Supplementary Information.

Improving Catalytic Activity towards the Direct Synthesis of H_2O_2 through Cu Incorporation into AuPd Catalysts

Alexandra Barnes [1,†], Richard J. Lewis [1,*,†], David J. Morgan [1,2], Thomas E. Davies [1] and Graham J. Hutchings [1,*]

[1] Max Planck-Cardiff Centre on the Fundamentals of Heterogeneous Catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK
[2] Harwell XPS, Research Complex at Harwell (RCaH) Didcot OX11 0FA, UK
* Correspondence: lewisr27@cardiff.ac.uk (R.J.L.); hutch@cardiff.ac.uk (G.J.H.)
† These authors contributed equally to this work.

Table S1. Synthesis details of the precursors used in the preparation of key bi- and tri-metallic 1%AuPd/ZSM-5 catalysts.

Catalyst	Au precursor	Precursor vol. / µL ($mgmL^{-1}$)	Au precursor	Precursor vol. / µL ($mgmL^{-1}$)	Tertiary metal precursor	Precursor vol. / µL ($mgmL^{-1}$)
$1\%AuPd_{(1.00)}/ZSM\text{-}5$	$HAuCl_4.3H_2O$	530 (12.25)	$PdCl_2$	585 (6.00)	-	-
$1\%AuPd_{(0.0975)}Cu_{(0.025)}/ZSM\text{-}5$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$CuCl_2$	106 (2.36)
$1\%AuPd_{(0.0975)}Zn_{(0.025)}/ZSM\text{-}5$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$Zn(NO_3)_2.6H_2O$	46 (5.43)
$1\%AuPd_{(0.0975)}Ni_{(0.025)}/ZSM\text{-}5$	$HAuCl_4.3H_2O$	517 (12.25)	$PdCl_2$	570 (6.00)	$Ni(NO_3)_2$	115 (2.18)

Note 1 : In the case of the tri-metallic catalysts the combined loading of Au and Pd is 0.975 wt.% (Au: Pd = (1:1 mol/mol)) and that of the tertiary metal (Cu, Zn or Ni) is 0.025 wt.%. In all cases catalyst are exposed to a reductive heat treatment prior to use (5%H_2/Ar, 400 °C, 4 h, 10°Cmin^{-1}). **Note 2:** values in parentheses for catalyst nomenclature refer to metal loading of (Au+Pd) or tertiary metal. In all instances total metal loading is 1 wt.% and Au: Pd: X = 1: 1 (mol/mol).

