Restructuring of AuPd nanoparticles studied by a combined XAFS/DRIFTS approach

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1. TEM-EDX results

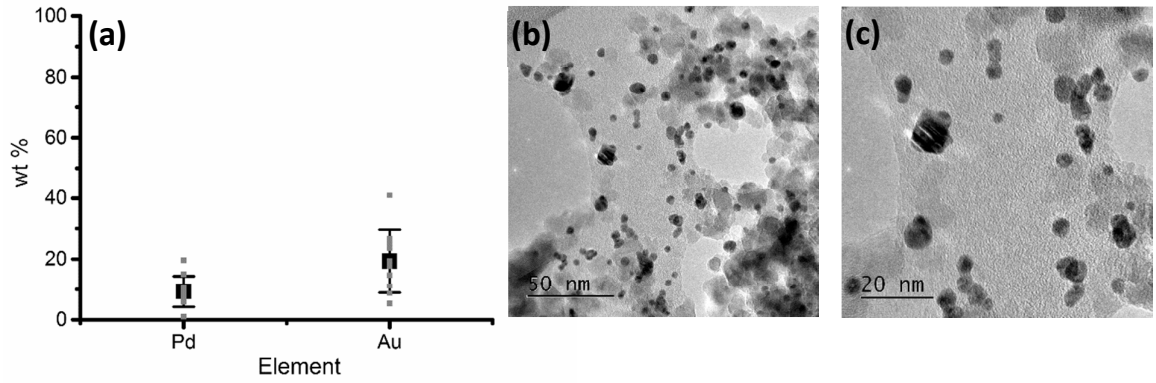

Figure S1 (a) The mean wt. % of Pd and Au (black squares), the standard deviation and the individual data for each particle (grey squares), representative TEM images of the AuPd/Al_2O_3 catalyst at (b) 50 nm and (c) 20 nm resolution.

EDX point measurements were performed on 10 particles, chosen at random. As the AuPd particles are approximately 4 nm the X-ray beam probed the bulk composition of the particles rather than their surface and so no information could be gathered as to the core-shell or alloy state using this technique. O and Al were also observed on these point measurements, however quantitative analysis of these elements is not reliable by EDX, so the values obtained are not shown here.

2. Determination of the σ^2 value

The same rate of change in σ^2 with temperature as calculated for Germanium by Dalba and Fornasini[1] was applied to the spectra collected during the CO oxidation experiment but starting from the σ^2 values determined from the fits of the spectra collected at 25°C at the Pd K-edge and Au L_3-edge. Figure S2 shows the change in σ^2 with temperature used for the Au and Pd data as shown by the green and blue data points, respectively, using the slope derived from the Germanium data.

