

Supporting Information

Site Requirements for Inhibition-free CO Oxidation over Silica-supported Bimetallic PdCu Alloys

Stephen Thomas Kristy^{1,2}, Scott Svadlenak¹, Adam S. Hoffmann², Simon R. Bare², Konstantinos A. Goulas^{1*}

1. School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR 97331
2. Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

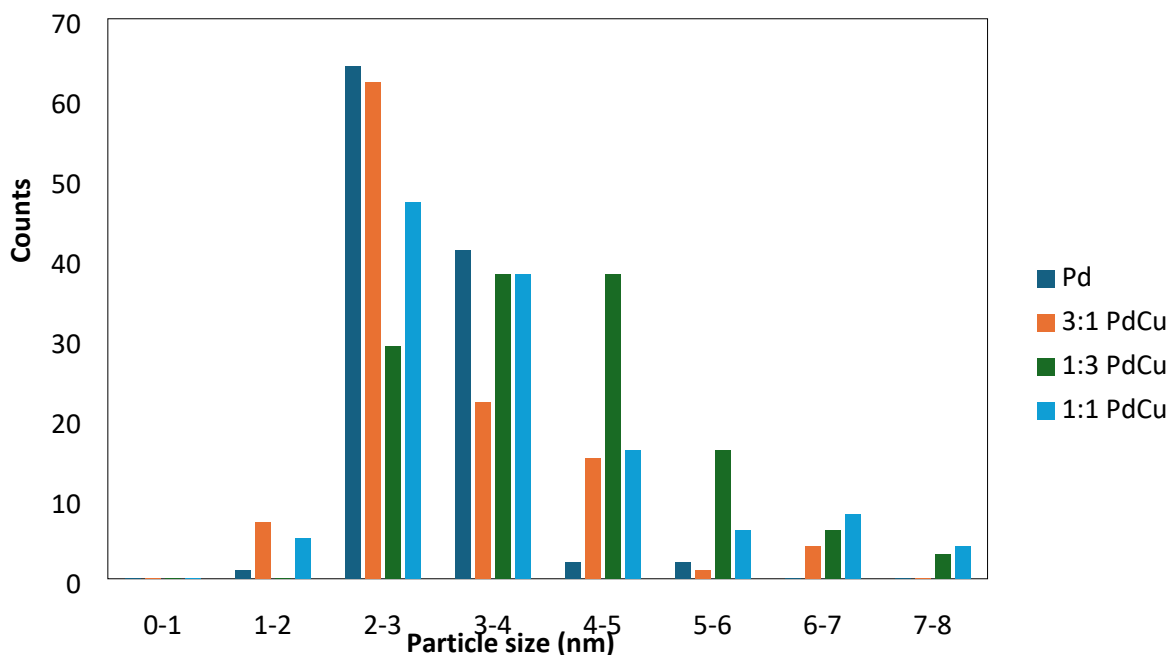


Figure S1: Particle size distribution of silica-supported catalysts, determined by TEM.

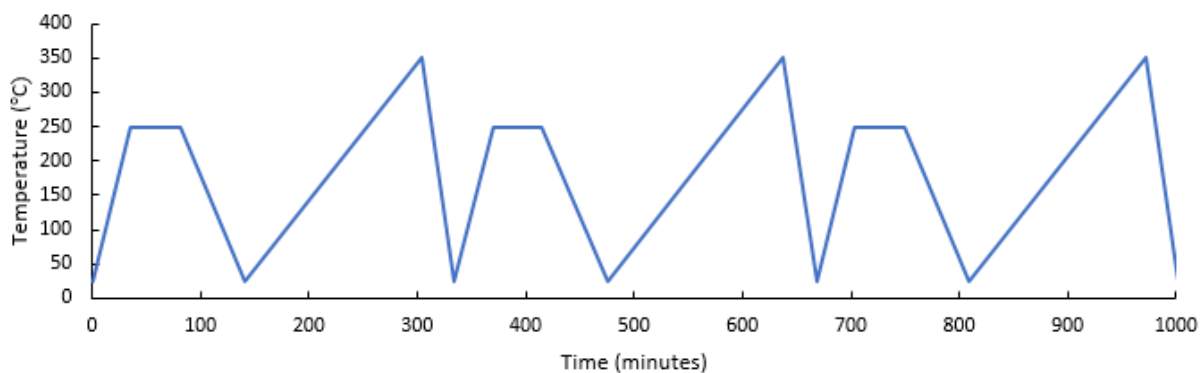


Figure S2 - Temperature profile for TPRs and TPOs performed on a single batch of catalyst loaded into the activity testing reactor system. This represents the heating profile for a series of three TPRs and TPOs we used to completely test catalyst activity.

Table S1: Catalyst and reactor loading parameters.

Catalyst	Pd	3:1 Pd:Cu	1:1 Pd:Cu	1:3 Pd:Cu
wt% Pd (nominal)	4	2.5	5.2	1.3
wt% Cu (nominal)	0	0.5	3.1	2.3
Average particle size (nm)	2.9	3.1	3.7	3.4
Standard deviation of particle size (nm)	0.6	1.0	1.6	1.3
Dispersion	0.34	0.33	0.27	0.29
Reactor mass loading (mg catalyst)	8.3	4.0	10.3	7.5
Space velocity ($\text{L g}^{-1} \text{h}^{-1}$)	990	832	2080	1109
Reactor metal loading (μmol)	7.8	8.1	9.8	9.1
Reactor surface metal loading (μmol)	2.7	2.7	2.7	2.6
Pd:Cu mol ratio (from ICP-OES)	-	2.7	0.79	0.35

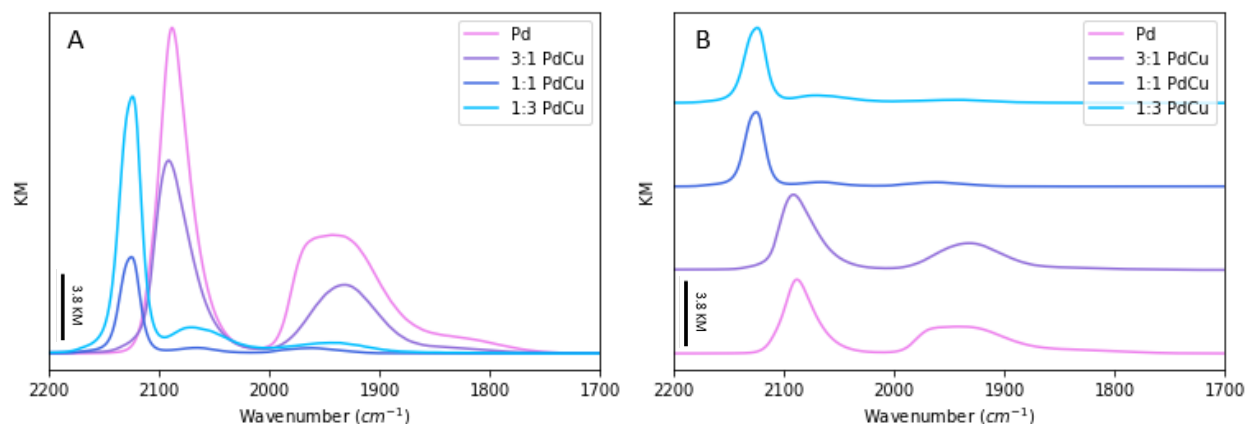


Figure S3 – CO TPD DRIFTS spectra at ambient temperature. (A) shows unadjusted/overlapping data, (B) shows unadjusted stacked data (same data). $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate used, 15-minute CO saturation ($20\text{ cm}^3 \text{ min}^{-1}$), 15 minute He purge ($20\text{ cm}^3 \text{ min}^{-1}$).

