Supplementary Information

CO oxidation activity of Pt, Zn and ZnPt nanocatalysts: a comparative study with *in situ* Near-Ambient Pressure X-ray Photoelectron Spectroscopy

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Supplementary information. STM images of ZnPt NPs after annealing in UHV at 500 K and after exposure to pure O_2 at 1 mbar pressure at 500 K. Gas phase CO core-level spectra at photon energies hν = 400 eV. In situ core-level spectra of Ti 2p at hν = 560 eV and Pt 4f at two photon energies, hν = 400 eV and hν = 165 eV. The fitting parameters of Pt 4f in pure Pt and ZnPt NPs at hν = 400 eV. In situ Core-level spectra in the binding energy region of Pt 4f and Zn 3p recorded at photon energies of hν = 400 eV and hν = 165 eV recorded on ZnPt samples.

S1. STM images after annealing in UHV at 500 K and after annealing at 500 K under 1 mbar of pure O_2 at 500 K

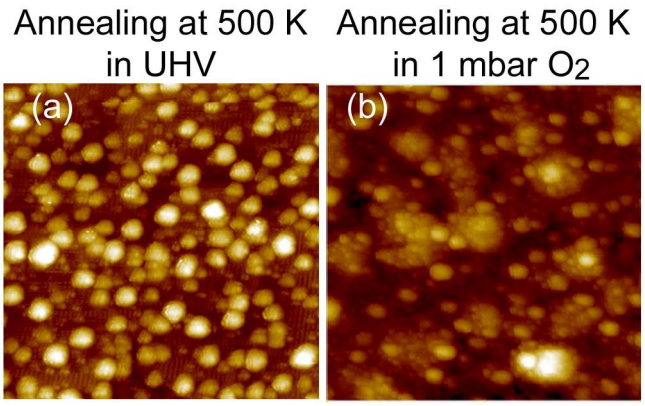

Figure S1: (50 nm × 50 nm) STM images of ZnPt NPs deposited on TiO_2(110). (a) after annealing at 500 K in UHV. (b) after annealing at 500 K under 1 mbar of O_2. The image (b) was recorded after pumping the gas. Note the strong roughening of the surface after annealing at 500 K under 1 mbar of O_2.

S2. Gas phase CO core-level spectra

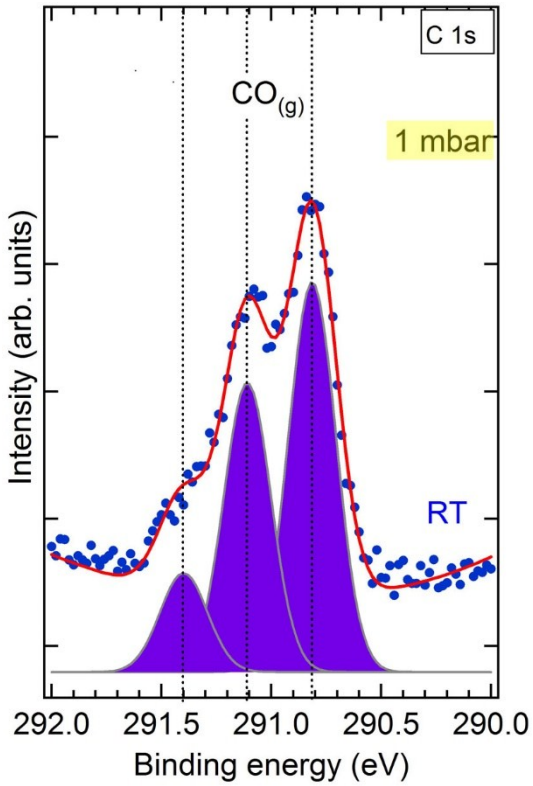

Figure S2. CO gas phase ($CO_{(g)}$) in C 1s spectrum measured at hν=400 eV fitted with a vibrational progression v'=0 (adiabatic peak), v'=1 and v'=2, distant by 300 meV each,[1] with a FWHM of 280 meV. This gas phase region is extracted from the C 1s spectra of Zn NPs at RT shown in Figure 3b. The spectrum was recorded under a pressure of 1 mbar and with a $CO:O_2$ ratio of 1:4.