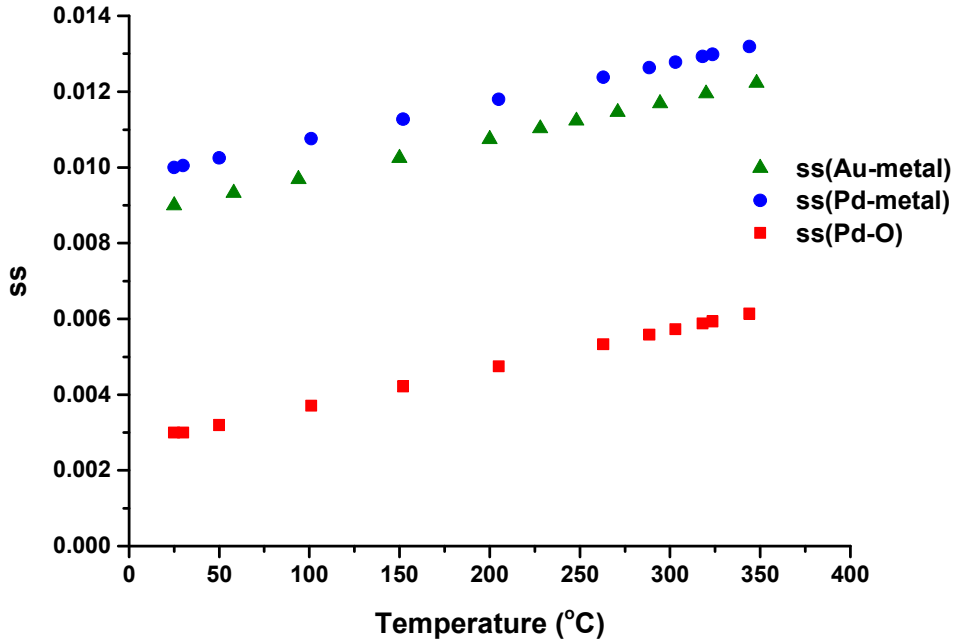

Figure S2 Change in the mean-squared relative displacement of absorber and backscatter atoms with temperature.

3. X

AFS fitting parameters

Refined Parameter	RT	50°C	101°C	152°C	205°C	263°C	[a] Merged 288.5°C	[a] Merged 324°C
$CN_{Pd(Pd)}$	5(1)	7(1)	8(1)	7(1)	7(1)	5(1)	4.3(4)	3.5(7)
$CN_{O(PdO)}$	2.4(2)	1.9(3)	1.1(3)			0.6(2)	0.8(2)	1.2(3)
$CN_{Pd(PdO)}$	8(3)	8(2)	5(3)					
$CN_{Pd2(PdO)}$	4(1)							
CN_{Au}	2(2)	3(2)	3(2)	4(1)	4(1)	5(1)	5(1)	5(1)
$R_{Pd(Pd)}$	2.86(4)	2.84(4)	2.79(3)	2.74(1)	2.75(1)	2.72(2)	2.69(2)	2.67(2)
$R_{O(PdO)}$	2.04(2)	2.02(3)	1.98(3)			1.94(3)	1.97(2)	1.95(2)
$R_{Pd(PdO)}$	3.07(3)	3.06(4)	3.01(4)					
$R_{Pd2(PdO)}$	3.43(3)							
R_{Au}	2.83(7)	2.82(7)	2.78(5)	2.75(3)	2.76(3)	2.75(3)	2.72(2)	2.71(2)
$SS_{Pd(Pd)}$	0.01	0.01025	0.01076	0.01127	0.0118	0.01238	0.01264	0.01299
$SS_{O(PdO)}$	0.03	0.032	0.00371			0.00533	0.00559	0.00594
$SS_{Pd(PdO)}$	0.01	0.01025	0.01076					
$SS_{Pd2(PdO)}$	0.01	0.01025						
SS_{Au}	0.01	0.01025	0.01076	0.01127	0.0118	0.01238	0.01264	0.01299
E_0	9(3)	6(2)	6(3)	2(1)	4(1)	2(1)	-2(1)	-3(1) (restrained -3 to 3)
R-factor	0.0035	0.0038	0.027	0.027	0.034	0.026	0.003	0.016

Table 1 The EXAFS fitting parameters for the Pd K-edge for spectra collected approximately every 50°C during the ramp to 350°C under CO oxidation conditions. Fitting parameters: S_0^2 = 0.85 as determined by the use of a Pd foil standard; Fit range 3<k<10, 1.15<R<3.85; number of independent points = 11.8, [a] Fitting parameters: R1.15 <R <3.6, 3.0<k<8.5, number of independent points = 8.4.

