

Supporting Information

Structural and Reactive Characterization of Oxidatively Grafted Pd Catalysts on MnO₂ for the Low-Temperature Oxidation of CO

Jacklyn N. Hall,^a A. Jeremy Kropf,^{*a} Uddhav Kanbur,^a Fulya Dogan,^a Carly Byron,^a Jianguo Wen,^b Massimiliano Delferro,^{* a} and David M. Kaphan^{*a}

^aChemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, USA

^bCenter for Nanoscale Materials, Argonne National Laboratory, Lemont, Illinois 60439, USA

*Corresponding author: kaphand@anl.gov, delferro@anl.gov, kropf@anl.gov

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S1. Experimental Procedures

S1.1. Pd/MnO₂ Synthesis

Pd/MnO₂ was synthesized by the oxidative grafting of bis(tricyclohexylphosphine)palladium(0) (Pd(PCy₃)₂) onto MnO₂ by an adaption of a previously reported synthesis method for Ni/LiMn₂O₄.¹ Briefly, MnO₂ (Carus Group, <https://www.carusllc.com/>) was dried under vacuum at 473 K overnight and transferred into a nitrogen filled glovebox (Vacuum Atmospheres). A solution of 60 mg of Pd(PCy₃)₂ (ThermoFisher Scientific, > 97% purity) dissolved in benzene (3 mL) was added to MnO₂ (500 mg) in benzene (roughly 6 – 7 mL) and stirred at room temperature for a minimum of 48 hours in the glovebox. The suspension was then filtered and washed with pentane (roughly 10 – 15 mL) to remove unreacted precursors and benzene. The solid was then dried under vacuum for 4 hours and stored in a glovebox freezer until further use. Metal analysis was performed at the Northwestern University Bio-element Imaging Center.

S1.2. N₂ Physisorption

N₂ physisorption (77 K) measurements to estimate the Brunauer-Emmett-Teller (BET) surface area were conducted using a Micromeritics ASAP 2020 instrument. Samples were degassed for 3 hours at 200 °C prior to analysis.

S1.3. CO Oxidation Reaction Experiments

Samples of Pd/MnO₂ (10 – 20 mg) were measured and loaded in air into an Inconel U-shaped tube (1/4 inch – outer diameter) using quartz wool as a support. The reactor tube was mounted vertically within a commercial Zeton Altamira (Model AMI-100) characterization system modified with a supplemental mass flow controller (Brooks 5850E Series) for multi-gas flow. The reaction temperature was determined by the placement of a K-type thermocouple (Omega) on the external surface of the reactor tube at the height of the catalyst bed. During temperature-programmed

reaction (TPRx) experiments, samples were exposed to 10% O₂/He (Airgas, 10.18 mol% O₂ actual, Certified Standard-Spec) and 10% CO/He (Airgas, 9.935 mol% CO actual, Primary Standard) for 1 hour (unless otherwise indicated) prior to heating to 323 K at a ramp rate of 5 K min⁻¹ (total gas flow rate = 50 mL min⁻¹). For isothermal reaction experiments at 323 K, samples were heated to the target temperature under 10% O₂/He at a rate of 5 K min⁻¹ and allowed 1 hour to equilibrate at 323 K before the introduction of 10%CO/He. Effluent gas concentrations were analyzed for CO, O₂, He, H₂O, and CO₂ using a Stanford Research Systems QMS200 Series Gas Analyzer.

S1.4. Sample Preparation for Ex-Situ Characterization

Pd/MnO₂ samples for ex-situ characterization were prepared on the Zeton Altamira instrument used for typical reaction experiments (as described in Section S1.3). Following sample treatment, materials were purged with He (Airgas, Ultra High Purity) at room temperature to flush out CO or O₂ then the reactor tube was closed off with two shut-off valves and transferred into a N₂-filled glovebox. Samples were stored in the glovebox and left without air exposure prior to characterization. Samples were prepared with three different conditions (1) reduced in CO, (2) post catalysis, and (3) post O₂ regeneration (1 cycle). The reduced sample was held at room temperature for 1 hour under CO flow (5% CO/He, 50 mL min⁻¹) and then ramped to 423 K at 5 K min⁻¹ and held at temperature for 1.5 hours. Following treatment, the sample was purged with He for 15 minutes at 423 K and then cooled to room temperature. The post catalysis sample was treated under CO/O₂ TPRx conditions (O₂/CO ratio: 3, room temperature to 323 K, ramp rate: 5 K min⁻¹) for 7 hours at 323 K. Post catalysis (7 hours reaction) samples were regenerated in 300 °C for 1.5 hours at 573 K and cooled to room temperature under He flow prior to being transferred for analysis to produce the O₂ regenerated material.

