Supporting Information

Improving time-resolution and sensitivity of in situ X-ray photoelectron spectroscopy of a powder catalyst by modulated excitation

M. Roger,[a,b] L. Artiglia,[a,*] A. Boucly,[a] F. Buttignol,[a,b] M. Agote-Arán,[a] J. A. van Bokhoven,[a,c] O. Kröcher,[a,b] D. Ferri[a]

[a] *Paul Scherrer Institut, Forschungsstrasse 111, CH-5232 Villigen PSI (Switzerland)*

[b] *École polytechnique fédérale de Lausanne (EPFL), Institute for Chemical Sciences and Engineering ; CH-1015 Lausanne (Switzerland)*

[c] *Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich (Switzerland)*

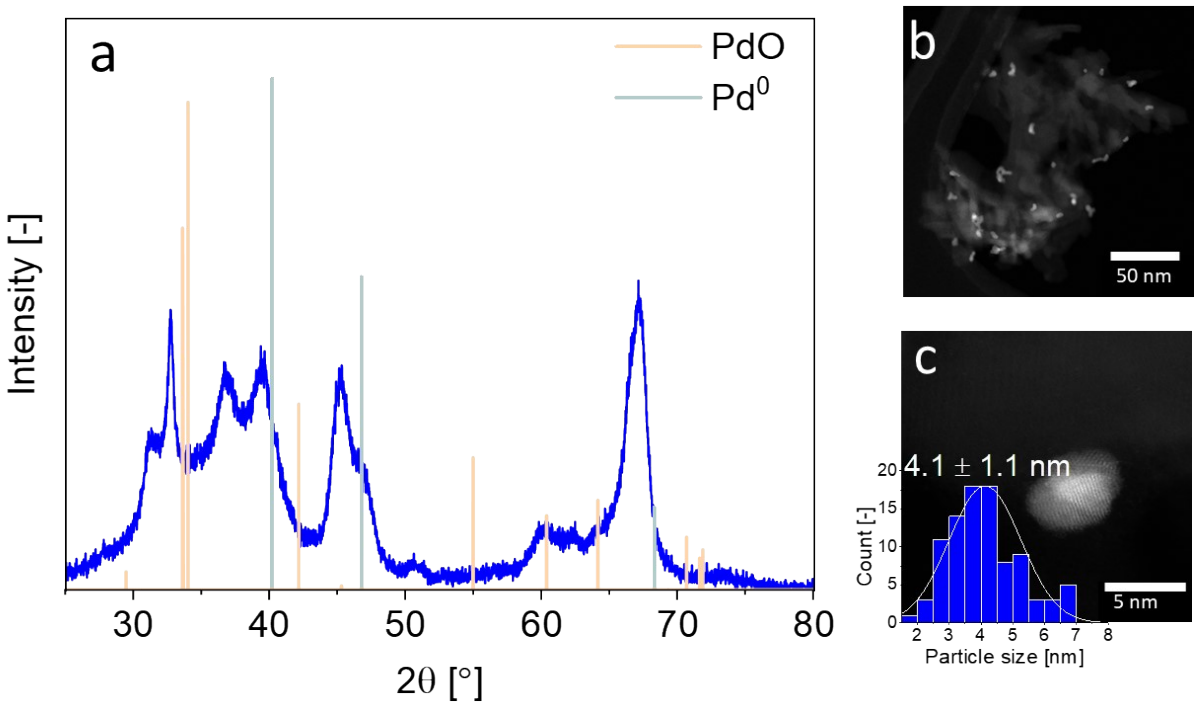

Figure S1. (a) Powder X-ray diffraction and (b-c) dark-field HAADF-STEM image and particle size distribution of pre-reduced 5 wt% Pd/Al_2O_3 catalyst.