Refined Parameter	304°C Merged	215°C	198°C	166°C	125°C	107°C	79°C	48°C	25°C	25°C O_2
$CN_{Pd(Pd)}$	2.9(8)	6.5(3)	7.0(4)	7.3(5)	7.4(4)	7.2(5)	7.5(5)	7.5(5)	7.7(5)	7.7(4)
$CN_{O(PdO)}$	1.7(4)									
$CN_{Pd(PdO)}$										
CN_{Pd_Au}	4(1)	4.9(5)	4.5(7)	4.6()	4.9(7)	4.9(7)	4.7(7)	4.8(7)	4.9(7)	4.7(7)
$R_{Pd(Pd)}$	2.69(3)	2.75(1)	2.74(1)	2.75(1)	2.75(1)	2.75(1)	2.75(1)	2.75(1)	2.75(1)	2.753(9)
$R_{O(PdO)}$	1.96 (2)									
$R_{Pd(PdO)}$										
R_{Pd_Au}	2.73(3)	2.76(5)	2.76(2)	2.76(2)	2.76(2)	2.76(2)	2.75(1)	2.76(2)	2.76(1)	2.75(1)
$SS_{Pd(Pd)}$	0.01279	0.0119	0.01173	0.01141	0.011	0.1082	0.01054	0.01023	0.01	0.01
$SS_{O(PdO)}$	0.0574									
$SS_{Pd(PdO)}$										
SS_{Pd_Au}	0.01279	0.0119	0.01173	0.01141	0.011	0.1082	0.01054	0.01023	0.01	0.01
E_0	-3 Restrained	2.9(6)	2.3(7)	2.3(8)	2.7(7)	2.8(7)	3.1(9)	2.7(7)	3.56)	2.4(6)
R-factor	0.022	0.0037	0.005	0.005	0.004	0.004	0.004	0.004	0.004	0.004

Table S2 The EXAFS fitting parameters for the Pd K-edge for spectra collected approximately every 50°C during the cooling step under CO oxidation conditions. Fitting parameters: S_0^2 = 0.85 as determined by the use of a Pd foil standard; Fit range 3<k<8.5, 1.15<R<3.6; number of independent points = 8.4,

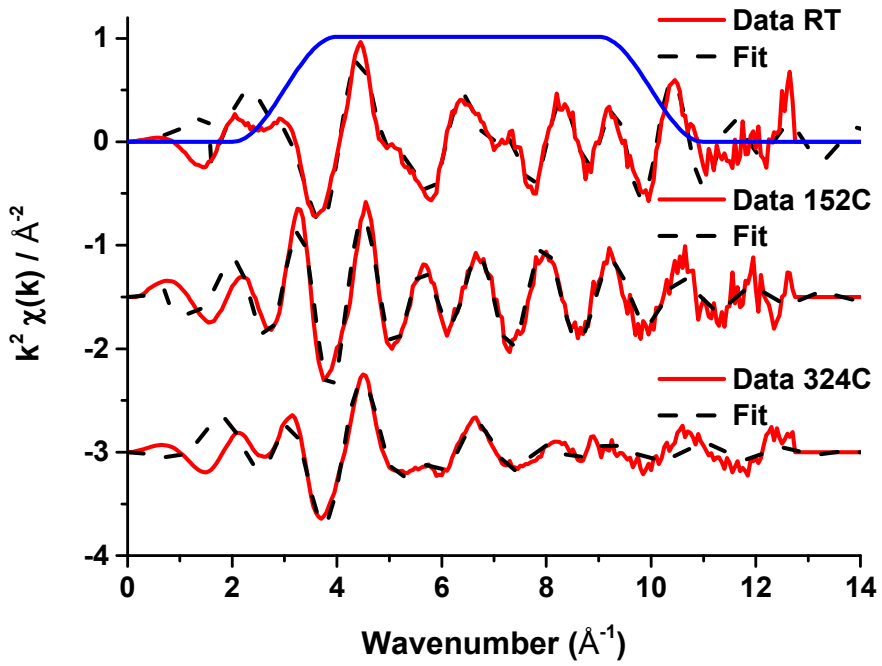

Figure S3 $k^2\chi$ data for RT, 152°C and 324°C, and their respective fits

RT-350	RT	58°C	94°C	150°C	200°C	228C	248C	271C	300C	320C	348°C
CN_{Au-Au}	6 (2)	7(1)	7(1)	8(1)	8(2)	7(1)	7(1)	7(1)	7(1)	6(1)	6(1)
CN_{Au-Pd}	4(3)	4(1)	4(1)	4(1)	4(1)	5(1)	4(1)	4(1)	4(1)	4(1)	4(1)
R_{Au-Au}	2.81(4)	2.80(2)	2.81(2)	2.82(2)	2.79(2)	2.80(3)	2.81(3)	2.81(3)	2.81(3)	2.80(3)	2.79(3)
R_{Au-Pd}	2.79(4)	2.79(3)	2.78(3)	2.78(3)	2.76(3)	2.77(3)	2.76(4)	2.76(3)	2.77(4)	2.76(3)	2.76(3)
ss_{Au-Au}	0.009(SET)	0.00933	0.00969	0.01025	0.01075	0.01103	0.01123	0.01146	0.01168	0.01195	0.01223
ss_{Au-Pd}	0.009(SET)	0.00933	0.00969	0.01025	0.01075	0.011	0.011	0.01146	0.01168	0.01195	0.01223
E_0	3(2)	5(1)	5(2)	5(2)	4(1)	4(2)	4(2)	4(2)	4(2)	4(2)	4(2)
R-factor	0.024	0.0269	0.0307	0.034	0.022	0.042	0.054	0.033	0.041	0.049	0.043