SI.5. X-ray Absorption Spectroscopy (XAS)

XAS measurements were completed at the 10ID and 10BM beamlines at the Advanced Photon Source (APS) at the Argonne National Laboratory. At 10ID, the beam is generated by an undulator source with a Si(111) double crystal monochromator (DCM) cooled with liquid nitrogen and a harmonic rejection mirror. The 10BM beamline uses a bending magnet source and a water-cooled Si(111) DCM detuned to 50% peak intensity for harmonic rejection. At both beamlines, spectra were collected with simultaneous measurement of the metal foil for calibration to 24352.6 eV and 6537.67 eV for the K edge of Pd and Mn,² respectively, at the zero-crossing of the second derivative spectra. Spectra normalization, background subtraction, calibration, and fitting were performed using the Demeter/Athena/Artemis suite of analysis software.³

Ex-situ samples for the Pd K edges were measured at beam line 10-ID in fluorescence mode using either a gas fluorescence ion chamber (5 grid, The EXAFS Company) or a 5x5 Si PIN diode array. Samples measured ex-situ were prepared in a N₂-filled glovebox and were hand pressed into a six-sample holder sealed with an O-ring and featuring Kapton film windows sealed with Torr Seal®. At the beamline, the sample holder was transferred to a cell purged with inert gas for the duration of sample measurements to further reduce the potential for air leaking into the sample holder.

Ex-situ samples for the Mn K edge were measured in transmission mode at the 10BM beamline. Samples were prepared in a N₂-filled glovebox and hand pressed into a six-sample holder and transferred into a quartz tube closed off with ultra-torr fittings and Kapton windows to maintain an air-free environment for the duration of the sample measurements. Based on analysis of the energy shifts of multiple spectra measured of the same sample, the relative energy scale and the Mn K edge has been corrected to within ± 0.015 eV using metallic iron foil spectra measured simultaneous with each sample as a reference for calibration. The typical metallic Mn reference

(from EXAFS Materials) is a 325 mesh powder. Spectra derived therefrom exhibit significant thickness effects that make it unsuitable for energy calibration, as well as high absorption, which makes it generally unsuitable for relative energy alignment in operando experiments in which the sample absorption is also quite high.

S1.6. Operando CO Oxidation XAS Measurements

Operando XAS measurements of Pd/MnO₂ during CO oxidation were conducted and the 10ID and 10BM beamlines at the APS for the Pd and Mn K edges, respectively. Due to the difference in the concentration of the metals in the material (approximately 1.1 wt.% Pd and 62 wt.% Mn), two different reactor configurations were employed for measurement in order to produce a desirable edge step and sufficient X-ray transmittance near the metal edge.

For Mn K edge experiments, approximately 2.7 mg of Pd/MnO₂ was diluted in vitreous, or glassy carbon (HTW, Sigradur G), with a composition of 5 wt.% Pd/MnO₂. The sample mixture was ground thoroughly with a mortar and pestle and then loaded into a polyimide capillary (Masterflex Transfer Tubing, Cole Parmer, 1.46 mm ID, 1.56 mm OD, 75 mm L) using quartz wool (CE Elantech) as a support. The capillary was prepared and stored in a N₂-filled glovebox until the time of measurement at which time it was loaded in air and transferred to the microreactor flow assembly. Details of the reactor have been provided in our previous work,^{4,5} with the design being inspired by plug flow in-situ cells described by Chupas and Figueroa.^{6,7} Brooks Instruments mass flow controllers were used to feed He, 10%CO/N₂, and 20% O₂/He into the reactor. A maximum flow rate of 10 mL min⁻¹ was used and gas flow rates were varied to produce concentrations of either 7.7 kPa O₂ or 7.7 kPa O₂ and 2.6 kPa CO during reaction experiments.

For Pd K edge measurements, approximately 30 mg of Pd/MnO₂ was diluted in glassy carbon with a composition of 33 wt.% Pd/MnO₂. The sample mixture was ground with a mortar and pestle and

then loaded into a 1/4-in OD borosilicate glass tube (McMaster-Carr 8729K31) using quartz wool as a support. The sample tube was prepared in a N₂-filled glovebox and then loaded into the microreactor flow assembly in air prior to the start of the experiment. Slight modifications were made to the reactor assembly to accommodate the large reactor tube and minimize the influence of axial and radial temperature gradients in the catalyst bed. Specifically, a K-type thermocouple placed at the end of the catalyst bed and was used to control the temperature. An insertion heater was utilized to heat the incoming gas mixture to 1 K below the set temperature of the catalyst bed by measurement with a secondary thermocouple located near the inlet of the reactor tube. Gas lines at the inlet to the reactor were also thoroughly insulated around the insertion heater to improve preheating of the incoming reactant gas. A maximum gas flow rate of 60 mL min⁻¹ was used for these measurements while maintaining the same partial pressures of O₂ and CO utilized for experiments completed for measuring the Mn K edge (7.7 kPa O₂ or 7.7 kPa O₂ and 2.6 kPa CO). A Pd K-edge step of approximately 0.12 was measured.