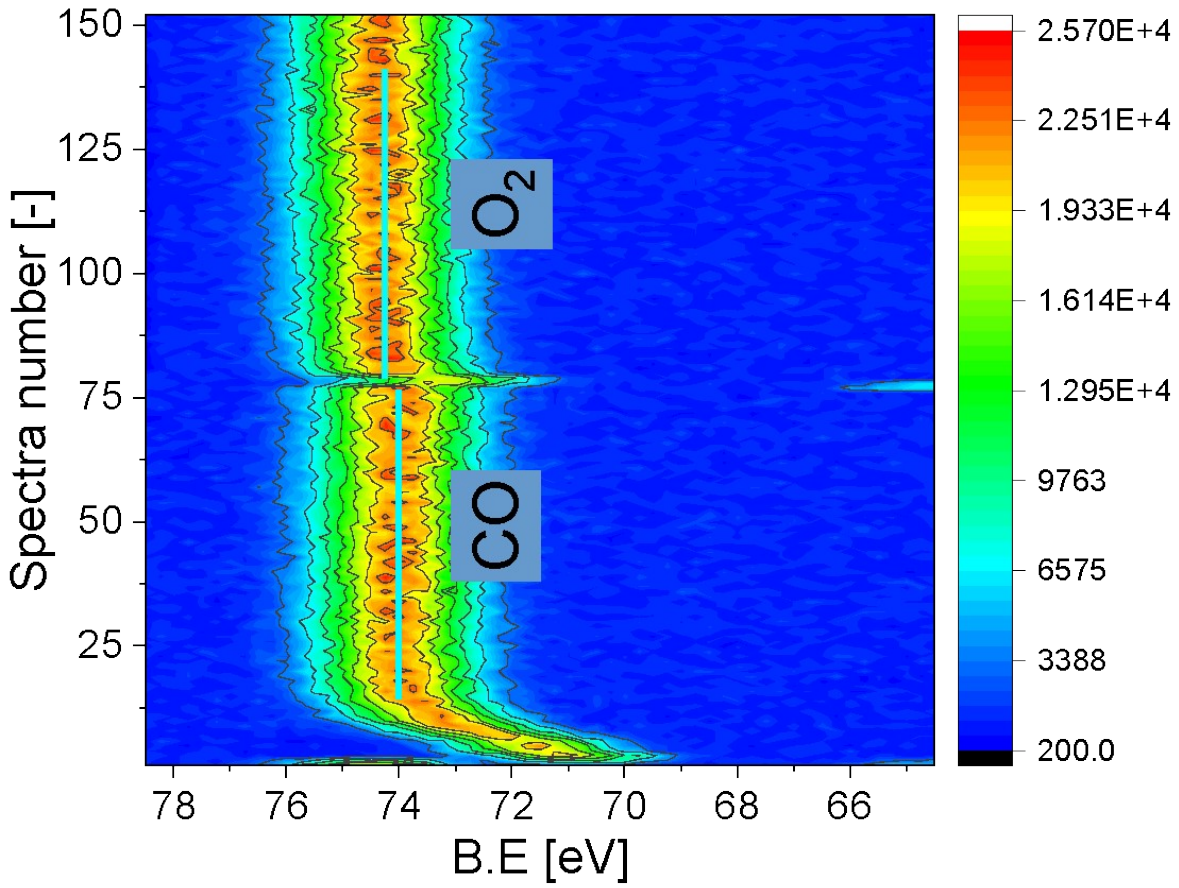

Figure S2. 2D representation of X-ray photoelectron spectra of 5 wt% Pd/Al_2O_3 at the Al 2p core level acquired with a 650 eV photon energy during repeated CO and O_2 pulses. The blue lines emphasize the center of the spectra.