DRIFTS spectral peaks below were fit using python, numpy, “spicy_optimize.curve_fit”, as Guassian, Lorentzian, or Voigt style peaks. An individual analysis was performed on each peak at each temperature to determine the appropriate style, and how many peaks were represented under the data. When in question, constrained fits were performed to disprove peak location.¹ Only three temperatures are shown here to save space, but the values of the peak crest and area under each curve are shown in respective tables for all temperatures. These tables were used to construct Figure 6 in the main test. Any values in the tables listed as “null” mean the peak was too small/wide to be fit properly.

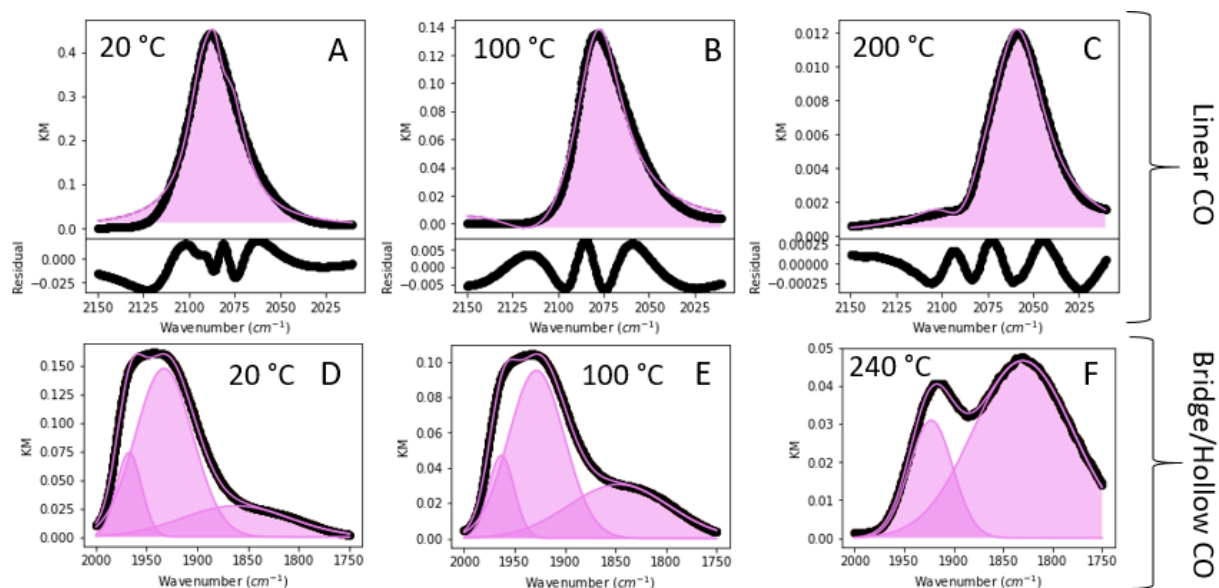


Figure S4 – Peak fitting analysis for Pd during TPD DRIFTS experiments for the Pd catalyst. Two bridge bound peaks were identified for Pd (lower panels). $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate used, 15-minute CO saturation ($20\text{ cm}^3\text{ min}^{-1}$), 15 minute He purge ($20\text{ cm}^3\text{ min}^{-1}$).

Table S2 – Peak position and area under each peak determined by fitting functions over the series of spectra collected during TPD DRIFTS experiments for the Pd catalyst. $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate used, 15-minute CO saturation ($20\text{ cm}^3\text{ min}^{-1}$), 15 minute He purge ($20\text{ cm}^3\text{ min}^{-1}$).

Temperature ($^{\circ}\text{C}$)	Hollow		Bridge				Linear	
	Peak Position (cm^{-1})	Integral	Peak 1 Position (cm^{-1})	Peak 1 Integral	Peak 2 Position (cm^{-1})	Peak 2 Integral	Peak 1 Position (cm^{-1})	Peak 1 Integral
20	1862	3.5	1933	10.4	1967	2.3	2087	17
40	1860	3.5	1932	9.8	1967	2.2	2086	15
60	1854	3.5	1931	8.8	1966	2.0	2083	11
80	1850	3.6	1930	7.7	1965	1.7	2080	7.6
100	1846	3.7	1928	6.7	1963	1.4	2077	5.1
120	1843	3.8	1927	5.7	1961	1.2	2074	3.4
140	1841	4.1	1925	4.8	1959	0.9	2071	2.2
160	1839	4.3	1924	4.1	1956	0.6	2067	1.4
180	1837	4.6	1924	3.3	1954	0.3	2062	0.9
200	1835	5.0	1924	2.8	1952	0.2	2059	0.6
220	1833	5.4	1924	2.2	null	null	2057	0.4
240	1830	5.7	1923	1.7	null	null	2055	0.3

