Operando Near Ambient Pressure XPS Study of the CO Oxidation Reaction on the Oxide/Metal Model Catalyst ZnO/Pt(111)

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Supporting Information

Table S1: *The normalized adsorbed CO intensities,* $R_{C1s}^{CO}(T) = \frac{I_{C\ 1s\ NAP-XPS}^{COads}(T)}{I_{C\ 1s\ NAP-XPS}^{COgas}(T)} \times p_{QMS}^{CO}(T)$*, as a function of the temperature. Time is the acquisition time of the* P_{QMS}^{CO} *corresponding to each C 1s XPS.* P_{QMS}^{CO} *indicates the corresponding pressure of CO monitored by QMS.* $I_{C\ 1s\ NAP-XPS}^{COgas}$ *and* $I_{C\ 1s\ NAP-XPS}^{COads}$ *are the integral intensities calculated from the fitting of the CO gas phase and the adsorbed CO peaks in C 1s XPS.*

Temperature (K)	Time (min)	P_{QMS}^{CO} (mbar)	$I_{C\ 1s\ NAP-XPS}^{COgas}$	$I_{C\ 1s\ NAP-XPS}^{COads}$	$Normalized\ R_{C1s}^{CO}$
293	19	0.25	1.20	6.81	1
410	330	0.22	1.09	6.53	0.89
445	485	0.16	1.00	7.26	0.80
465	681	0.13	0.80	6.86	0.74

Table S2: *The fitting parameters of the formate and the carboxyl in C 1s XPS of ZnO/Pt(111) and the evolution of the $I_{Formate}$ / $I_{Carboxyl}$ ratio as a function of the temperature.*

	Formate		Carboxyl		
	BE	FWHM	BE	FWHM	$I_{Formate}$ / $I_{Carboxyl}$
293 K	289.51	0.99	288.79	1.00	0.43
410 K	289.59	0.95	288.92	1.00	0.66
445 K	289.57	0.99	288.83	1.00	1.51
465 K	289.65	1.00	288.95	1.00	1.65
485 K	289.65	0.99	288.91	1.00	3.31
520 K	289.53	1.10	288.80	1.10	3.54

Table S3: *The calibrated formate/carboxyl intensities as a function of the temperature,* $R_{C1s}^{carboxyl/formate}(T) = \frac{I_{C\ 1s\ NAP-XPS}^{carboxyl/formate}(T)}{I_{C\ 1s\ NAP-XPS}^{COgas}(T)} \times p_{QMS}^{CO}(T)$. *Time is the acquisition time of the* P_{QMS}^{CO} *corresponding to each C 1s XPS.* P_{QMS}^{CO} *indicates the corresponding pressure of CO monitored by QMS.* $I_{C\ 1s\ NAP-XPS}^{COgas}$ *is the integral intensity obtained from the fitting of the CO gas phase peaks in the XPS C 1s spectra, and* $I_{C\ 1s\ NAP-XPS}^{carboxyl/formate}$ *is the ratio of carboxyls/formates integral intensities as obtained from the fitting the carboxyls and formates peaks in the C 1s XPS spectra.*

Temperature (K)	Time (min)	p_{QMS}^{CO} (mbar)	$I_{C\ 1s\ NAP-XPS}^{COgas}$	$I_{C\ 1s\ NAP-XPS}^{COads}$	$I_{C\ 1s\ NAP-XPS}^{carboxyl/formate}$	$R_{C1s}^{carboxyl/formate}$
293	28	0.25	2.19	3.88	2.6	0.30
410	571	0.18	1.45	3.84	2.0	0.25
445	732	0.17	1.30	3.38	2.07	0.27
465	914	0.13	1.15	4.06	2.07	0.23
485	1108	0.09	0.83	4.4	2.74	0.29