S3. Ti 2p core-level spectra

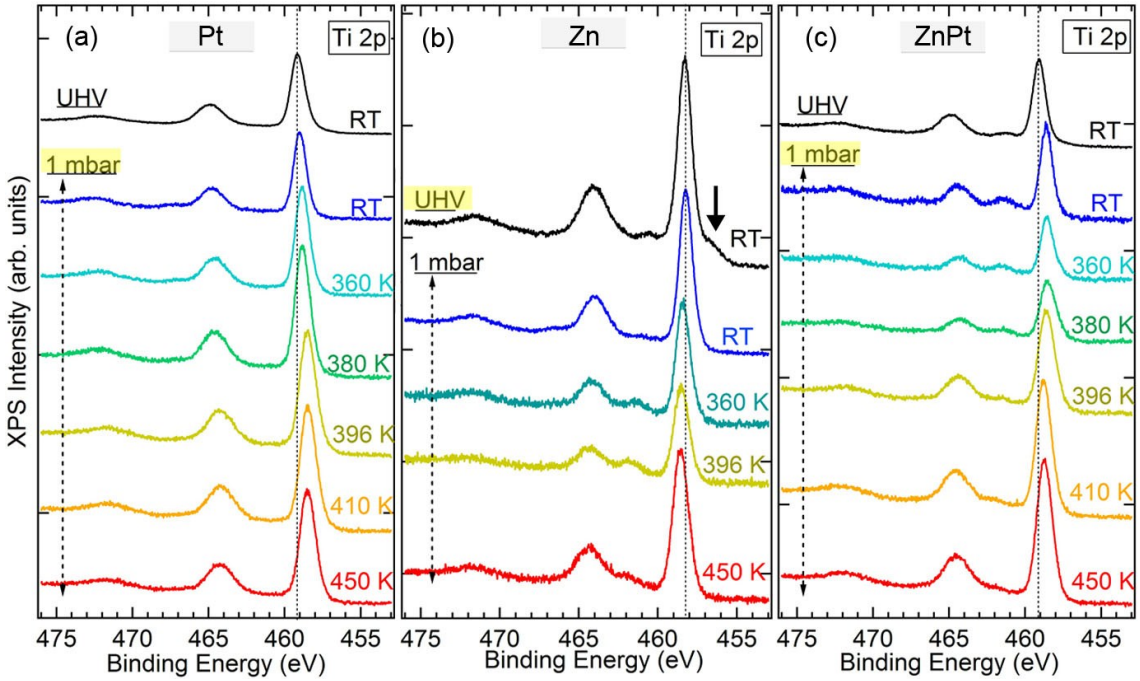

Figure S3: Temperature dependence of the Ti 2p core-level spectra of the pure Pt NPs (a) pure Zn NPs (b) and bimetallic ZnPt NPs (c) supported on TiO_2(110) in a mixture of $CO:O_2$ (1:4) under a total pressure of 1 mbar. The spectra recorded at a photon energy hν of 560 eV. The spectrum denoted "UHV" was recorded at room temperature (RT) before exposure to gases. In panel (b) the shoulder to the right of the Ti $2p_{3/2}$ component (arrow) indicates the formation of Ti^{3+} after Zn deposition at room temperature. An exposure to the oxygen rich mixture quenches this component. RT=293 K.

S4. Pt 4f spectra at photon energy hν = 400 eV

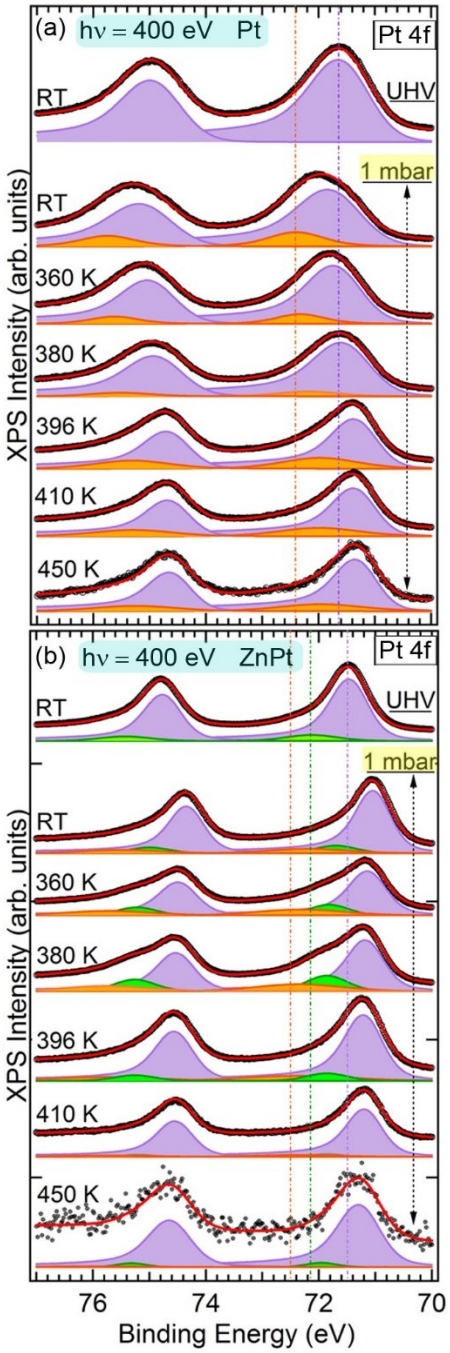

Figure S4. Pt 4f spectra of the pure Pt and ZnPt NPs measured at hν = 400 eV in a mixture of $CO:O_2$ (1:4) under a total pressure of 1 mbar. The spectra denoted UHV are recorded at room temperature (RT) before exposure to gases. RT = 293 K.