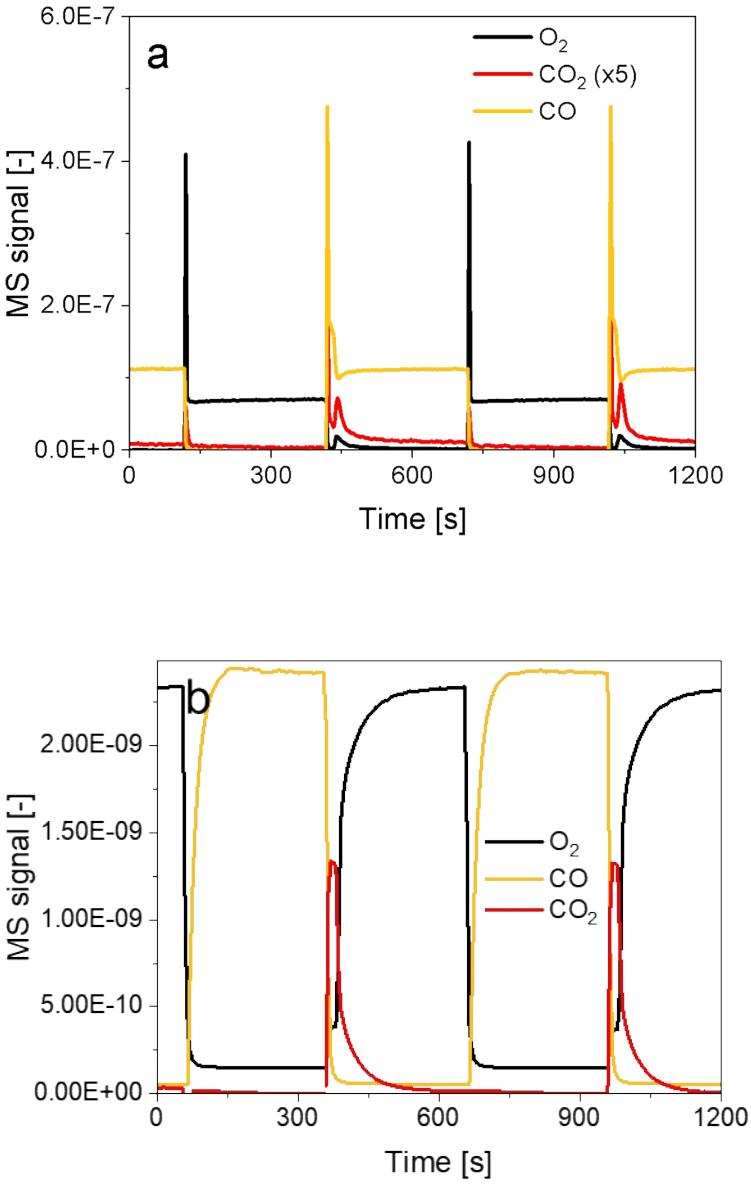

Figure S3. O_2, CO, and CO_2 mass spectrometer signals measured during (a) X-ray photoelectron spectroscopy measurements and (b) in a quartz plug-flow reactor in the laboratory during identical O_2 and CO pulses of 5 min.

