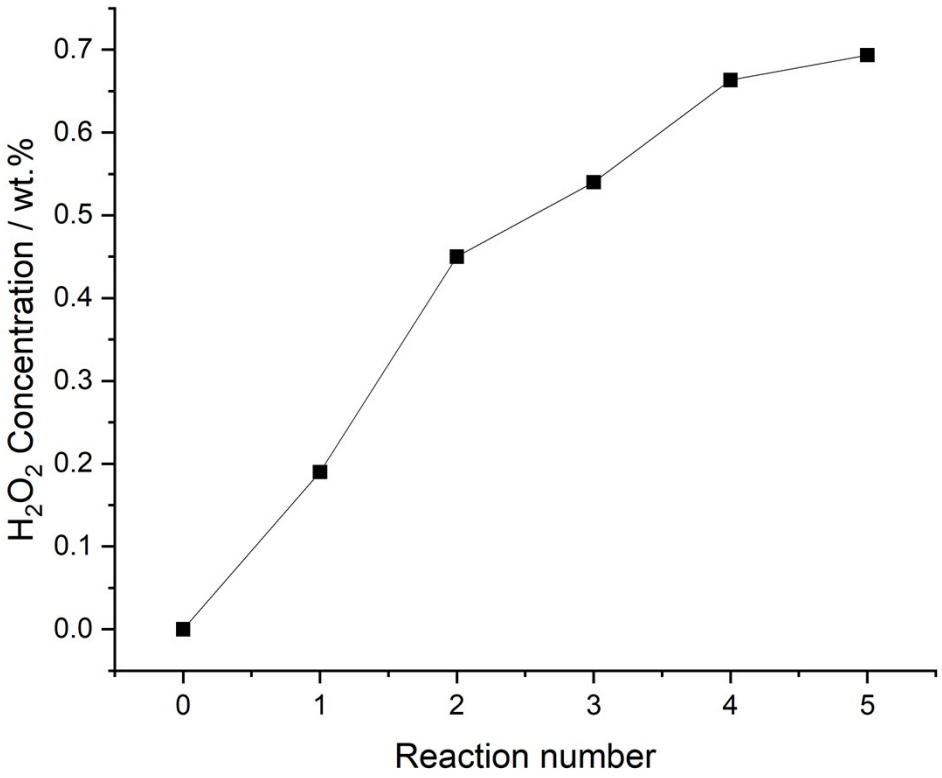

Figure S.3. Activity of the 0.25%Pd-2.25%Sn/TiO2 catalyst over sequential H_2O_2 synthesis reactions. **H_2O_2 direct synthesis reaction conditions:** catalyst (0.01 g), H_2O (2.9 g), MeOH (5.6 g), 5% H_2/CO_2 (420 psi), 25% O_2/CO_2 (160 psi), 0.5 h, 20 °C, 1200 rpm.