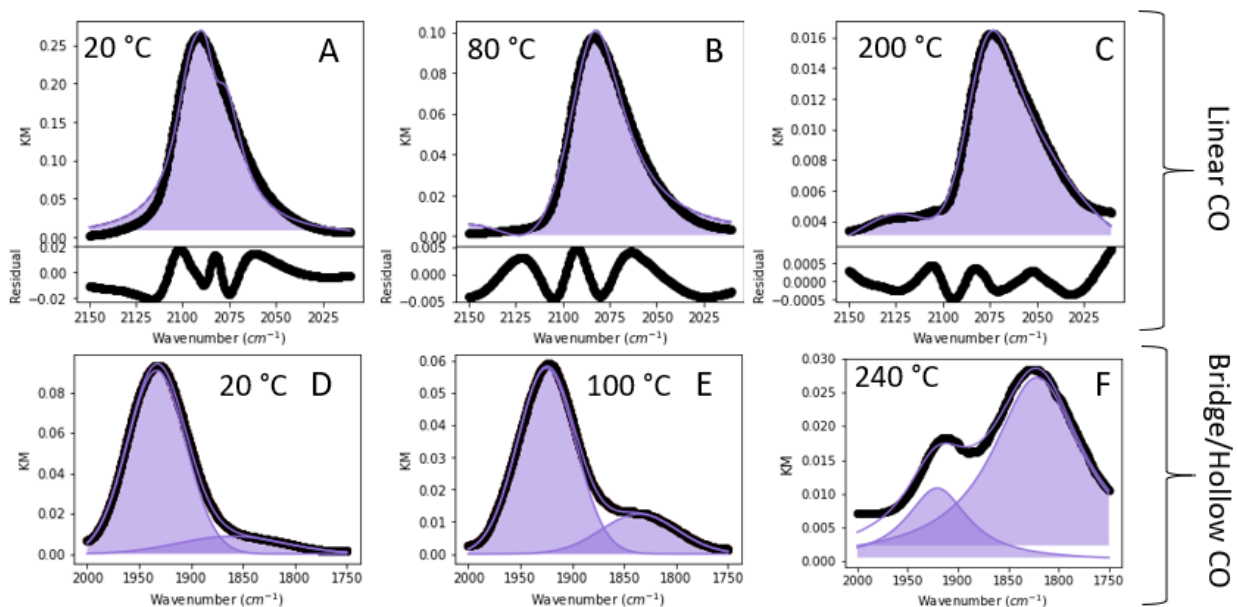


Figure S5- Peak fitting analysis for Pd during TPD DRIFTS experiments for the 3:1 PdCu catalyst. A single bridge bound peaks was identified. 10 °C min⁻¹ heating rate used, 15-minute CO saturation (20 cm³ min⁻¹), 15 minute He purge (20 cm³ min⁻¹).

Table S3 - Peak position and area under each peak determined by fitting functions over the series of spectra collected during TPD DRIFTS experiments for the 3:1 PdCu catalyst. 10 °C min⁻¹ heating rate used, 15-minute CO saturation (20 cm³ min⁻¹), 15 minute He purge (20 cm³ min⁻¹).

Temperature (°C)	Hollow		Bridge		Linear	
	Peak Position (cm ⁻¹)	Integral	Peak Position (cm ⁻¹)	Integral	Peak 1 Position (cm ⁻¹)	Peak 1 Integral
20	1862	1.1	1933	6.3	2090	11
40	1859	1.1	1932	5.9	2088	10
60	1845	1.0	1930	5.4	2088	6.8
80	1839	1.1	1927	4.7	2082	4.3
100	1836	1.2	1925	4.0	2079	2.5
120	1836	1.6	1923	3.2	2076	1.4
140	1828	1.5	1918	3.3	2073	1.1
160	1828	2.0	1917	2.7	2066	1.0
180	1827	2.4	1916	2.1	2061	1.0
200	1825	2.7	1915	1.7	null	null
220	1824	3.1	1917	1.3	null	null
240	1822	3.6	1920	1.0	null	null

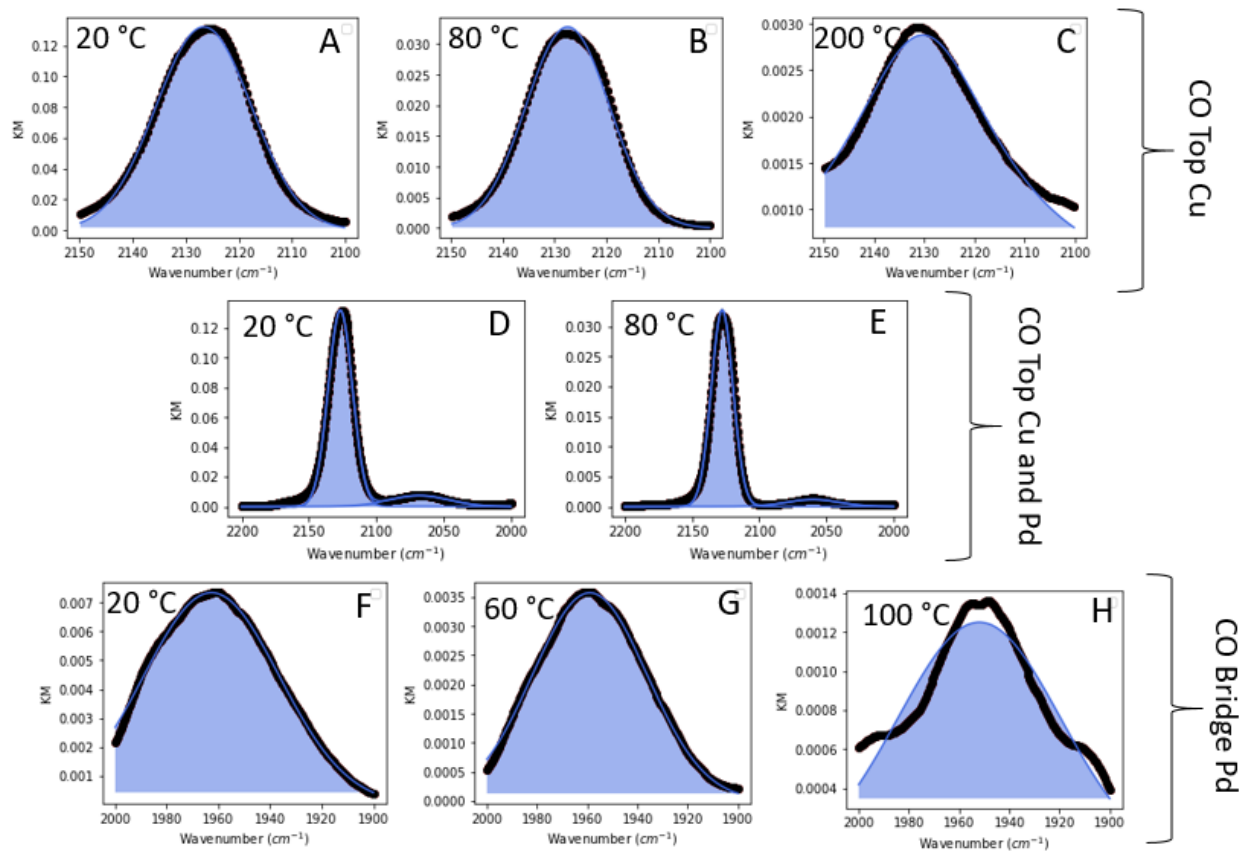


Figure S6 - Peak fitting analysis for Pd during TPD DRIFTS experiments for the 1:1 PdCu catalyst. A single bridge bound peaks was identified. $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate used, 15-minute CO saturation ($20\text{ cm}^3\text{ min}^{-1}$), 15 minute He purge ($20\text{ cm}^3\text{ min}^{-1}$).

Table S4 - Peak position and area under each peak determined by fitting functions over the series of spectra collected during TPD DRIFTS experiments for the 1:1 PdCu catalyst. 10 °C min⁻¹ heating rate used, 15-minute CO saturation (20 cm³ min⁻¹), 15 minute He purge (20 cm³ min⁻¹).