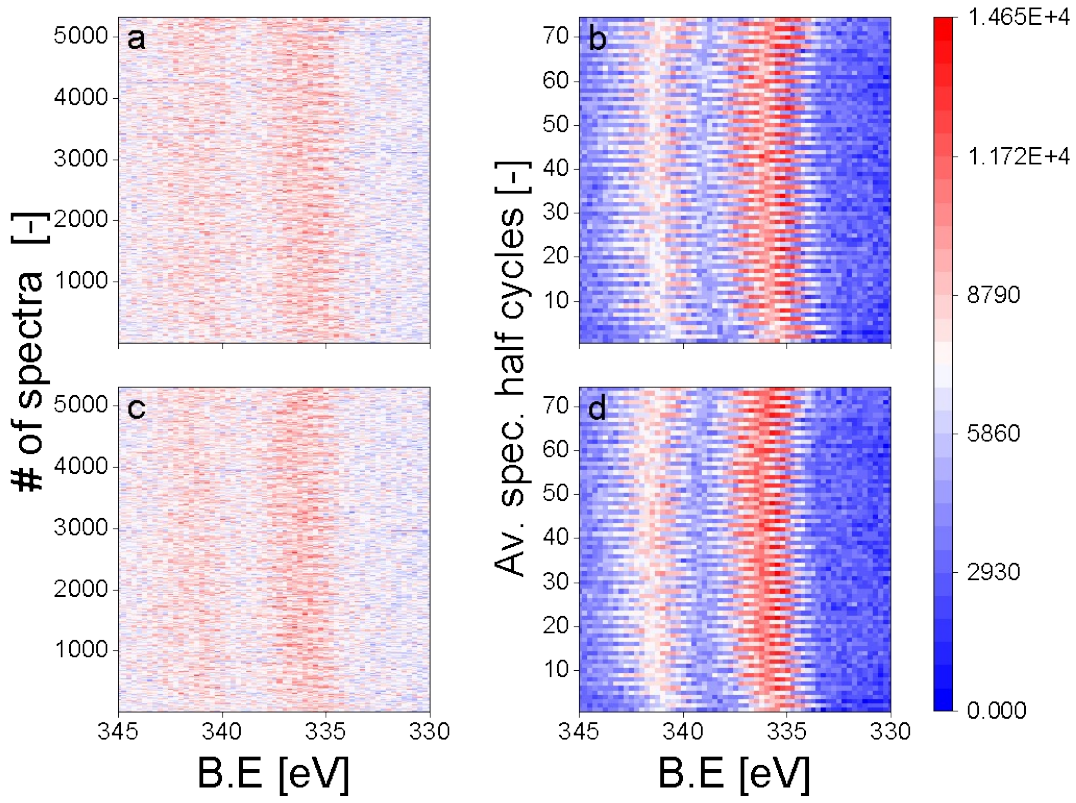

Figure S4. 2D representation of X-ray photoelectron spectra of 5 wt% Pd/Al_2O_3 at the Pd 3d core level acquired with a 300 eV kinetic energy. (a-b) Non-aligned spectra, (c-d) aligned spectra. (a, c) Heat map of all spectra acquired during the 6 h measurement. (b, d) Heat maps of the averaged spectra.

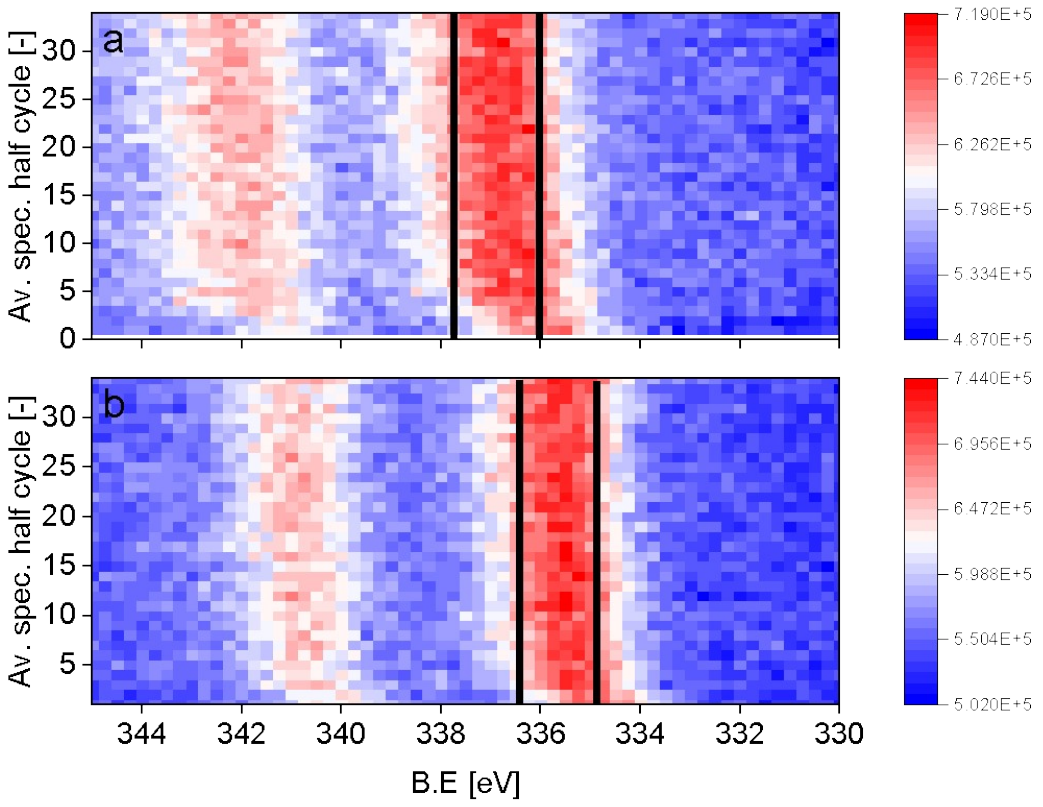

Figure S5. 2D representation of X-ray photoelectron spectra of 5 wt% Pd/Al_2O_3 at the Pd 3d core level acquired in (a) O_2. (b) CO with a 300 eV kinetic energy . Spectra are averaged over each half cycle of the 6 h measurement and aligned.