Table S1: fitting parameters of Pt 4f spectra in pure Pt NPs recorded at hν = 400 eV and shown in Fig. S 4(a)

	Pt^0 (Pt_{met})		Pt^{2+} (PtO)	
	FWHM = 0.124 Asym = 0.205		FWHM = 0.41	
	BE ($Pt\ 4f_{7/2}$)	**BE ($Pt\ 4f_{5/2}$)**	**BE ($Pt\ 4f_{7/2}$)**	**BE ($Pt\ 4f_{5/2}$)**
UHV	71.52	74.87	--	--
RT	71.70	75.05	72.40	75.75
360 K	71.44	74.74	72.17	75.63
380 K	71.48	74.81	72.18	75.51
396 K	71.29	74.62	71.99	75.32
410 K	71.30	74.60	72.00	75.30
450 K	71.26	74.56	71.96	75.26

Table S2: fitting parameters of Pt 4f spectra in bimetallic ZnPt NPs recorded at hν = 400 eV and shown in Fig. S 4(b)

	Pt^0 (Pt_{met})		**Pt (ZnPt alloy)**		**Pt^{2+} (PtO)**	
	FWHM = 0.271 Asym = 0.115		FWHM = 0.1		FWHM = 0.05	
	BE ($Pt\ 4f_{7/2}$)	**BE ($Pt\ 4f_{5/2}$)**	**BE ($Pt\ 4f_{7/2}$)**	**BE ($Pt\ 4f_{5/2}$)**	**BE ($Pt\ 4f_{7/2}$)**	**BE ($Pt\ 4f_{5/2}$)**
UHV	71.43	74.73	72.13	75.43	--	--
RT	71.01	74.31	71.70	75.00	72.19	75.49
360 K	71.10	74.45	71.82	75.22	72.32	75.72
380 K	71.14	74.49	71.86	75.26	72.35	75.75
396 K	71.17	74.52	71.86	75.26	72.38	75.78
410 K	71.16	74.51	71.85	75.20	72.37	75.72
450 K	71.25	74.60	71.96	75.32	72.52	75.93

S5. Pt 4f spectra recorded at photon energy hν = 165 eV

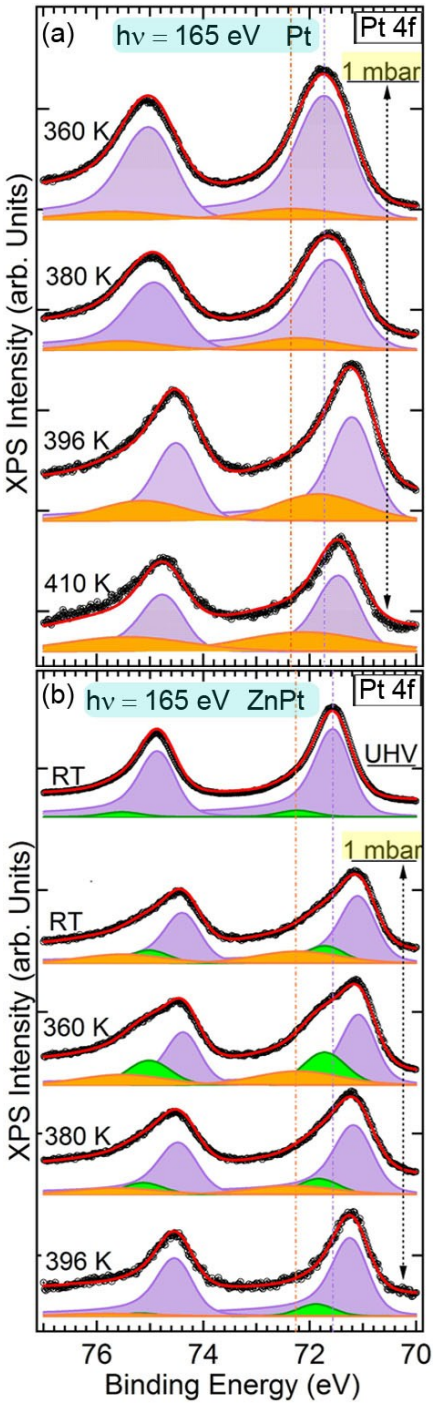

Figure S5. Pt 4f spectra of the pure Pt and ZnPt NP samples measured at hν = 165 eV in a mixture of $CO:O_2$ (1:4) under a total pressure of 1 mbar. The spectra denoted UHV are recorded at room temperature (RT) before exposure to gases. RT = 293 K.