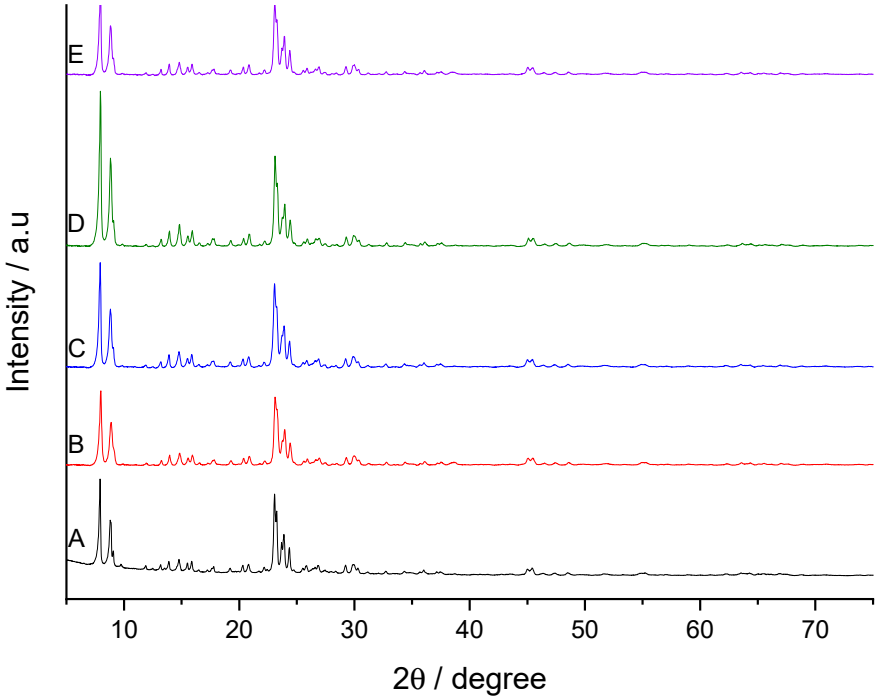

Figure S1. X-ray diffractograms of 1%$AuPd_{(0.0975)}X_{(0.025)}$/ZSM-5 catalysts. **(A)** ZSM-5, **(B)** 1%$AuPd_{(1.00)}$/ZSM-5, **(C)** 1%$AuPd_{(0.0975)}Cu_{(0.025)}$/ZSM-5, **(D)** 1%$AuPd_{(0.0975)}Ni_{(0.025)}$/ZSM-5 and **(E)** 1%$AuPd_{(0.0975)}Zn_{(0.025)}$/ZSM-5.

Supplementary text associated with Figure S1.

No significant change in the MFI structure of the SZM-5 support is observed upon metal impregnation and exposure to a reductive heat treatment (flowing 5%H_2/Ar, 400 °C, 4h, 10°Cmin^{-1}), based on the main reflections associated with ZSM-5 (θ = 7.8, 8.8,14.8, 23.14, 23.91 and 24.5°).

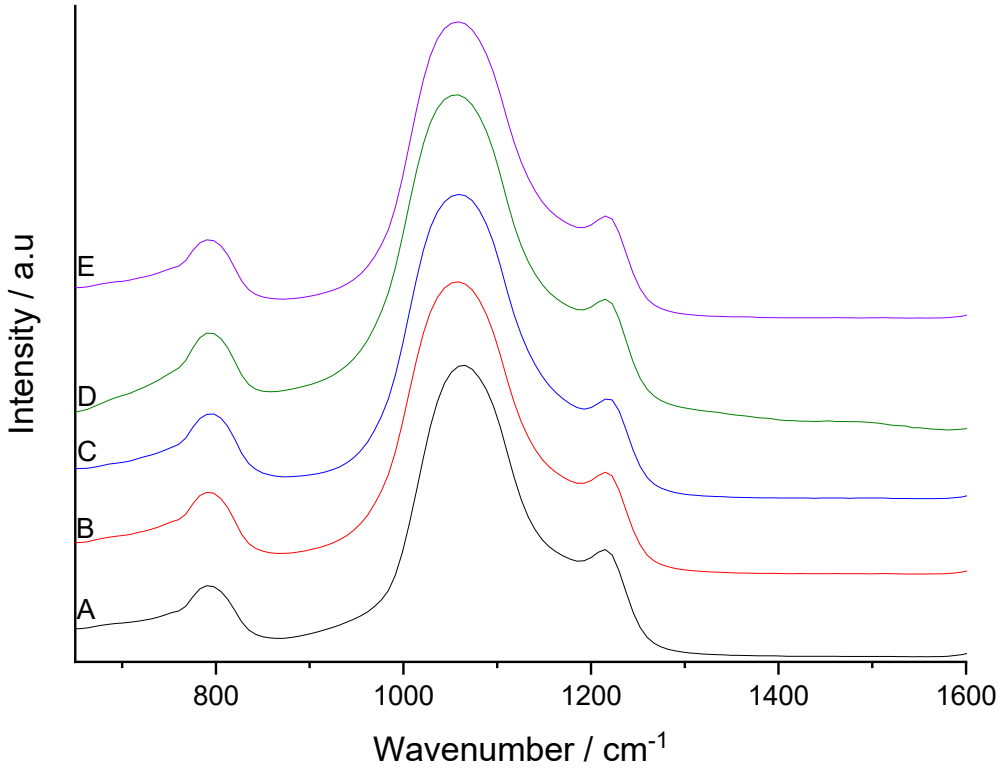

Figure S2. Fourier-transform infrared spectroscopy of 1%AuPd$_{(0.975)}$X$_{(0.025)}$/ZSM-5 catalysts. **(A)** ZSM-5, **(B)** 1%AuPd$_{(1.00)}$/ZSM-5, **(C)** 1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/ZSM-5, **(D)** 1%AuPd$_{(0.975)}$Ni$_{(0.025)}$/ZSM-5 and **(E)** 1%AuPd$_{(0.975)}$Zn$_{(0.025)}$/ZSM-5.