For both analyses, spectra of the starting material were collected under He flow and then under 7.7 kPa O₂/He. CO (2.6 kPa) was added to gas stream at room temperature (~ 297 K) and held for 1 hour prior to completing temperature-programmed reaction (TRPx) measurements up to 323 K. Specifically a ramp rate of 0.24 K min⁻¹ was used to obtain sufficient resolution in temperature for spectra collected during ramping. After reaching 323 K the sample was held for up to 2 hours with simultaneous monitoring of the metal K edge spectra. An on-line residual gas analyzer (RGA) was employed to monitor the relative CO₂ formation rate as a function of time.

On the 10ID beamline, it was observed that enhanced Pd particle growth could be directly attributable to the beam interaction during operando experiments. To mitigate this effect for the experimental results reported, the beam intensity was reduced by tapering the undulator and then

measuring the spectra at different positions in an A-B-A-B-A-C repeated pattern with the beam shutter closed for 8 minutes between each scan for the duration of the experiment.

S1.7. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS measurements were completed using a Thermo Scientific Nicolet iS50 FT-IR spectrometer featuring a MCT-A detector cooled to 77 K. The Harrick Praying Mantis™ Diffuse Reflection Accessory and Praying Mantis™ High Temperature Reaction Chamber equipped with ZnSe windows was utilized for in-situ sample measurements. Measurement of KBr under inert atmosphere at the analysis temperature were used as a background. Approximately 10 mg of Pd/MnO₂ was placed on top of a KBr bed and loaded into the Harrick reaction cell either in air or in a N₂-filled glovebox (when indicated). Gas flows to the cell were regulated by Brooks mass flow controllers and gases included 20% O₂/N₂ (house air line), 10% CO/He (Airgas, 9.935 mol% CO actual, Primary Standard), He (Airgas, Ultra High Purity) or N₂ (house nitrogen line). For monitoring the changes in the concentration of carbonates during reaction, the total carbonate area was determined as the integrated area of the infrared spectra from 800 – 1740 cm⁻¹ using *Origin 2021*.

S1.8. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and Energy-Dispersive X-ray Spectroscopy (EDS) was performed using the FEI Talos F200X TEM/STEM at 200 kV in the Center for Nanoscale Materials at Argonne National Laboratory. High Angle Annular Dark Field (HAADF) STEM images and TEM Bright Field (BF) images were collected to determine the presence of nanoparticles on as-prepared and post-reaction catalysts and to determine the morphology of MnO₂. EDS was used to map Pd, Mn, and O for as-prepared and

post-reaction catalysts. Samples were prepared by dry loading powder catalyst onto lacey carbon TEM grids (Electron Microscopy Sciences, Lacey carbon film on 400 mesh Cu, 100 micron).

For Pd/MnO₂ analyzed post reaction, the Pd nanoparticle size distribution was measured for N=10 nanoparticles from bright field TEM images using the ImageJ processing software,⁸ and the mean diameter was determined to be 10.8 ± 4.5 nm.

SI.9. ³¹P Solid State Nuclear Magnetic Resonance (NMR)

³¹P solid state NMR experiments were performed at 7.02 Tesla (300 MHz) on a Bruker Avance III HD spectrometer operating at a Larmor frequency of 121.494 MHz, using a 1.3 mm MAS probe. All spectra were acquired at 50 kHz with a rotor synchronized echo pulse sequence ($90^\circ\tau 180^\circ\tau$ -acq), where $\tau = 1/\nu_r$. A $\pi/2$ pulse width of 1.5 μ s was used with sufficiently long pulse recycle delays of 0.2 s. All spectra were collected at a constant temperature of 283 ± 0.1 K (crucial for accurate and consistent determination of NMR shift trends). Chemical shifts were referenced to 85% H₃PO₄ at 0 ppm. The spectra were normalized by the total number of scans which was the same for all runs and the weight of active materials packed in the rotors for the best possible quantitative analyses of intensity changes.

SI.10. High Resolution X-ray Diffraction

High resolution synchrotron powder X-ray diffraction measurements were made at APS beam line 11-BM using the mail-in program. The average X-ray wavelength was 0.458987 Å. Data were collected using a step size of $0.001^\circ 2\theta$ at a scan speed of $0.01^\circ/\text{s}$. For the analysis, a Kapton capillary was filled with MnO₂ powder and sealed with epoxy.