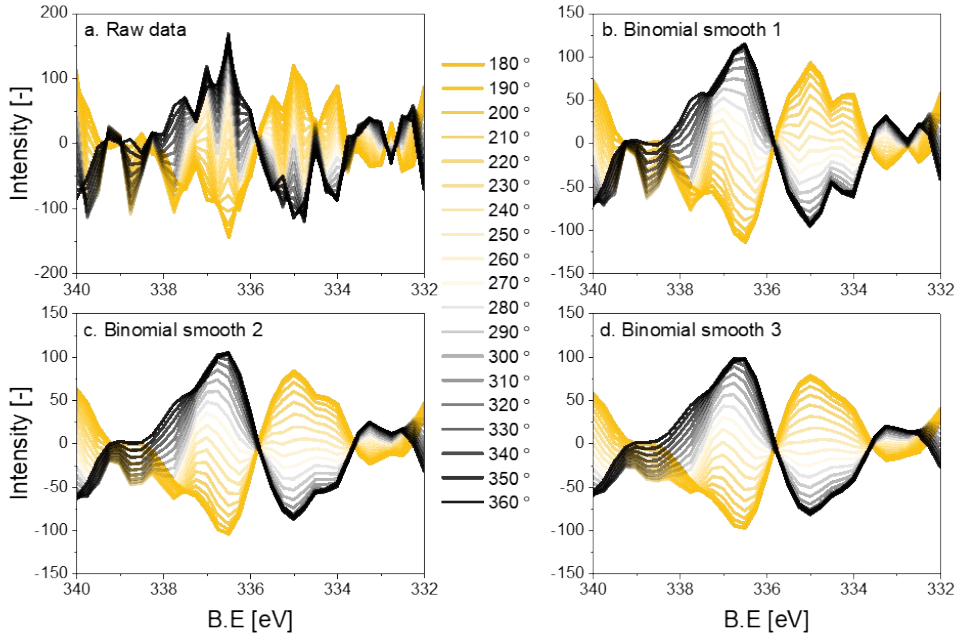

Figure S6. Phase domain analysis performed on (a) aligned, (b) binomial smoothed 1, (c) binomial smoothed 2, (d) binomial smoothed 3 of X-ray photoelectron spectra of 5 wt% Pd/Al_2O_3 at the Pd 3d core level acquired with a 300 eV kinetic energy during repeated CO and O_2 pulses. Only the Pd $3d_{5/2}$ core level is shown.