Table S3 The EXAFS fitting parameters for the Au L_3-edge for spectra collected approximately every 50°C during the temperature ramp under CO oxidation conditions. Fitting parameters: S_0^2 = 0.83 as determined by the use of a Au foil standard; Fit range 3<k<8.5, 1.15<R<4; number of independent points = 9.8.

Refined Parameter	305°C	272°C	243°C	203°C	148°C	101°C	53°C	25°C	25°C O_2
CN_{Au-Au}	6(1)	6(1)	7(2)	7(2)	7(1)	7(1)	7(1)	7(1)	7(1)
CN_{Au-Pd}	4(1)	4(2)	5(1)	5(1)	5(1)	5(1)	5(1)	5(1)	5(1)
R_{Au-Au}	2.80(4)	2.80(3)	2.81(3)	2.80(2)	2.80(2)	2.80(2)	2.79(2)	2.80(2)	2.80(3)
R_{Au-Pd}	2.76(4)	2.77(3)	2.78(3)	2.78(3)	2.78(2)	2.78(2)	2.78(2)	2.78(2)	2.78(3)
ss_{Au-Au}	0.01180	0.01147	0.01118	0.01078	0.01023	0.00976	0.00928	0.009	0.009
ss_{Au-Pd}	0.01180	0.01147	0.01118	0.01078	0.01023	0.00976	0.00928	0.009	0.009
E_0	4(2)	4(2)	4(2)	4(1)	5(1)	5(1)	4(1)	5(2)	5(2)
R-factor	0.036	0.033	0.050	0.028	0.025	0.031	0.024	0.033	0.038

Table S4 The EXAFS fitting parameters for the Au L_3-edge for spectra collected approximately every 50°C during the cooling stage under CO oxidation conditions. Fitting parameters: S_0^2 = 0.83 as determined by the use of a Au foil standard; Fit range 3<k<8.5, 1.15<R<4; number of independent points = 9.8