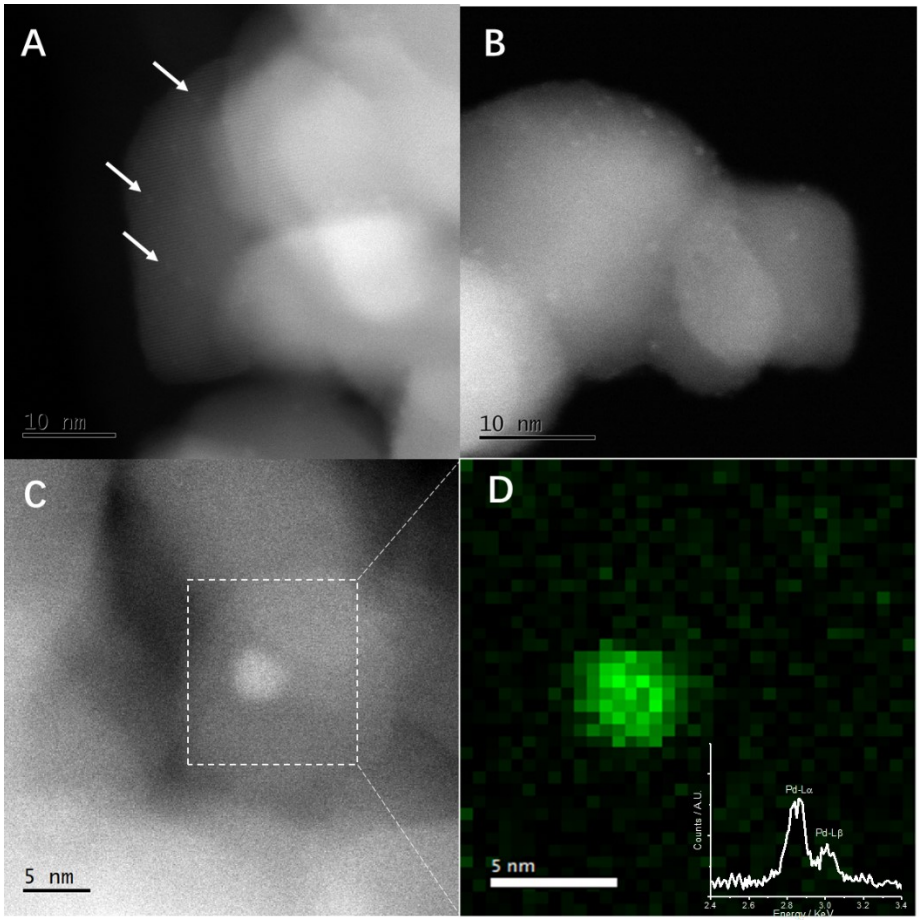

Figure S.4. Aberration corrected STEM images and XEDS mapping of the 0.25%Pd/TiO_2 catalyst **(A-B)** HAADF images showing the small, predominant <1nm Pd particles. **(C)** HAADF image of one of the few larger Pd particles suitable for **(D)** XEDS mapping to confirm the presence of Pd. **Note:** In all cases, active metallic species are identified by high Z-contrast (*i.e.* brighter regions of the micrograph).