Supplementary text associated with Figure S2.

As with analysis via XRD (Figure S.1), investigation of the 1%AuPd$_{(0.975)}$X$_{(0.025)}$/ZSM-5 catalysts by FTIR indicates no significant changes in the structure of the ZSM-5 structure is observed after metal impregnation and exposure to a reductive heat treatment (flowing 5%H_2/Ar, 400 °C, 4h, 10°Cmin^{-1}). It is possible to observe three distinct infrared bands in the FTIR spectra of 1%AuPd$_{(0.975)}$X$_{(0.025)}$/ZSM-5 catalysts at 800, 1060 and 1220 cm^{-1} characteristic of SiO_4 tetrahedron units. The adsorption band around 1060 cm^{-1} is attributed to the internal asymmetric stretching vibration of Si-O linkage. While the adsorption band at 1220 cm^{-1} have been assigned to the 5-membered rings present in the structure of the ZSM-5 zeolite and the band at 800 cm^{-1} can be assigned the symmetric stretching of the external linkages of the SiO_4 tetrahedron.

Table S2. Summary of porosity and surface area of key 1%AuPd$_{(0.0975)}$X$_{(0.025)}$/ZSM-5 catalysts and HZSM-5(30).

Catalyst	Surface area / m^2g^{-1}	$V_{Micropore}$ / cm^3g^{-1}
ZSM-5(30)	493	0.185
1%AuPd$_{(1.00)}$/ZSM-5	446	0.170
1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/ZSM-5	440	0.171

Note: ZSM-5 support exposed to calcination prior to metal immobilisation (flowing air, 550 ˚C, 3 h, 20 ˚Cmin^{-1})