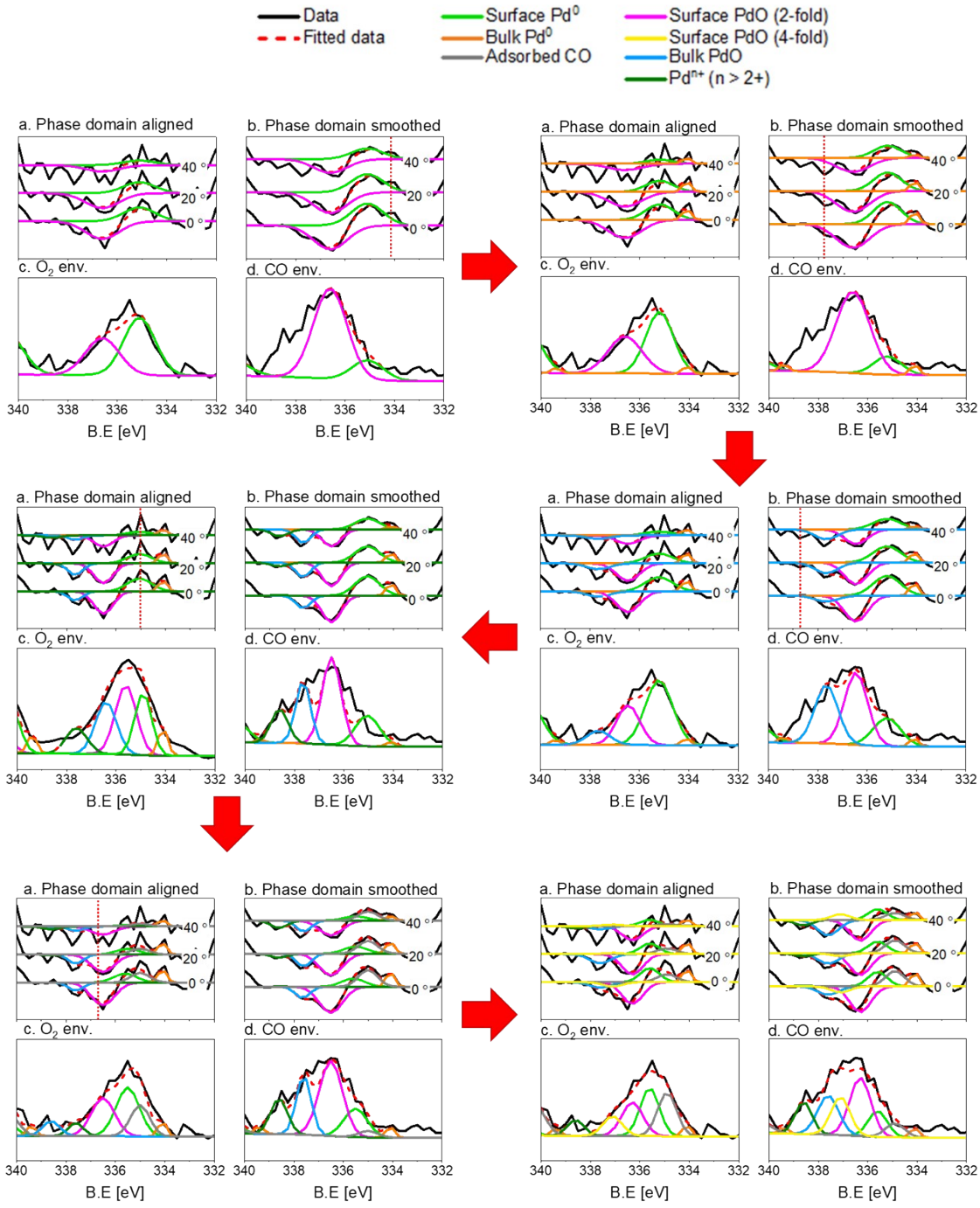

Figure S7. Fitting strategy to determine the peak features (fitting the data by identifying the missing peaks in the phase domain). (a-b) Phase domain spectra at 0, 20 and 40 °, of (a) raw and (b) smoothed (binomial 1) data. (c-d) Time domain spectra, under (c) O_2 and (d) CO. Only the Pd $3d_{5/2}$ core level is shown.