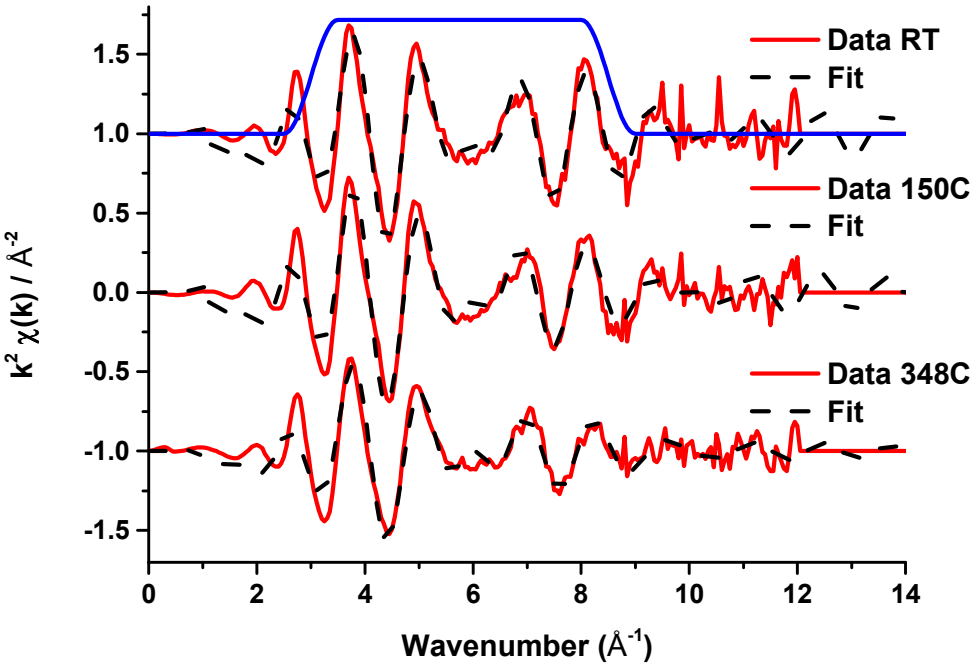

Figure S4 $k^2\chi$ data for RT, 152°C and 324°C, and their respective fits

4. Cowley Short-Range Order Parameter

As discussed in references 3 and 4 the coordination numbers determined form the EXAFS analysis can be used in the Cowley short-range order parameter (Equation 1)[2] to interpret the extent of clustering or alloying in the structure.[3, 4]

$$a_{Au} = 1 - \frac{N_{AuPd}A/N_{AuM}}{X_{Pd}} \quad (1)$$

Where X_B is the molar ratio of Pd, this can be calculated from Equation 2.[3]

$$N_{PdAu}/N_{AuPd} \sim x_{Au} : x_{Pd} \sim \gamma$$

$$\frac{1}{1+\gamma} = x_{Pd} \quad (2)$$

The values of α calculated from our data at 150°C and on cooling are shown in Table S5. Comparing to those in reference 4, at 150°C our nanoparticles are more consistent with an alloy and on cooling the nanoparticles have a more core-shell character.

Temperature	α_{Au}	α_{Pd}
~150°C	0.34	0.83
~200°C cooling	0.27	0.86

Table S5 Cowley short range order parameters calculated from the coordination numbers of the AuPd nanoparticle at 150°C and at approximately 200°C on cooling.

5. DRIFTS spectra recorded during CO oxidation

Figure S5 shows selected spectra taken during CO oxidation, during the CO oxidation experiment performed at the Pd K-edge. The band assigned to CO adsorbed on Au^0 appears (2112cm^{-1}) as the bands for CO adsorbed on PdO disappear (2157 and 2137 cm^{-1}). This CO on Au starts to disappear itself at 166°C which is consistent with the Au EXAFS analysis which shows an increasing Au-Au coordination at 150°C.