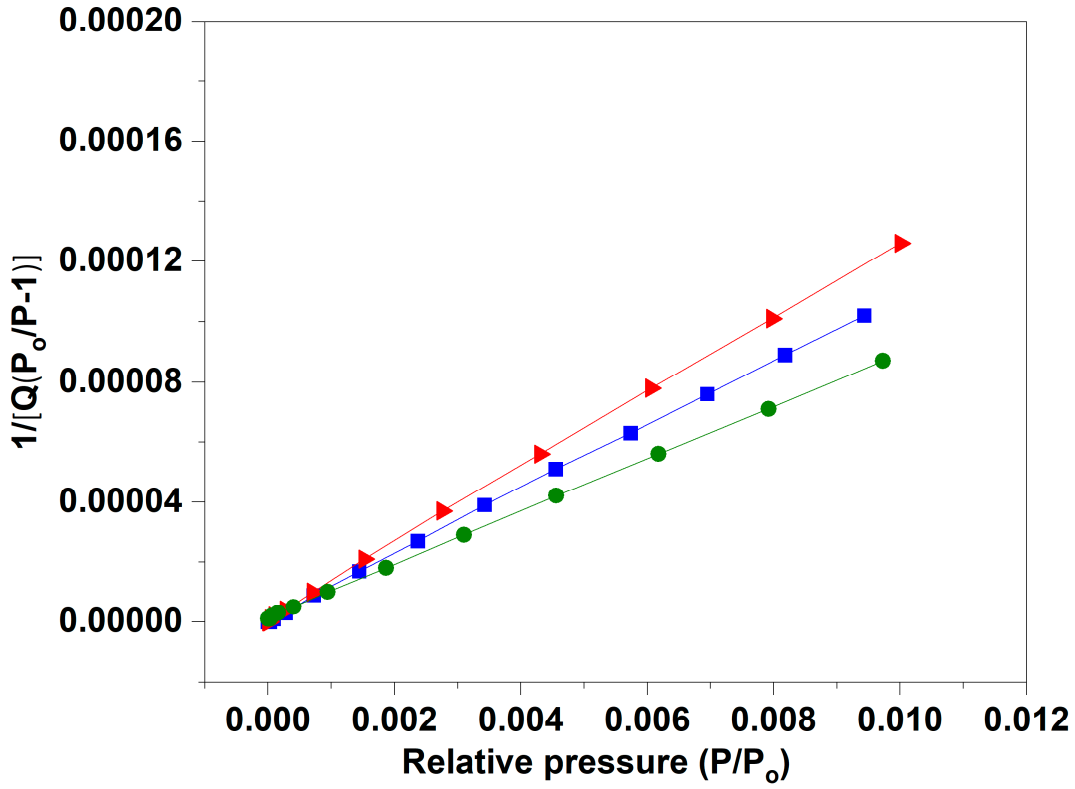

Figure S3. BET analysis plots for key 1%AuPd$_{(0.0975)}$X$_{(0.025)}$/ZSM-5 catalysts and HZSM-5(30). ***Key:*** ZSM-5(30) (*red triangles*), 1%AuPd$_{(1.00)}$/ZSM-5 (*blue squares*), 1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/ZSM-5 (*green circles*). **Note:** ZSM-5 support exposed to calcination prior to metal immobilisation (flowing air, 550 ˚C, 3 h, 20 ˚Cmin^{-1})

Table S3. Comparison of initial H_2O_2 synthesis rates over 1%$AuPd_{(0.0975)}X_{(0.025)}$/ZSM-5 (X=Cu, Ni, Zn) catalysts, as a function of Cu loading.

Catalyst	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	H_2O_2 Conc. / wt.%	Initial rate of reaction / $mmol_{H2O2}mmol_{metal}^{-1}min^{-1}$	Degradation / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$
ZSM-5(30)	0	0	0	0
1%$AuPd_{(1.00)}$/ZSM-5	69	0.14	37.6	320
1%$AuPd_{(0.975)}Cu_{(0.025)}$/ZSM-5	115	0.23	48.5	529
1%$AuPd_{(0.975)}Ni_{(0.025)}$/ZSM-5	81	0.16	36.4	281
1%$AuPd_{(0.975)}Zn_{(0.025)}$/ZSM-5	77	0.16	39.6	361

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, 2° C, 1200 rpm. **Note 1:** Initial reaction rates are determined after a reaction time of 0.083 h and are calculated based on theoretical metal loading. **Note 2:** ZSM-5 support exposed to calcination prior to metal immobilisation (flowing air, 550 ˚C, 3 h, 20 ˚$Cmin^{-1}$)

Table S4. The effect of tertiary metal introduction upon the surface atomic composition of 1%$AuPd_{(0.975)}X_{(0.025)}$/ZSM-5 catalysts (X= Cu, Ni, Zn) , as determined by XPS.

Catalyst	Au: Pd	Pd^{2+} : Pd^0	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$
1%$AuPd_{(1.00)}$/ZSM-5	0.78	0.30	69
1%$AuPd_{(0.975)}Cu_{(0.025)}$/ZSM-5	0.81	1.06	115
1%$AuPd_{(0.975)}Ni_{(0.025)}$/ZSM-5	0.83	2.13	81
1%$AuPd_{(0.975)}Zn_{(0.025)}$/ZSM-5	0.28	1.13	77

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, 2° C, 1200 rpm.

Table S5. Comparison of initial H_2O_2 synthesis rates over 1%AuPdCu/ZSM-5 catalysts, as a function of Cu loading.

Catalyst	Productivity / $mol_{H2O2}kg_{cat}^{-1}h^{-1}$	H_2O_2 Conc. / wt.%	Initial rate of reaction / $mmol_{H2O2}mmol_{metal}^{-1}min^{-1}$
1%AuPd/ZSM-5	69	0.14	37.6
1%$AuPd_{(0.988)}Cu_{(0.012)}$/ZSM-5	111	0.22	45.1
1%$AuPd_{(0.981)}Cu_{(0.019)}$/ZSM-5	116	0.23	45.7
1%$AuPd_{(0.975)}Cu_{(0.025)}$/ZSM-5	115	0.23	48.5
1%$AuPd_{(0.963)}Cu_{(0.037)}$/ZSM-5	75	0.15	29.7

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, 2° C, 1200 rpm. **Note:** Initial reaction rates are determined after a reaction time of 0.083 h and are calculated based on theoretical metal loading.