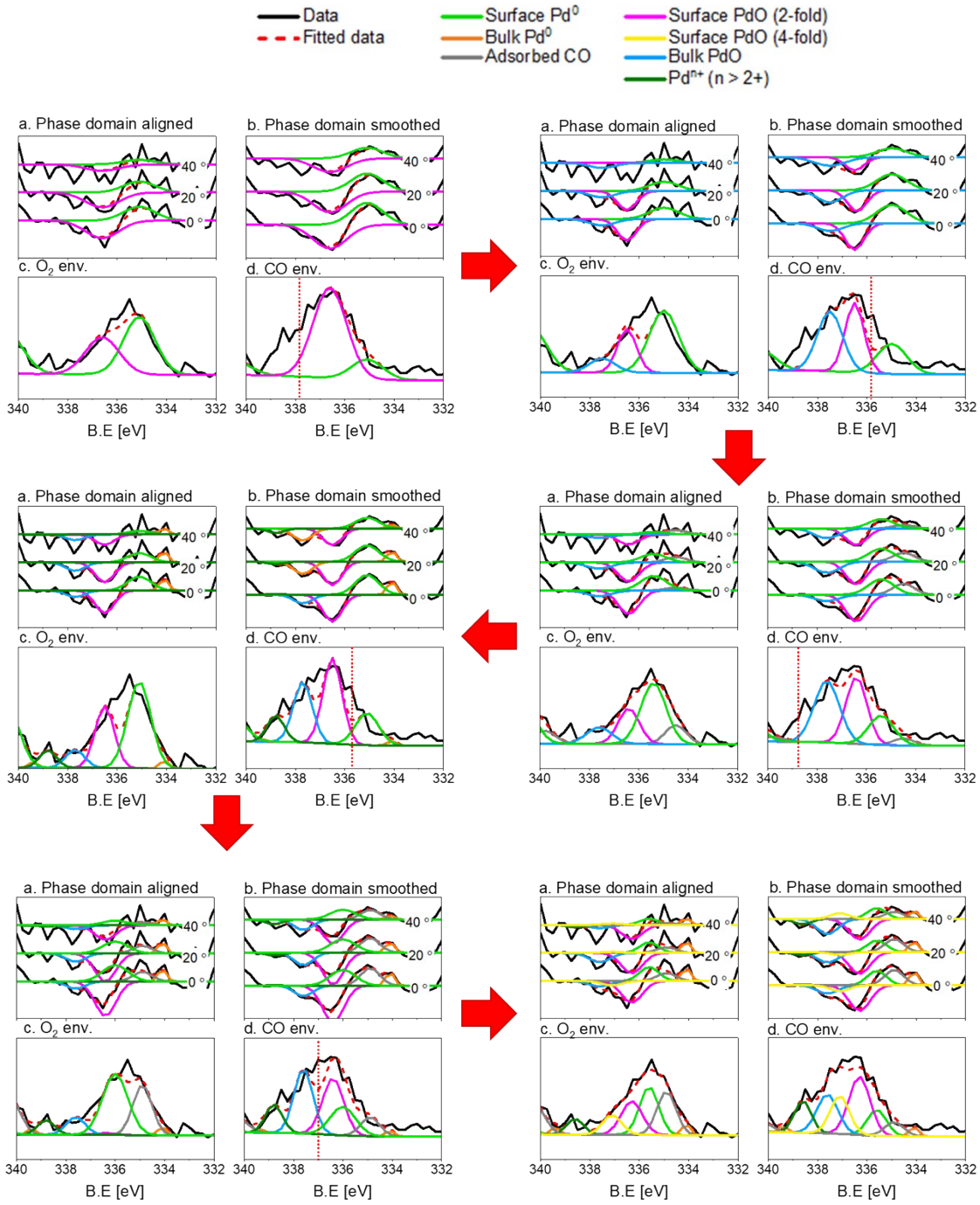

Figure S8. Fitting strategy to determine the peak features (fitting the data by identifying the missing peaks in the time doamin). (a-b) Phase domain spectra at 0, 20 and 40 °, of (a) raw and (b) smoothed (binomial 1) data. (c-d) Time domain spectra, under (c) O_2 and (d) CO. Only the Pd $3d_{5/2}$ core level is shown.