Temperature (°C)	Pd Bridge		Pd Linear		Cu Linear	
	Peak Position (cm ⁻¹)	Integral	Peak Position (cm ⁻¹)	Peak Integral	Peak Position (cm ⁻¹)	Integral
20	1963	0.4	2068	0.4	2127	3.0
40	1961	0.1	2066	0.3	2127	2.3
60	1959	0.1	2064	0.1	2127	1.3
80	1955	0.1	2060	0.1	2127	0.7
100	1952	0.4	2057	0.0	2128	0.3
120	1952	0.1	2053	0.1	2129	0.1
140	1948	0.1	2046	0.1	2130	0.1
160	null	null	2044	0.3	2132	0.1
180	null	null	null	null	2131	0.1
200	null	null	null	null	2131	0.1

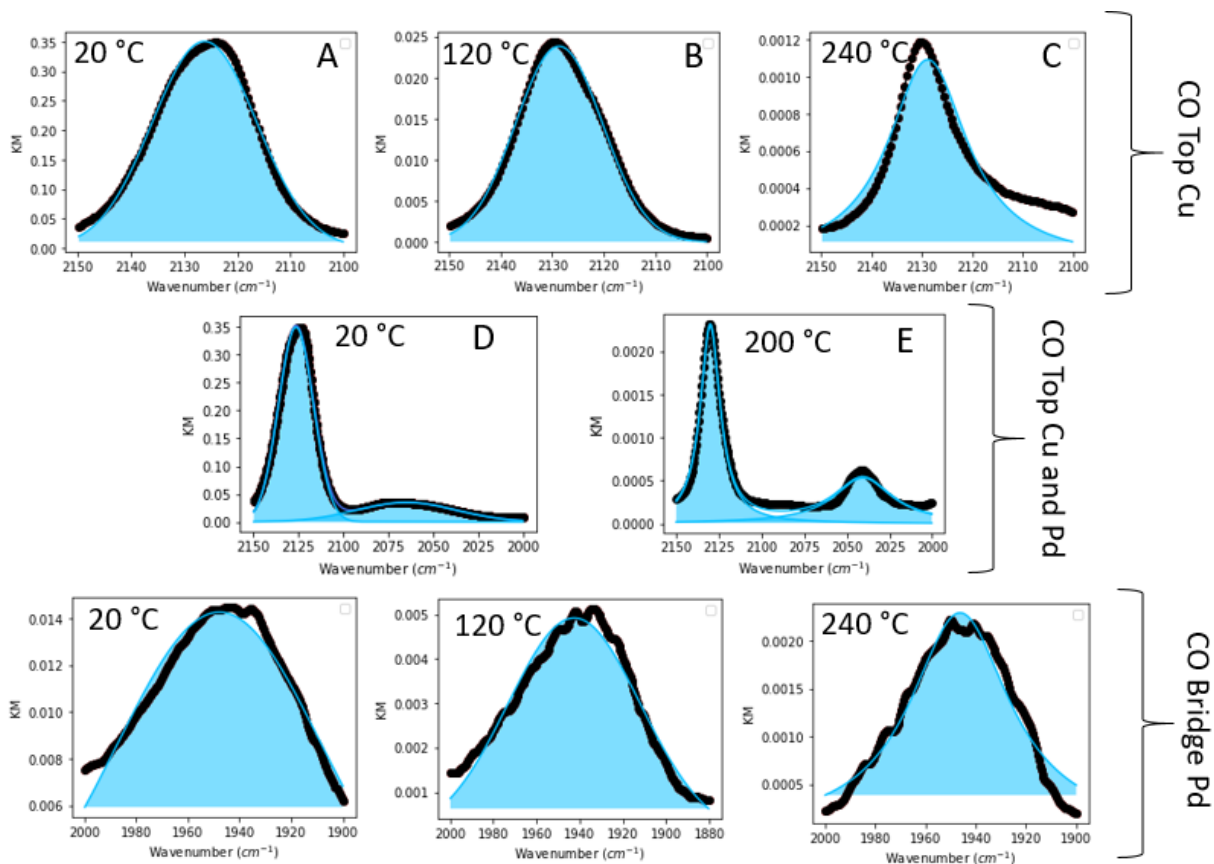


Figure S7 - Peak fitting analysis for Pd during TPD DRIFTS experiments for the 1:3 PdCu catalyst. A single bridge bound peaks was identified. 10 °C min⁻¹ heating rate used, 15-minute CO saturation (20 cm³ min⁻¹), 15 minute He purge (20 cm³ min⁻¹).

Table S5 - Peak position and area under each peak determined by fitting functions over the series of spectra collected during TPD DRIFTS experiments for the 1:3 PdCu catalyst. 10 °C min⁻¹ heating rate used, 15-minute CO saturation (20 cm³ min⁻¹), 15 minute He purge (20 cm³ min⁻¹).

Temperature (°C)	Pd Bridge		Pd Linear		Cu Linear	
	Peak Position (cm ⁻¹)	Integral	Peak Position (cm ⁻¹)	Peak Integral	Peak Position (cm ⁻¹)	Integral
20	1948	1.1	2065	2.4	2126	8.6
40	1948	1.0	2063	2.1	2126	7.3
60	1947	0.8	2060	1.4	2126	4.9
80	1947	0.6	2054	0.8	2128	0.9
100	1944	0.4	2048	0.4	2129	0.5
120	1942	0.3	2045	0.2	2129	0.2
140	1939	0.3	2042	0.1	2129	0.3
160	1936	0.3	2040	0.1	2130	0.1
180	1937	0.1	2041	0.0	2130	0.1
200	1940	0.1	2040	0.0	2130	0.04
220	1943	0.1	null	null	2130	0.03
240	1946	0.1	null	null	2128	0.03