S6. Pt 4f and Zn 3p spectra recorded at photon energy hν = 400 eV and hν = 165 eV

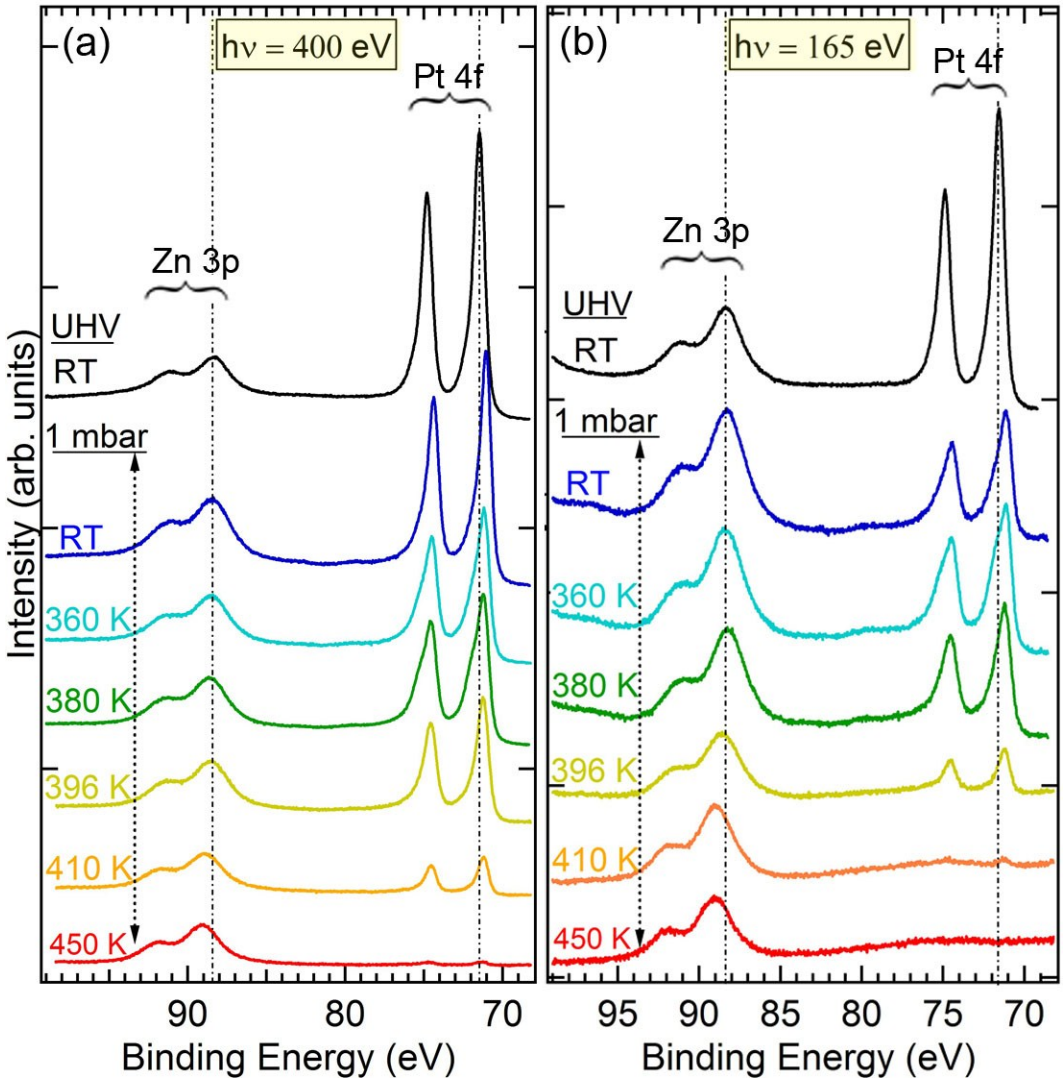

Figure S6**.** Pt 4f and Zn 3p binding energy region of the pure Pt and ZnPt NP samples measured at hν = 400 eV (bulk sensitive conditions) and 165 eV (surface sensitive conditions) in a CO:O_2 mixture (1:4) and under a total pressure of 1 mbar. The spectra denoted UHV are recorded at room temperature (RT) before exposure to gases. RT = 293 K.

References

1. Kempgens, B.; Maier, K.; Kivimaki, A.; Koppe, H. M.; Neeb, M., Vibrational excitation in C 1s and O 1s photoionization of CO. *J Phys B-at Mol Opt* **1997,** *30*, L741-L747.