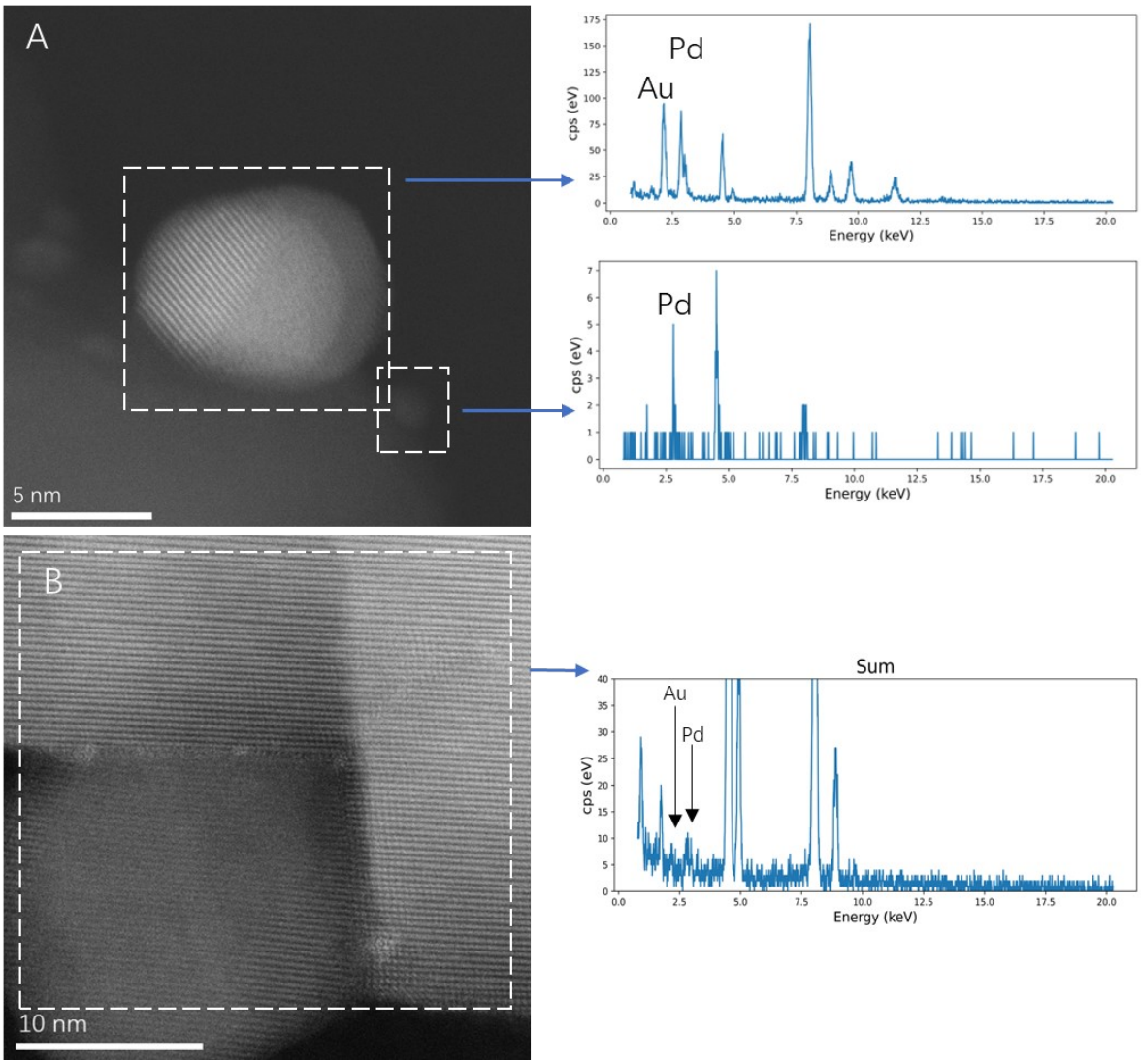

Figure S.5. Aberration corrected HAADF-STEM images and XEDS analysis of the 0.25%Pd-0.25%Au/TiO_2. catalyst. **(A)** XED spectra of areas indicated showing both Au and Pd in the larger particles and predominately Pd in the smaller particle highlighted. **(B)** HAADF-STEM image of the smaller clusters and associated XED spectra highlighting the presence of Au in a limited number of the smaller clusters. **Note:** In all cases, active metallic species are identified by high Z-contrast (*i.e.* brighter regions of the micrograph). Unlabelled signals in the XED spectra are those corresponding to the TiO_2 support, copper sample holder and Au-L transitions.