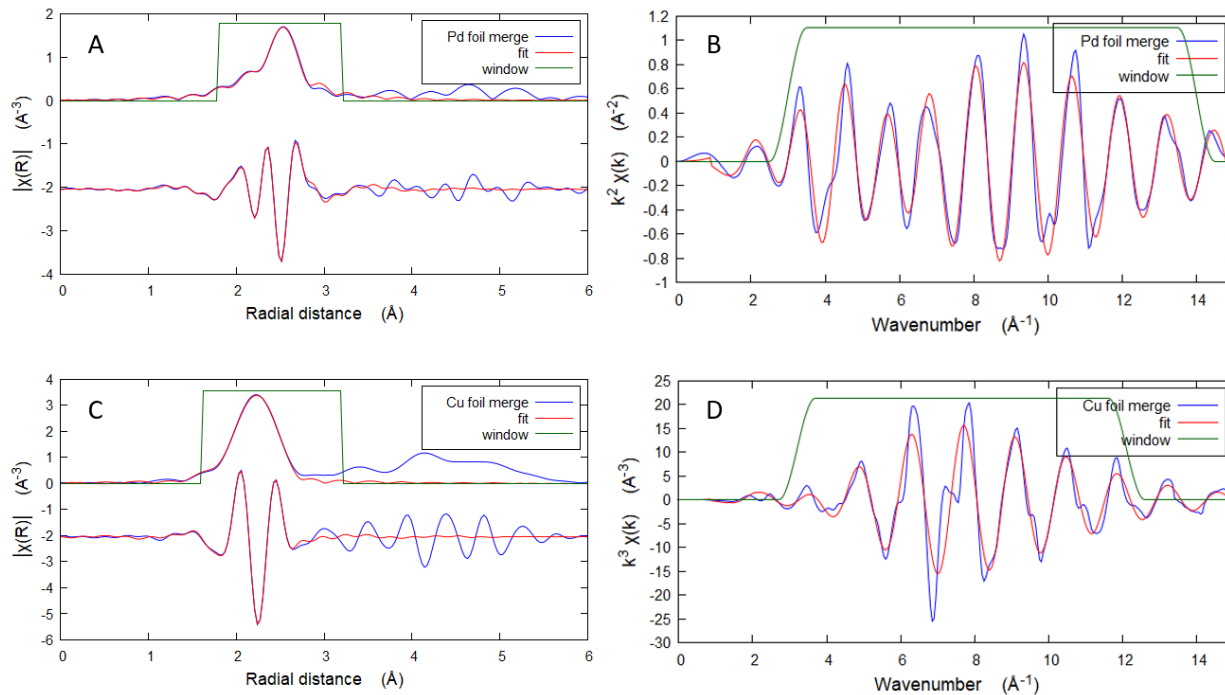


Figure S8 – (A and B – Pd Foil): Pd edge and (C and D – Cu Foil) Cu edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Pd Foil fitting ranges: k : 3.0-13.0 \AA^{-1} , r : 1.75-3.2 \AA . Cu Foil fitting ranges: k : 3.0-11.5 \AA^{-1} , r : 1.6-3.2 \AA .

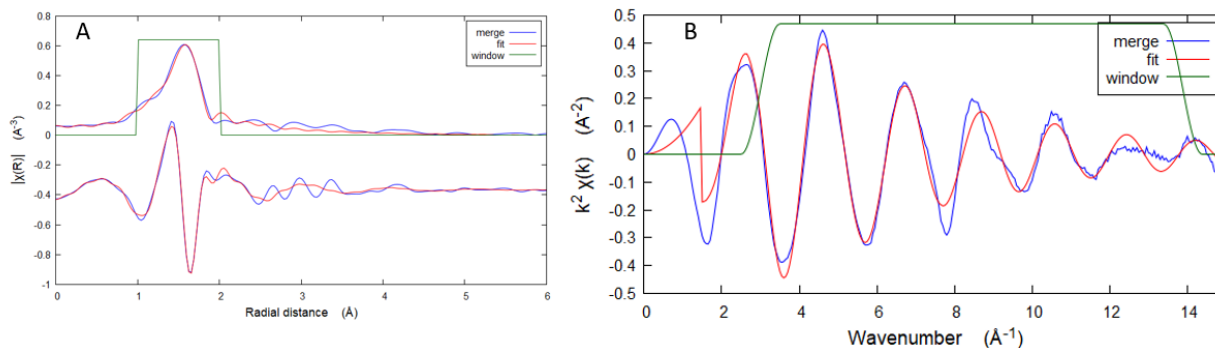


Figure S9 – (Pd/SiO₂): As Prepared Pd edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 3.0-13.0 \AA^{-1} , r : 1.0-2.0 \AA .

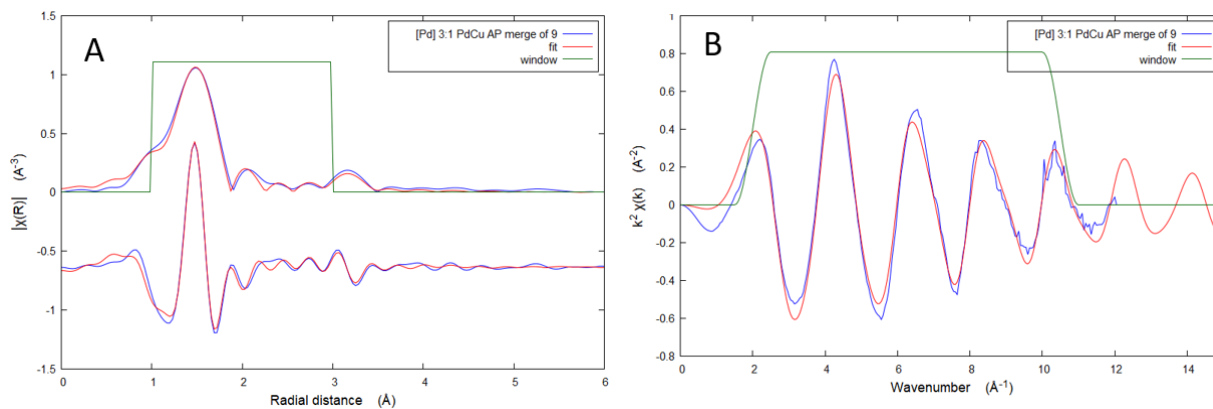


Figure S10 – (3:1 PdCu/SiO₂): As Prepared Pd edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 2.0-10.0 Å⁻¹; r : 1.0-3.0 Å.

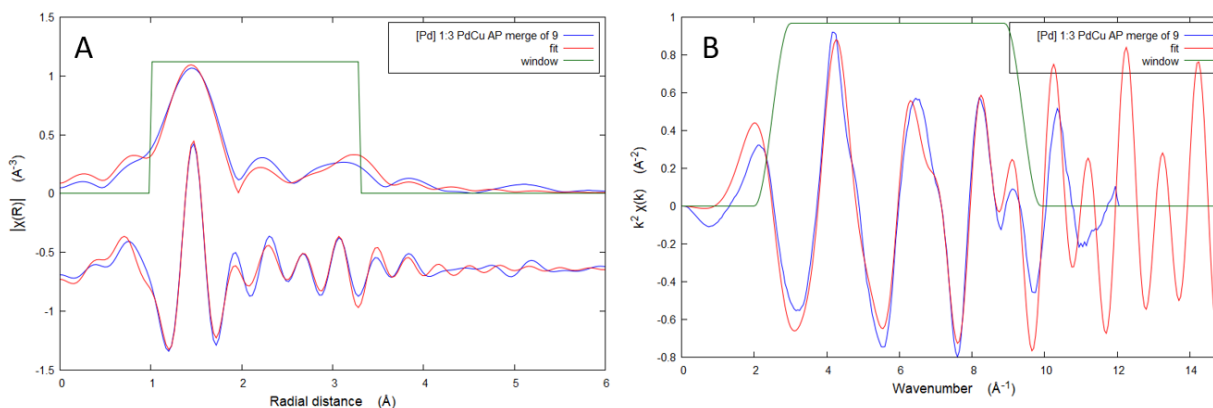


Figure S11 - (1:3 PdCu/SiO₂): As Prepared Pd edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 2.0-10.0 Å⁻¹; r : 1.0-3.0 Å.