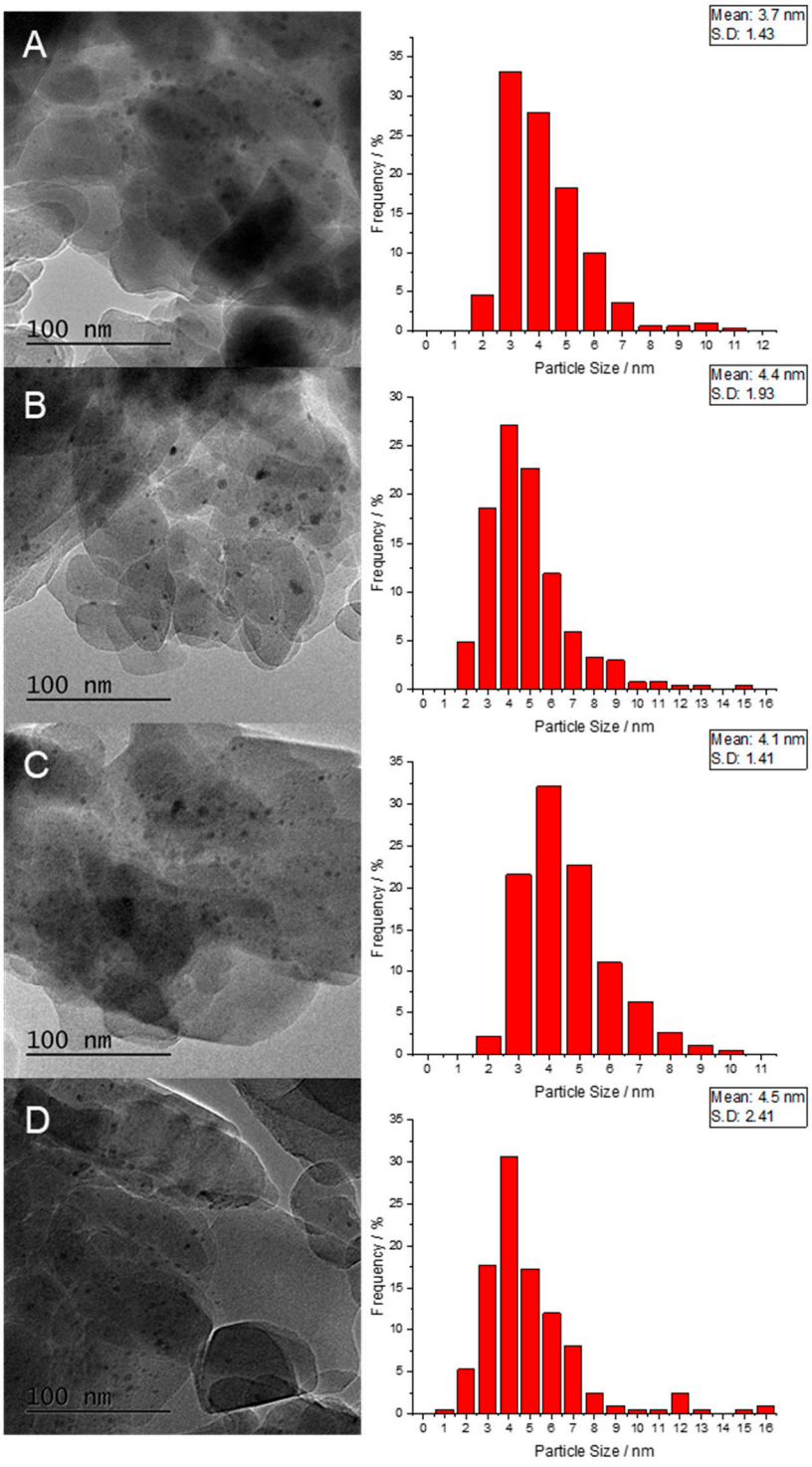

Figure S4. Representative bright field transmission electron micrographs and corresponding particle size histograms of as-prepared **(A)** 1%AuPd$_{(1.00)}$/ZSM-5 and **(C)** 1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/ZSM-5 catalysts and analogous **(B)** 1%AuPd$_{(1.00)}$/ZSM-5 and **(D)** 1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/ZSM-5 samples after use in the direct synthesis reaction. **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, 2° C, 1200 rpm.