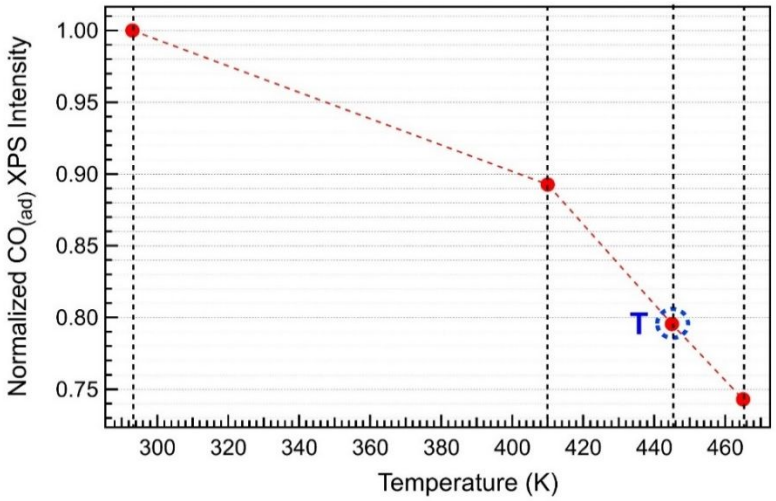

Figure S1. *The normalized adsorbed CO intensities on Pt(111) as a function of the heating temperature.*

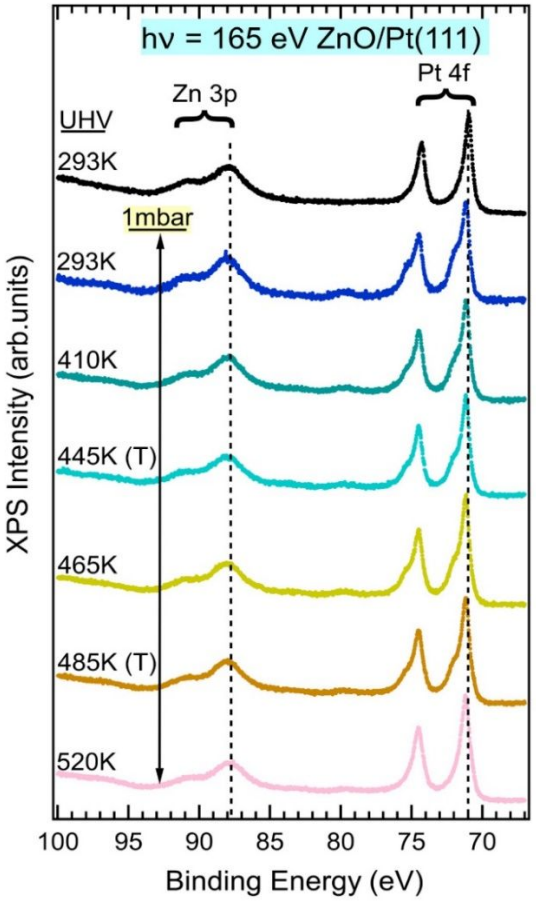

Figure S2. *Pt 4f and Zn 3p binding energy region of the ZnO/Pt(111) sample measured at hυ = 165 eV in a ($CO:O_2$) mixture (1:4) under a total pressure of 1 mbar. The spectra denoted UHV are recorded at 293 K before exposure to gases.*