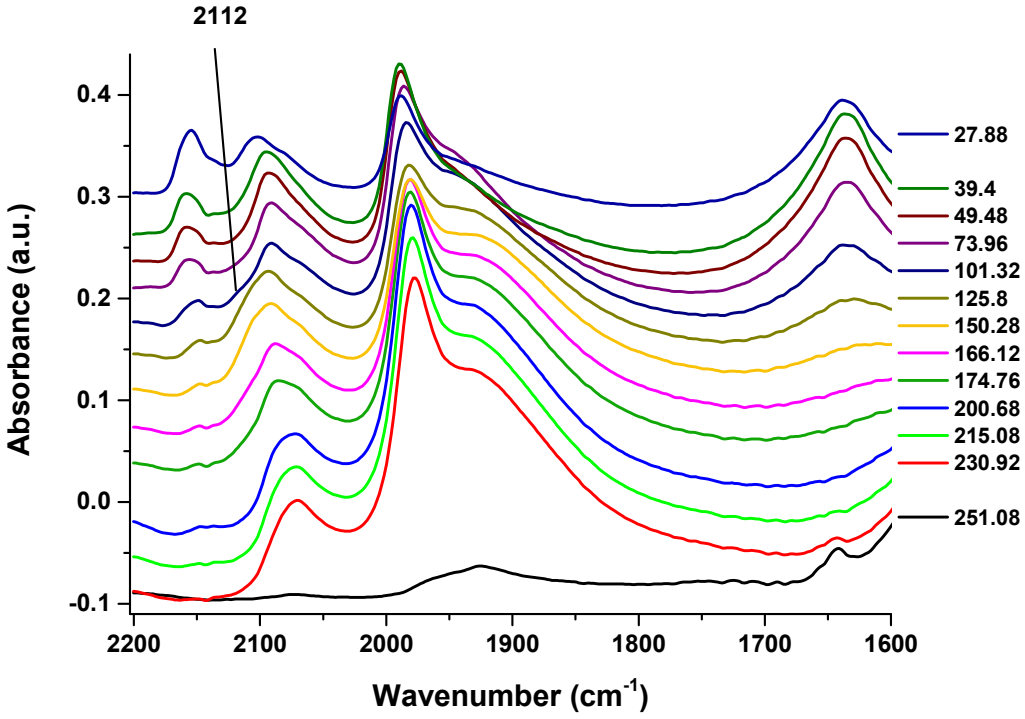

Figure S5 Selected DRIFTS spectra taken between 27-251°C during the CO oxidation experiment performed at the Pd K-edge.

Temperature Programmed Desorption of CO

The sample was heated to 125°C to remove water then cooled to RT before flowing 10%CO/He. The cell was flushed of gas phase CO by flowing He for 10 minutes at 25°C. The spectra shown in Figures S4 and S5 have had the spectrum recorded at RT after initial heating to 125°C subtracted, additionally the spectra in Figure S6 have also had the CO gas phase subtracted.

The band at 2123 cm^{-1} which can be tentatively assigned to CO-Au^+ desorbs after only 2 minutes under flowing He. The sample was then heated to 200°C, Figure S7, during which the band at 2109cm^{-1} for CO-Au linear desorbs as does the CO-Pd^{2+} (2152 cm^{-1}), by 95 and 167°C respectively. Linearly adsorbed CO-Pd^0 shown by the bands at 2096 and 2065 cm^{-1} remain on the surface even at 200°C. The increase in intensity of the broad shoulder near 1950 cm^{-1} is consistent with CO adsorbed on 3-fold Pd sites, which can occur at lower coverage, as observed from the reduction in intensity of the linear CO bands. A shift in the doubly bridged species also occurs on reduced coverage, the band at 1970 shifts to 1945 cm^{-1}.[5] Please note, the temperatures measured during the TPD are slightly

overestimated compared with those during CO oxidation using the XAFS/DRIFTS cell, as the cell used for the TPD measurements does not have an independent thermocouple in the catalyst bed.

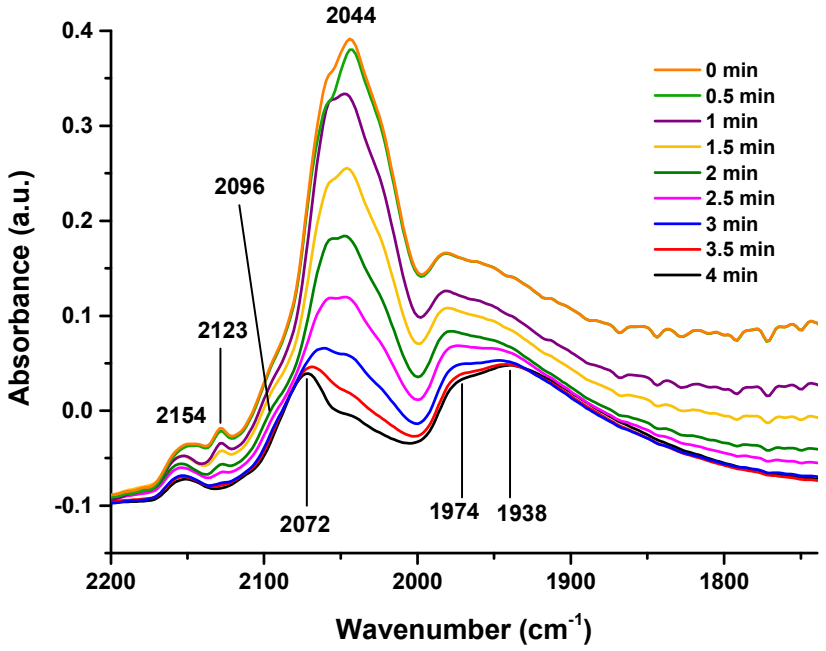

Figure S6 DRIFTS spectra taken during the helium purge after CO adsorption at room temperature.