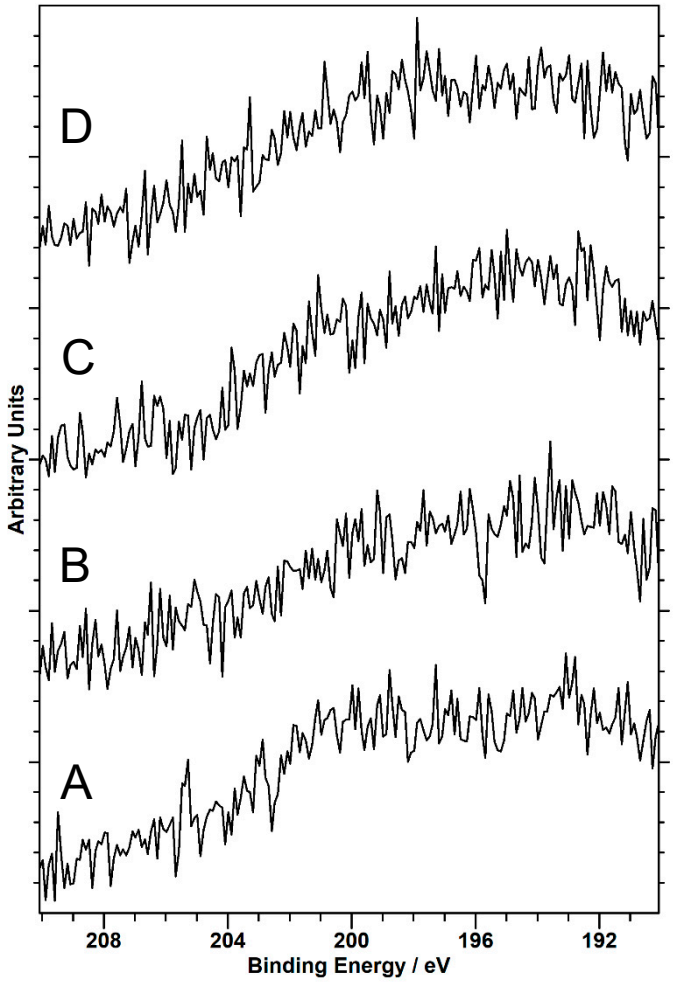

Figure S5. Comparison of surface atomic Cl content of the as-prepared **(A)** and **(B)** used 1%AuPd$_{(1.00)}$/ZSM-5 catalyst and the fresh **(C)** and **(D)** used 1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/ZSM-5 analogue. **Note:** No signal is observed for any catalyst formulation within the expected energy window for Cl(2p) (approx. 200 eV).