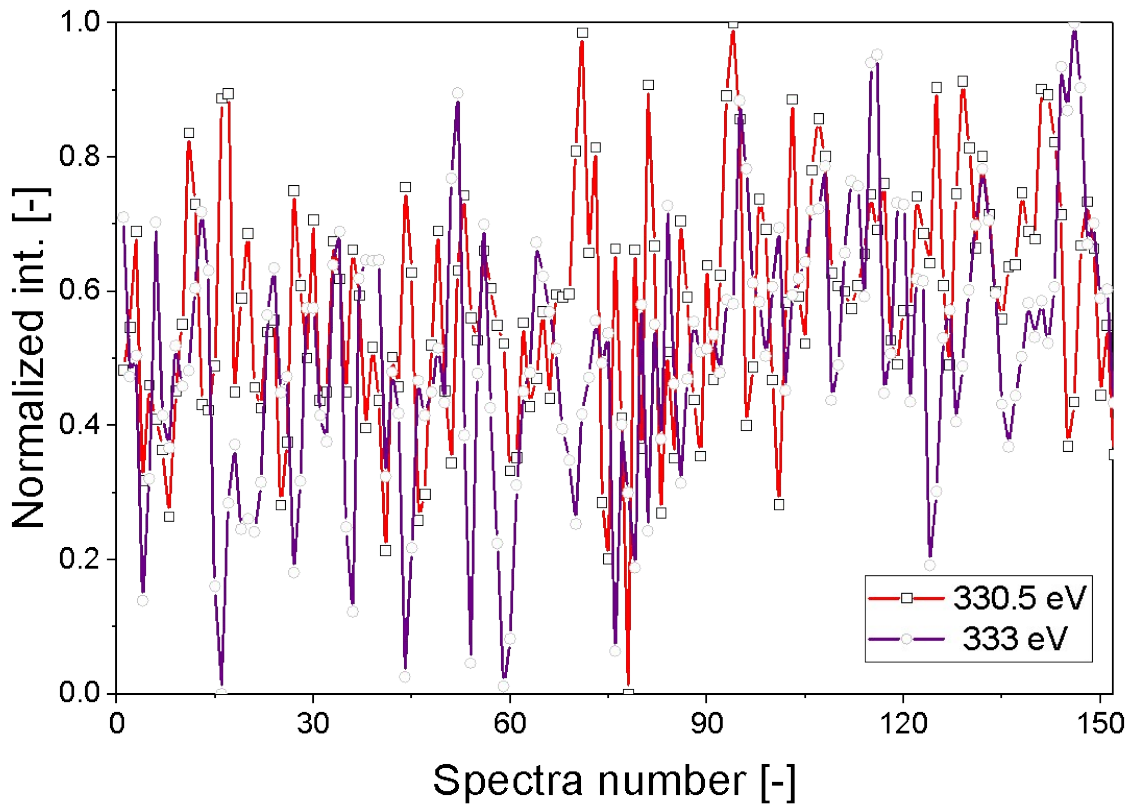

Figure S9. Normalized intensity of selected time resolved signals from the raw data. The X-ray photoelectron spectra of 5 wt% Pd/Al_2O_3 were acquired at the Pd 3d core level with a 300 eV kinetic energy during repeated CO and O_2 pulses.

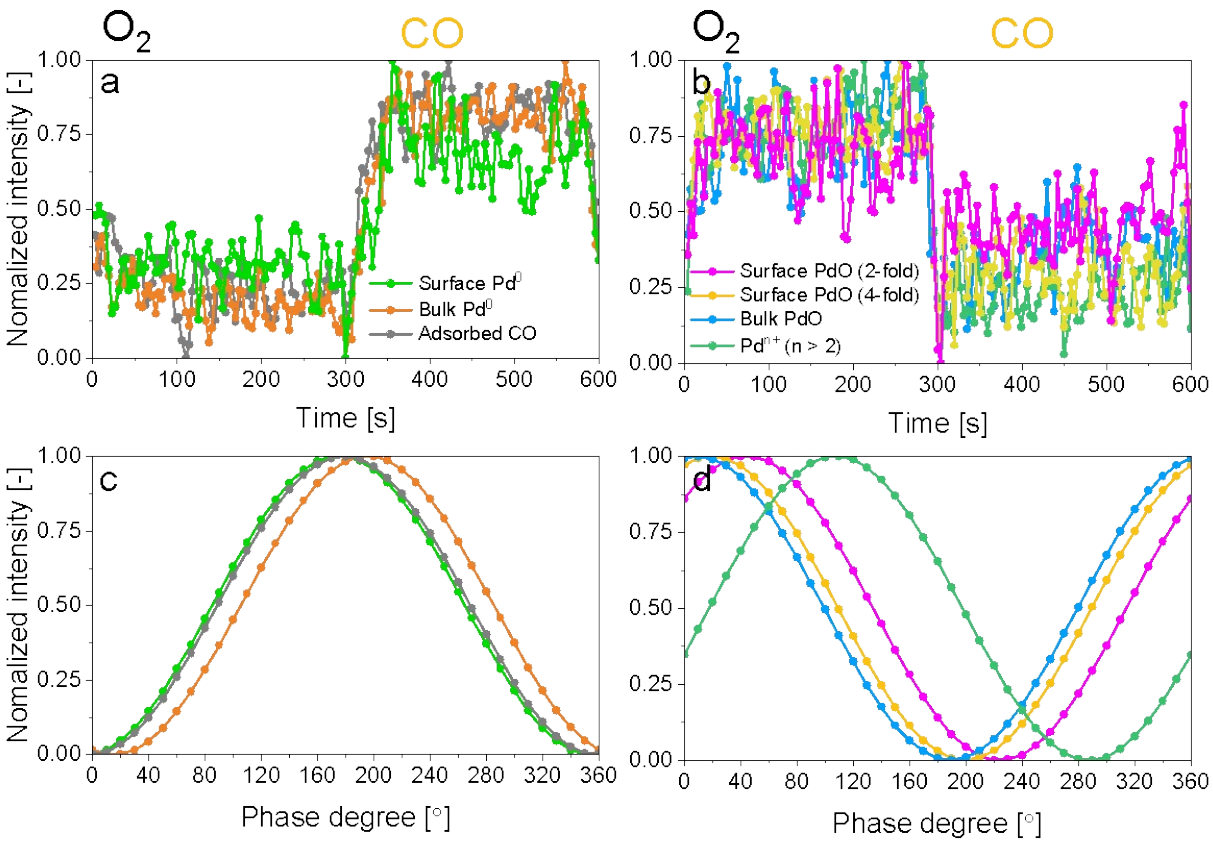

Figure S10. Behaviour of normalised (a, c) time domain and (c, d) phase domain intensities of (a, c) all reduced Pd species and (b, d) all oxidized Pd species from the aligned data set.