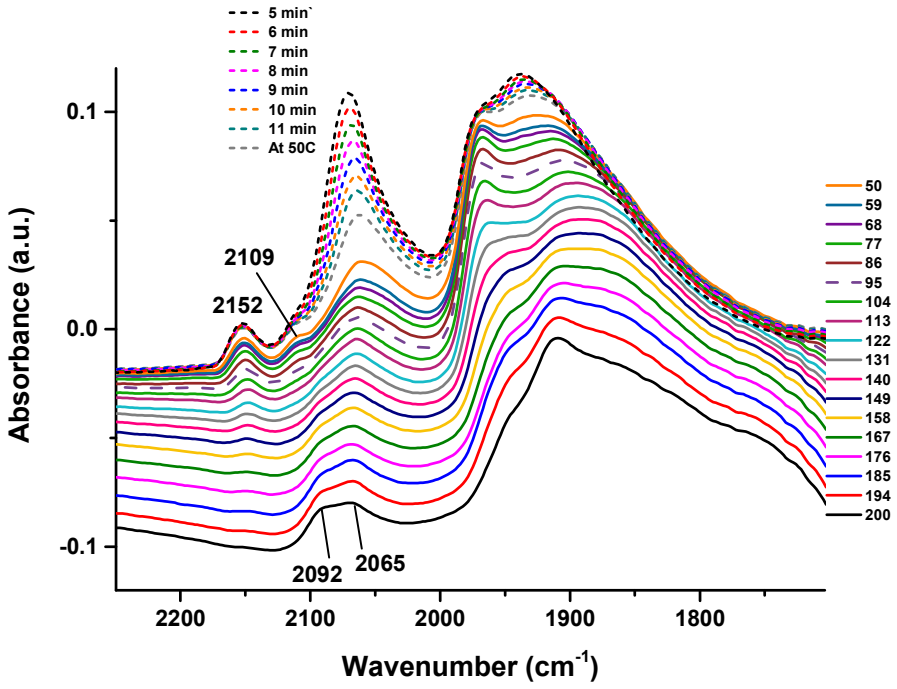

Figure S7 DRIFTS spectra taken during the temperature ramp to 200°C under helium after CO adsorption at room temperature.

6. DRIFTS spectra during the cooling stage of the CO oxidation experiment

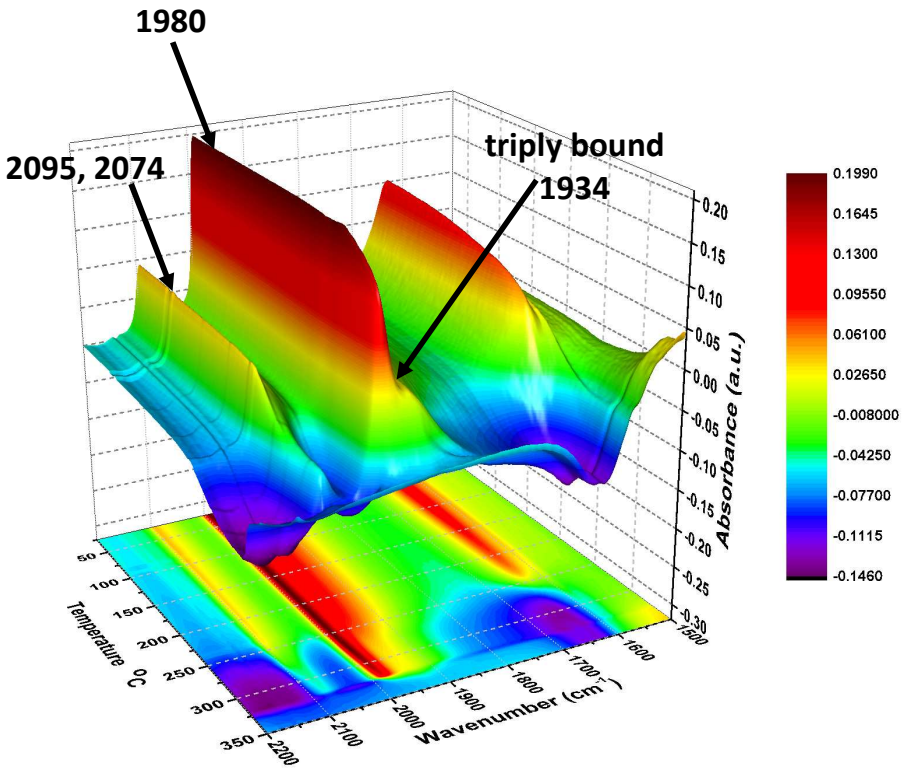

Figure S8 DRIFTS spectra recorded during the cooling step of the Pd K-edge experiment under CO oxidation conditions.