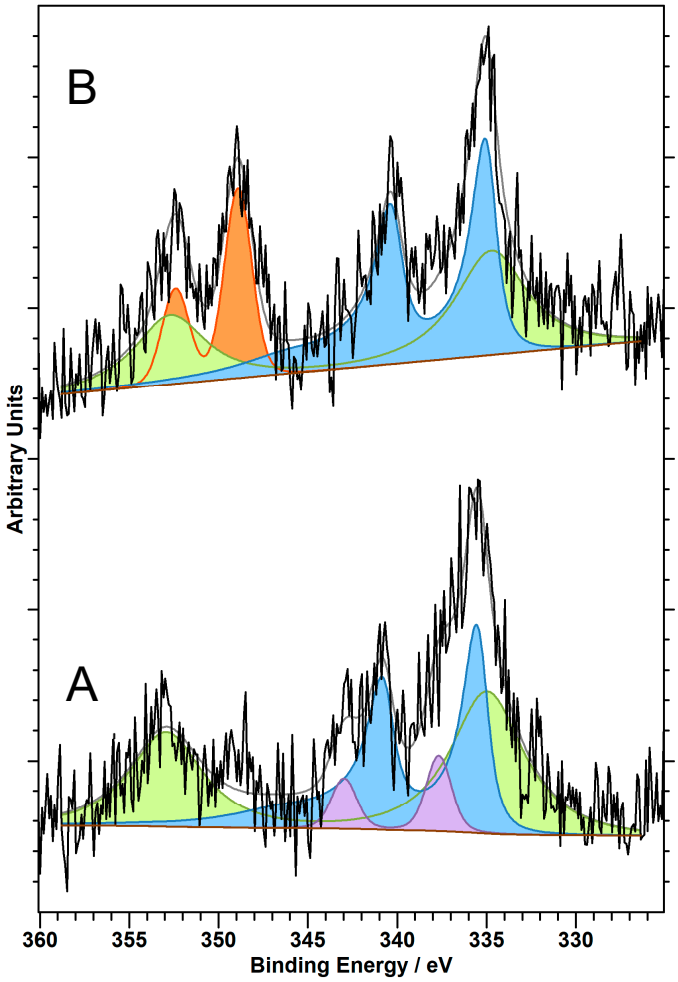

Figure S6. XPS spectra of Pd(3d) regions for the **(A)** as-prepared and **(B)** used 1%AuPd$_{(1.00)}$/ZSM-5 catalyst, after use in the H_2O_2 direct synthesis reaction. ***Key:*** Au(4d) (green), Pd^0(blue), Pd^{2+}(purple), Ca^{2+} (orange).

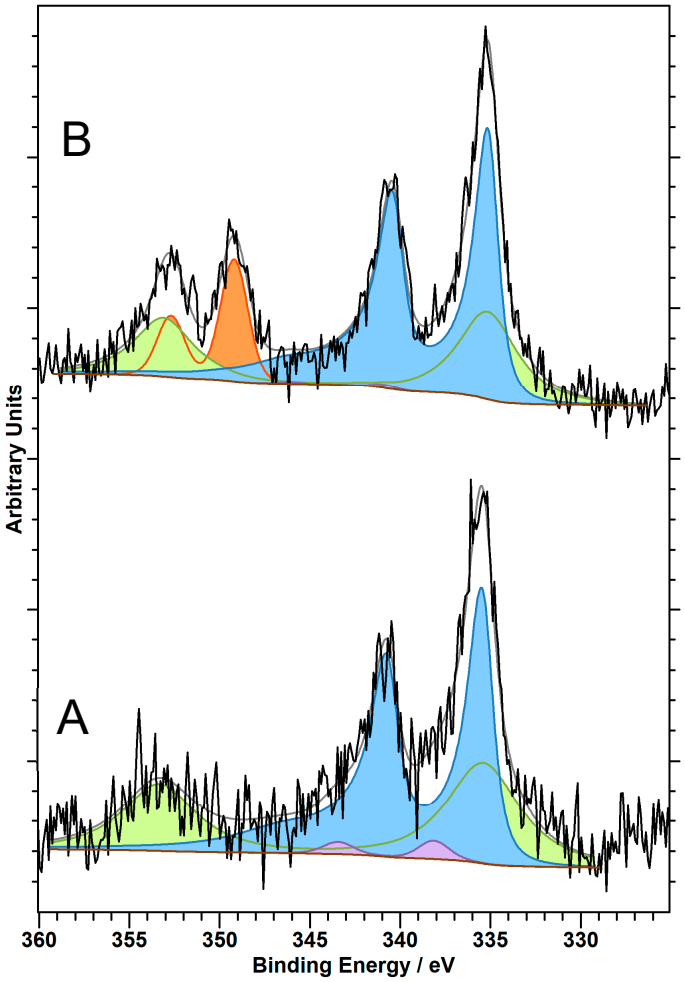

Figure S7. XPS spectra of Pd(3d) regions for the **(A)** as-prepared and **(B)** used 1%AuPd$_{(0.975)}$Cu$_{(0.025)}$/ZSM-5 catalyst, after use in the H_2O_2 direct synthesis reaction. ***Key:*** Au(4d) (green), Pd^0(blue), Pd^{2+}(purple), Ca^{2+} (orange).