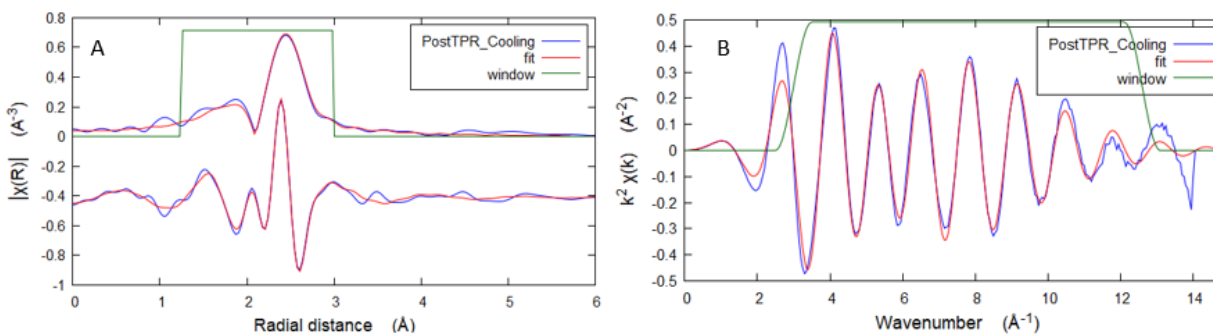


Figure S12 – (Pd/SiO₂): Post reduction Pd edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 3.0-13.0 Å⁻¹; r : 1.0-3.0 Å.

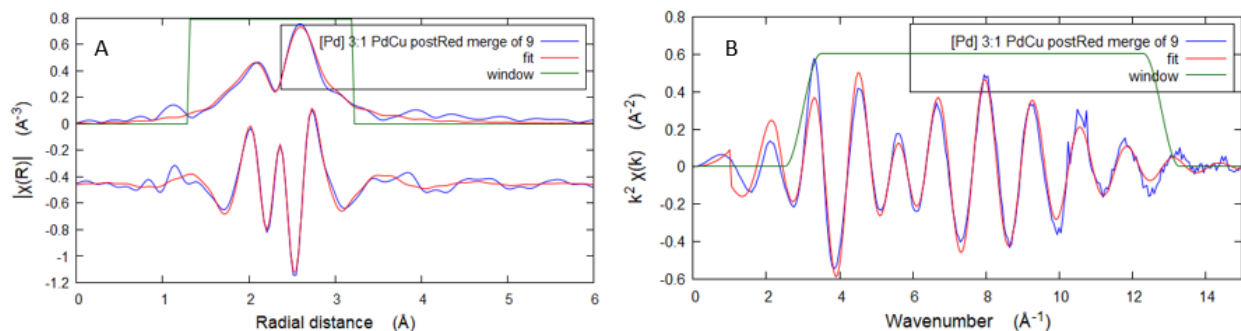


Figure S13 – (3:1 PdCu/SiO₂): Post reduction Pd edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 3.0-13.0 Å⁻¹, r : 1.2-3.2 Å.

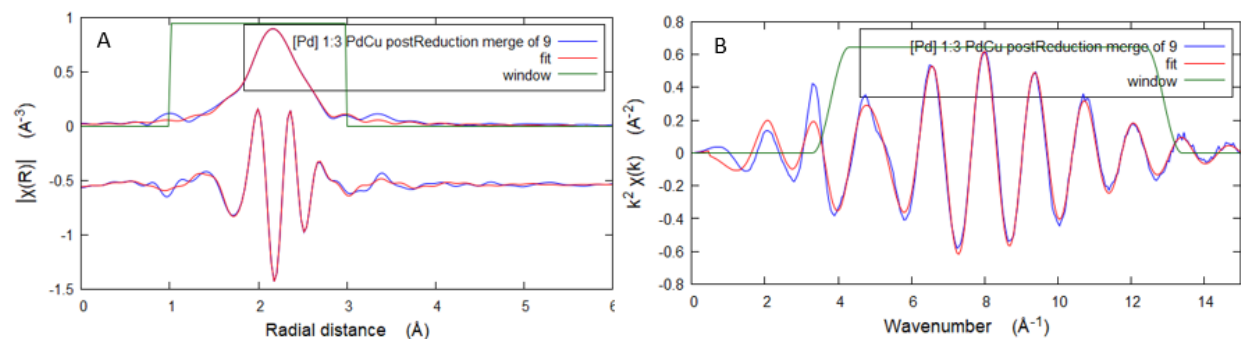


Figure S14 - (1:3 PdCu/SiO₂): Post reduction Pd edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 4.0-13.0 Å⁻¹, r : 1.0-3.0 Å.

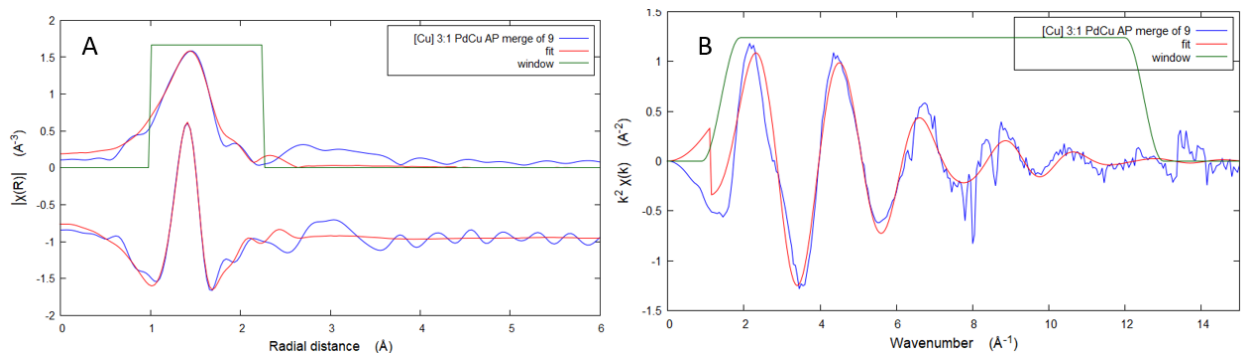


Figure S15 - (3:1 PdCu/SiO₂): As Prepared Cu edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 1.5-12.0 Å⁻¹, r : 1.0-2.25 Å.

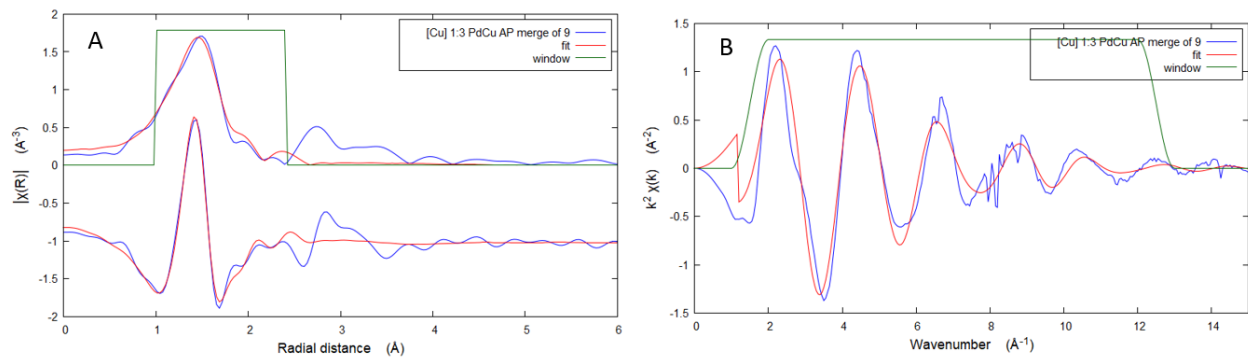


Figure S16 - (1:3 PdCu/SiO₂): As Prepared Cu edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 2.0-12.5 Å⁻¹, r : 1.1-2.6 Å.