During the cooling stage of the CO oxidation reaction performed at the Pd K-edge, bands for CO linearly, bridge-onded and triply bonded to Pd were observed. No bands for CO adsorbed on PdO or on Au were observed. This can be more clearly observed by comparing individual spectra taken during the CO TPD measurement, the CO oxidation experiment and the cooling stage, as shown in Figure S9.

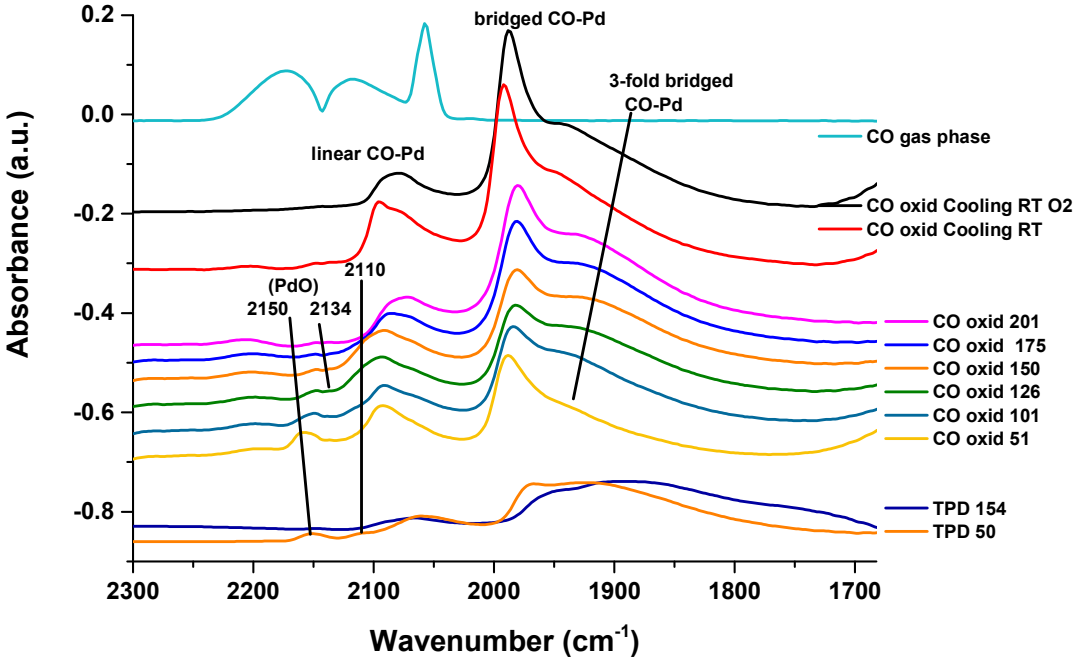

Figure S9 Selected DRIFTS spectra recorded during the CO TPD experiment, the reaction and cooling stages of the CO oxidation experiment and the CO gas phase spectrum.

1. G. Dalba and P. Fornasini, *J. Synchrotron Rad.*, 1997, 4, 243-255.
2. J. M. Cowley, *Physical Review*, 1965, 138, A1384-A1389.
3. B. M. W. Andrew M. Beale, *Physical Chemistry Chemical Physics*, 2010, 12, 5562-5574.
4. A. I. Frenkel, Q. Wang, S. I. Sanchez, M. W. Small and R. G. Nuzzo, *The Journal of Chemical Physics*, 2013, 138, 064202-064207.
5. S. Marx, F. Krumeich and A. Baiker, *Journal of Physical Chemistry C*, 2011, 115, 8195-2025.