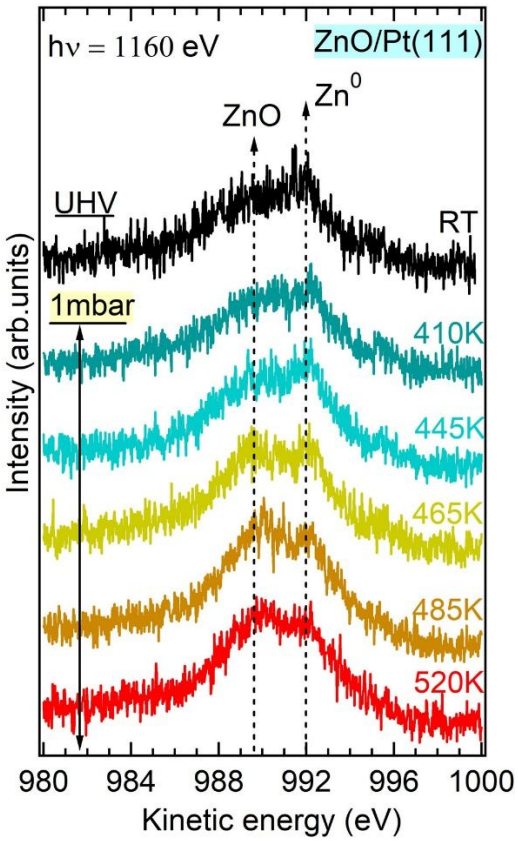

Figure S3. *Zn LMM Auger-electron spectra of the ZnO/Pt(111) sample measured at photon energy hν = 1160 eV in a ($CO:O_2$) mixture (1:4) under a total pressure of 1 mbar. The spectrum denoted UHV was recorded at room temperature (RT) on the sample as prepared in UHV before exposure to gases.*

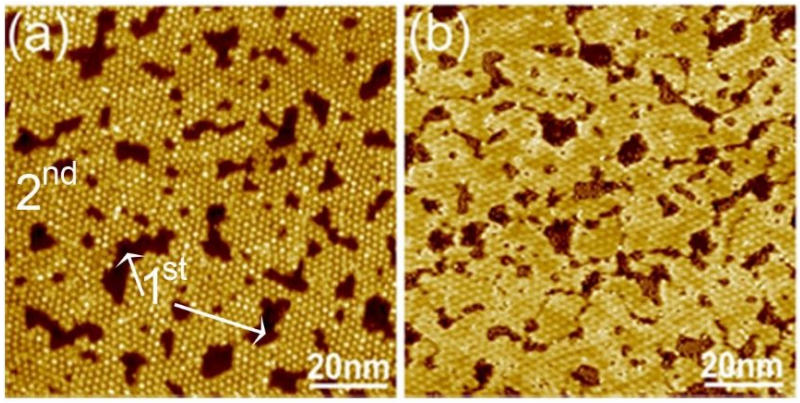

Figure S4*. (a) STM image (2.6 V, 190 pA) of the as-deposited ZnO film on Pt(111) (~1.8 ML coverage); (b) STM image (2.4 V, 190 pA) of the same sample as (a) but after exposure to 1 mbar of the ($CO:O_2$) mixture (1:4) at room temperature, followed by pumping down to UHV. 2^{nd} and 1^{st} indicate the second and first ZnO layers on Pt(111), respectively.*

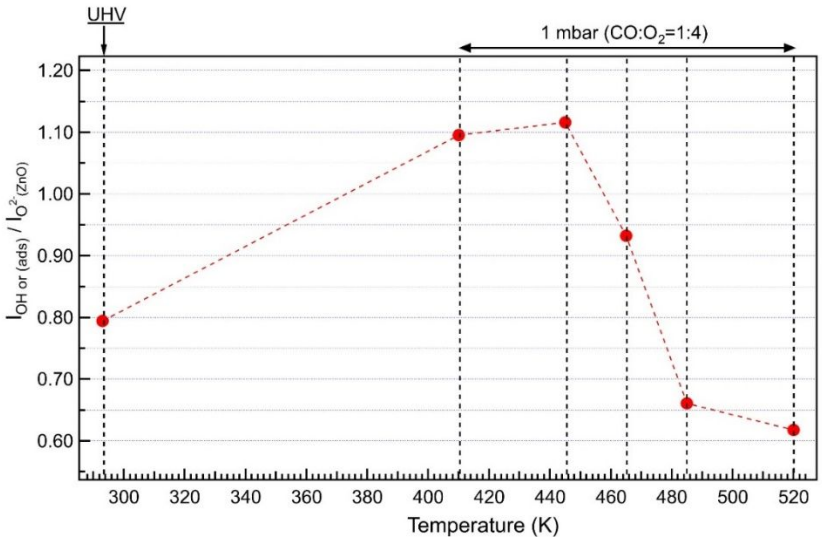

Figure S5. *The evolution of the* $I_{OH\ or\ (ads)}/\ I_{O^{2-}(ZnO)}$ *ratio as a function of the temperature at 1 mbar of (CO: O_2) mixture (1: 4) calculated from the O 1s spectra of the ZnO/Pt(111).*