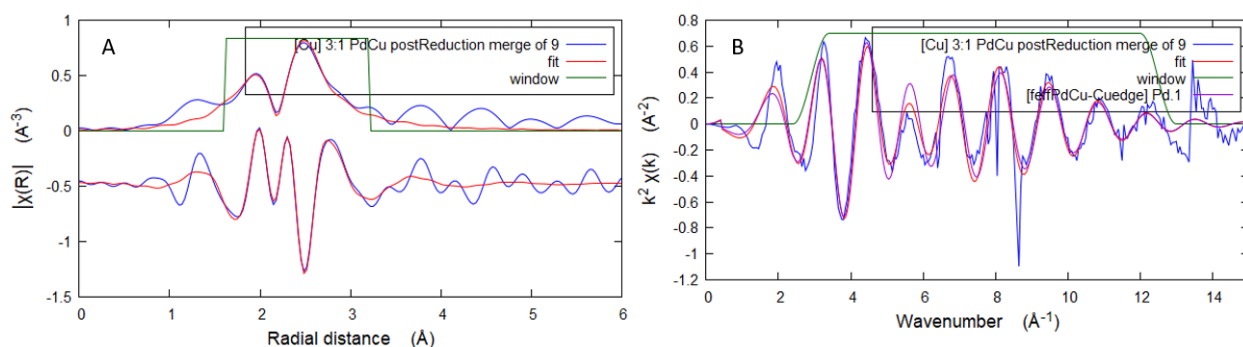


Figure S17 - (3:1 PdCu/SiO₂): Post reduction Cu edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 3.0-13.0 Å⁻¹, r : 1.6-3.2 Å.

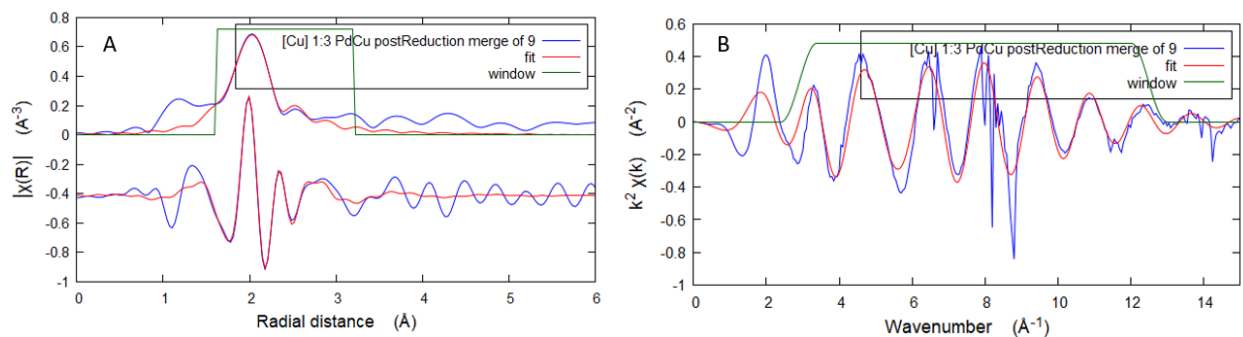


Figure S18 - (1:3 PdCu/SiO₂): Post reduction Cu edge XAS scans shown in k^2 -weighted EXAFS, and the respective fit. Fitting ranges: k : 3.0-12.0 Å⁻¹, r : 1.6-3.2 Å.

Table S6 – EXAFS fitting parameters for the as-prepared catalyst. Fitting ranges included in above

	Sample	Path	C.N.	R (Å)	$10^3 \cdot \sigma^2$ (Å ²)	ΔE_0 (eV)	Reduced χ^2
Pd Edge	Pd Foil	Pd-Pd	12 ± N/A	2.74 ± 0.01	5.4 ± 0.3	3.4 ± 0.4	6539
	Pd	Pd-O	1.9 ± 0.1	2.01 ± -0.05	2.7 ± 1.0	8.3 ± 1.0	1396
	3:1 PdCu	Pd-O	3.1 ± 0.3	2.02 ± 0.01	1.0 ± 1.3	-3.4 ± 1.0	771
	3:1 PdCu	Pd-Pd	1.2 ± 2.2	3.42 ± 0.08	6.5 ± 12.3	-3.4 ± 1.0	771
	1:3 PdCu	Pd-O	3.5 ± 0.2	2.01 ± 0.01	0.2 ± N/A	-4.7 ± 1.6	7036
	1:3 PdCu	Pd-Pd	2.4 ± 0.5	3.41 ± 0.02	0.2 ± N/A	-4.7 ± 1.6	7036
Cu Edge	Cu Foil	Cu-Cu	12 ± N/A	2.54 ± 0.01	8.4 ± 1.1	3.0 ± 1.3	1727
	3:1 PdCu	Cu-O	4.0 ± 0.5	1.88 ± 0.02	8.6 ± 3.3	4.9 ± 1.1	264
	3:1 PdCu	Cu-Cu	0.4 ± 0.8	2.54 ± 0.14	8.6 ± 3.3	4.9 ± 1.1	264
	1:3 PdCu	Cu-O	4.1 ± 0.5	1.90 ± 0.01	7.7 ± 2.6	5.0 ± 0.9	280
	1:3 PdCu	Cu-Cu	0.4 ± 0.6	2.57 ± 0.09	7.7 ± 2.6	5.0 ± 0.9	280

figures.

Table S7 - EXAFS fitting parameters for the post-reduction catalyst. Fitting ranges included in above figures.

	Sample	Path	C.N.	R (Å)	$10^3 \cdot \sigma^2$ (Å ²)	ΔE_0 (eV)	Reduced χ^2
Pd Edge	Pd	Pd-Pd	6.5 ± 0.3	2.74 ± 0.00	13 ± 0.40	-12 ± 0.4	414
	3:1 PdCu	Pd-Pd	7.1 ± 0.7	2.75 ± 0.01	12 ± 1.0	3.9 ± 0.8	355
	3:1 PdCu	Pd-Cu	2.7 ± 0.7	2.63 ± 0.02	16 ± 1.3	3.9 ± 0.8	355
	1:3 PdCu	Pd-Pd	3.1 ± 0.3	2.71 ± 0.00	8.4 ± 0.5	0.9 ± 0.9	291
	1:3 PdCu	Pd-Cu	5.5 ± 0.4	2.59 ± 0.01	11 ± 0.6	0.9 ± 0.9	291
Cu Edge	3:1 PdCu	Cu-Cu	1.5 ± 0.4	2.48 ± 0.01	15 ± 1.2	0.7 ± 0.7	14
	3:1 PdCu	Cu-Pd	4.8 ± 0.4	2.59 ± 0.02	12 ± 0.9	0.7 ± 0.7	14
	1:3 PdCu	Cu-Cu	2.9 ± 0.5	2.48 ± 0.01	11 ± 1.9	-1.2 ± 1.5	20
	1:3 PdCu	Cu-Pd	1.4 ± 0.3	2.55 ± 0.02	8.2 ± 1.5	-1.2 ± 1.5	20