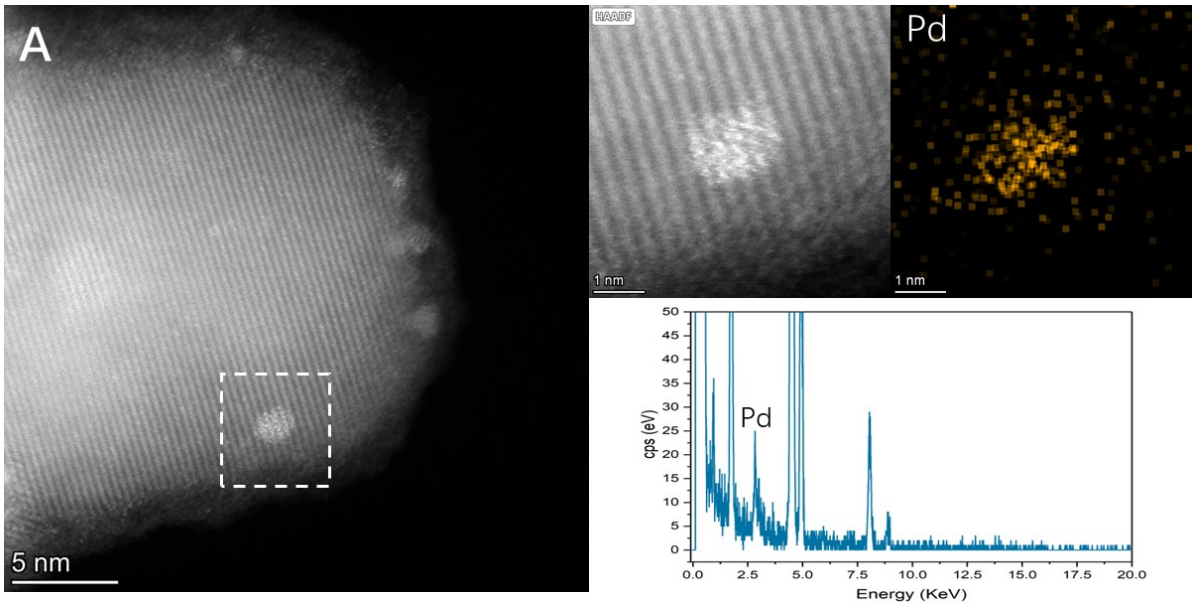

Figure S.6. Aberration corrected HAADF-STEM images and XEDS analysis of the 0.25%Pd-2.25%Sn/TiO_2 catalyst. **(A)** HAADF-STEM and XED spectra of area indicated showing the smaller particles present to be Pd. **Note:** In all cases, active metallic species are identified by high Z-contrast (*i.e.* brighter regions of the micrograph). Unlabelled signals in the XED spectra are those corresponding to the TiO_2 support, copper sample holder and Au-L transitions.

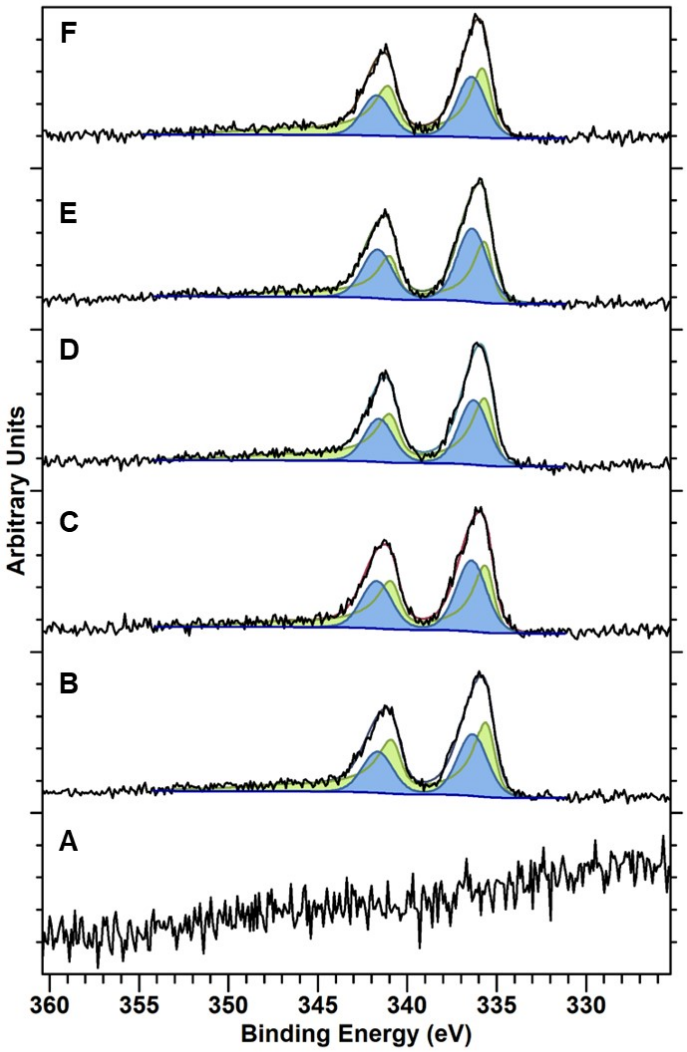

Figure S.7. XPS spectra of Pd(3d) regions of the as-prepared **(A)** 0.5%Sn/TiO_2, **(B)** 0.25%Pd-0.25%Sn/TiO_2 and **(C)** 0.25%Pd-0.5%Sn/TiO_2 **(D)** 0.25%Pd-0.5%Sn/TiO_2 **(E)** 0.25%Pd-0.5%Sn/TiO_2 and **(F)** 0.25%Pd-0.5%Sn/TiO_2 catalysts. ***Key:*** Pd^0 (*green*) Pd^{2+} (*blue*).