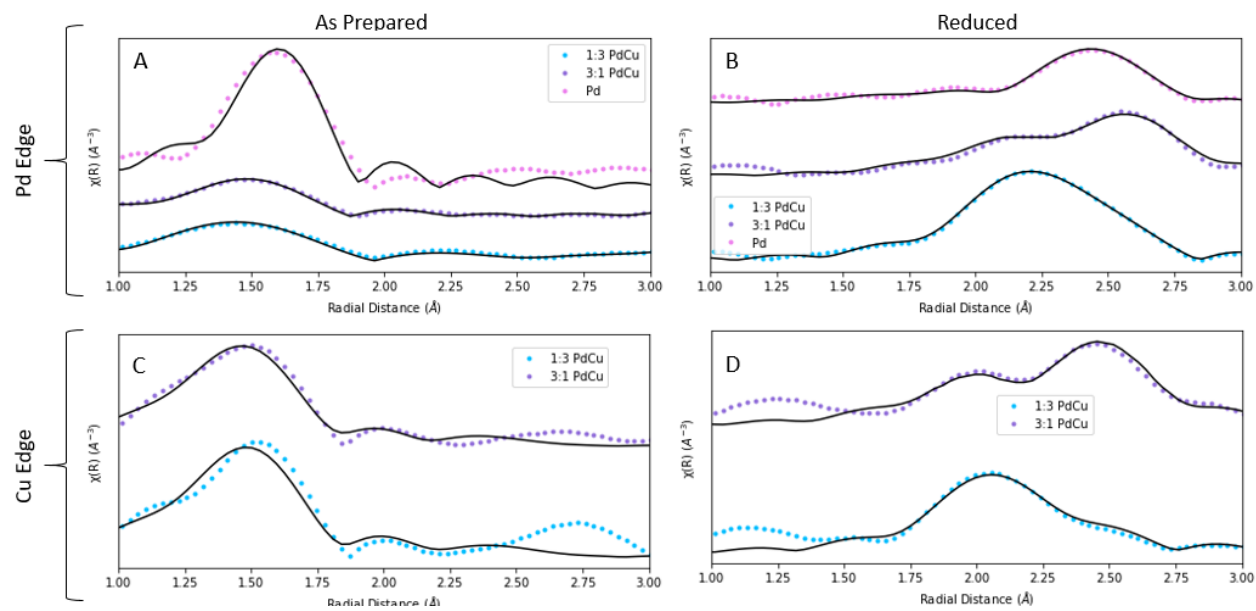


Figure S19 - EXAFS region XAS spectra in Radial Space performed on As Prepared, and Post reduction catalyst samples. The top panels (A and B) show Pd edge data, the bottom show Cu edge data. Panels A and C are As Prepared, B and D are Post reduction.

Table S8 – Linear Combination Fitting Parameters obtained for Pd and Cu edge XANES spectra collected for the as-prepared catalyst samples. PdO and Pd foil references used in Pd edge data. CuO and Cu foil references used in Cu edge data.

		Standard	Catalyst		
			Pd	3:1 PdCu	1:3 PdCu
Pd Edge	Pd Foil	0.43 ± 0.03	0.42 ± 0.05	0.35 ± 0.05	
	PdO	0.57 ± 0.03	0.58 ± 0.05	0.65 ± 0.05	
Cu Edge	Cu Foil	NA	0.27 ± 0.01	0.16 ± 0.01	
	CuO	NA	0.73 ± 0.01	0.84 ± 0.01	

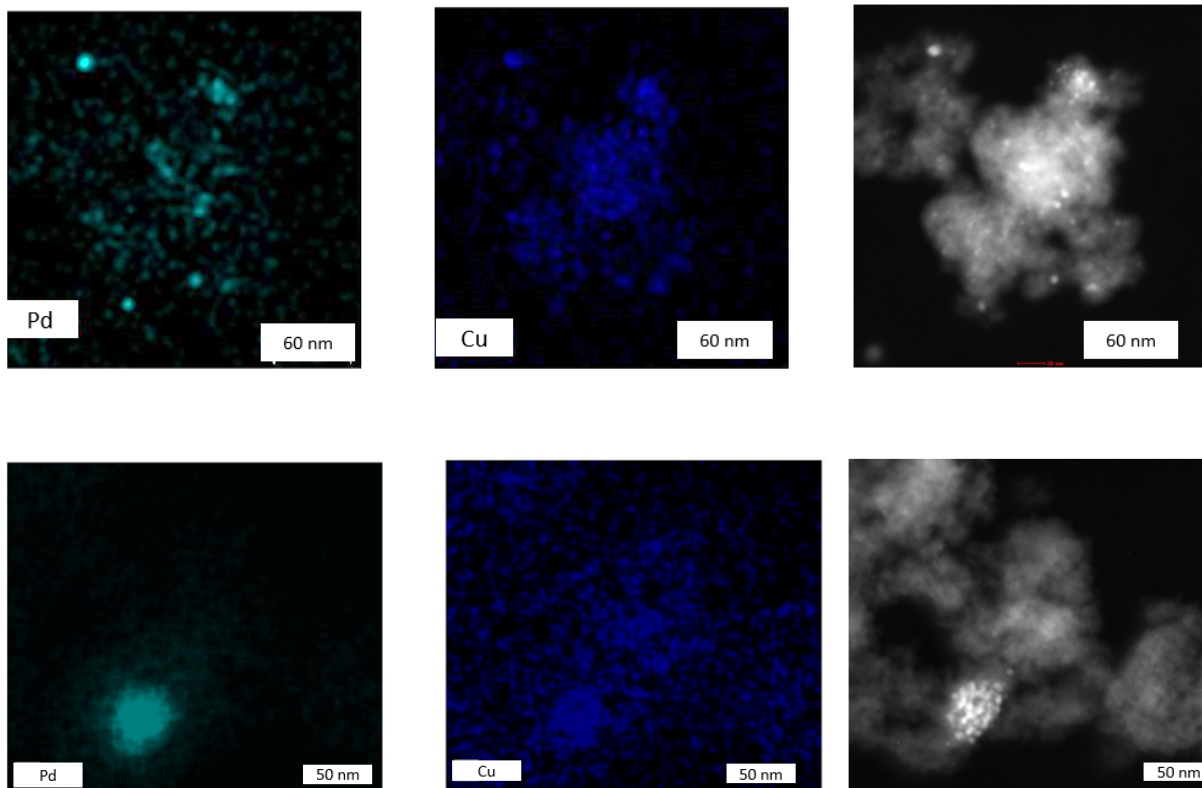


Figure S20: STEM/EDX micrographs of $\text{PdCu}_3/\text{SiO}_2$ catalyst (top) and $\text{Pd}_3\text{Cu}/\text{SiO}_2$ catalyst (bottom)