S2. Supplementary Results

S2.1. Supplementary Characterization

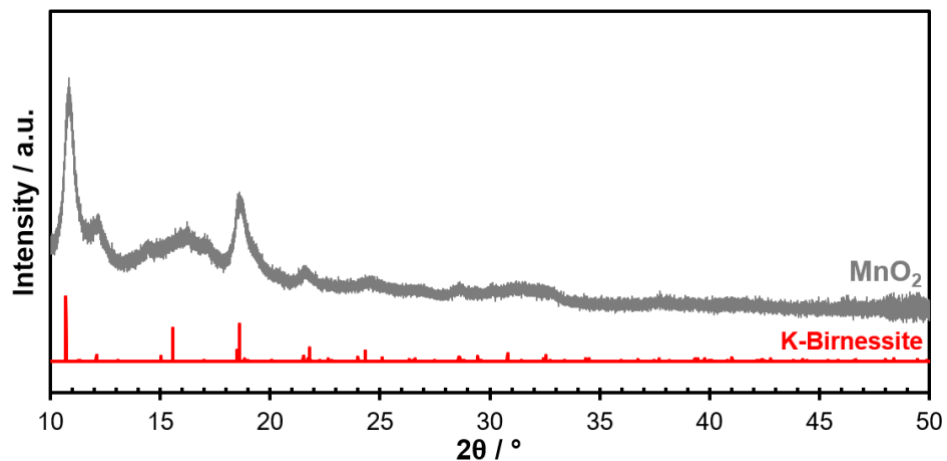


Figure S1. X-ray diffraction pattern of MnO₂ in comparison to the simulated diffraction pattern of K-birnessite from COD entry 4000330 and Reference 9. (X-ray wavelength, $\lambda = 0.458987\text{\AA}$)

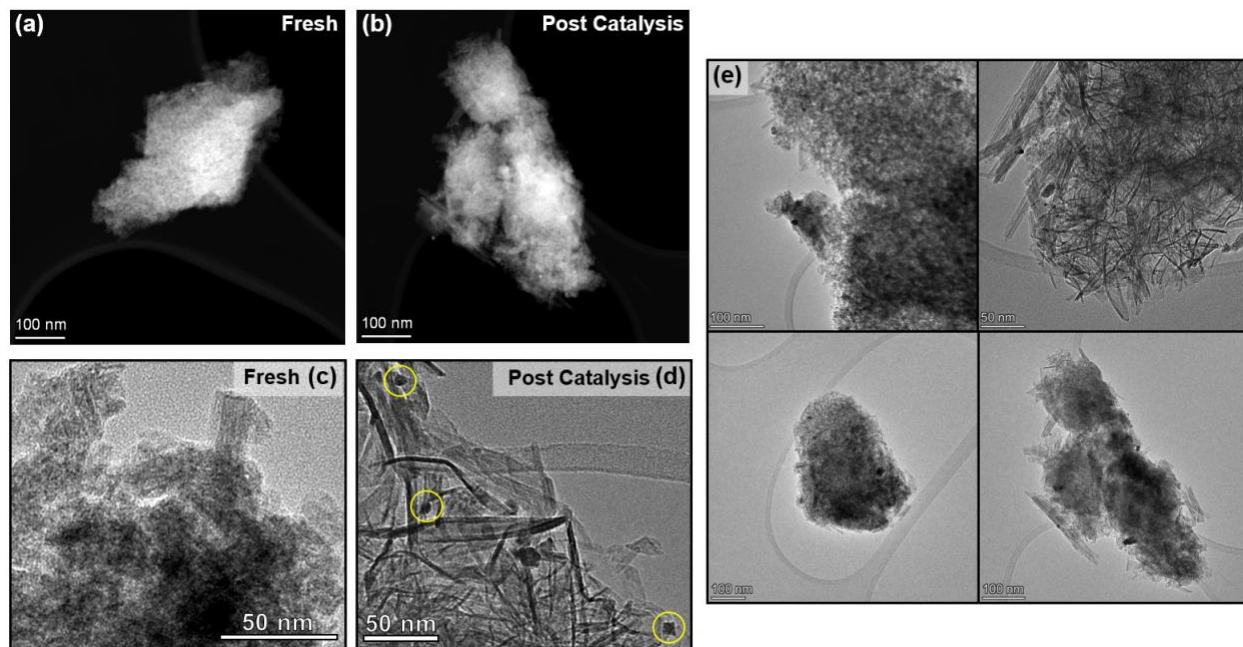


Figure S2. STEM HAADF micrographs of (a) fresh Pd/MnO₂ and (b) post catalysis Pd/MnO₂. TEM of (c) fresh Pd/MnO₂ and (d) post catalysis Pd/MnO₂ with the Pd nanoparticles highlighted. (e) For post catalysis Pd/MnO₂, TEM images used to estimate the average Pd particle size (10.8 ± 4.5 nm). The post catalysis sample was prepared following reaction for 7 h at 323 K (7.7 kPa O₂, 2.6 kPa CO).

S2.2. Ex-Situ X-ray Absorption Fine Structure (XAFS) Results

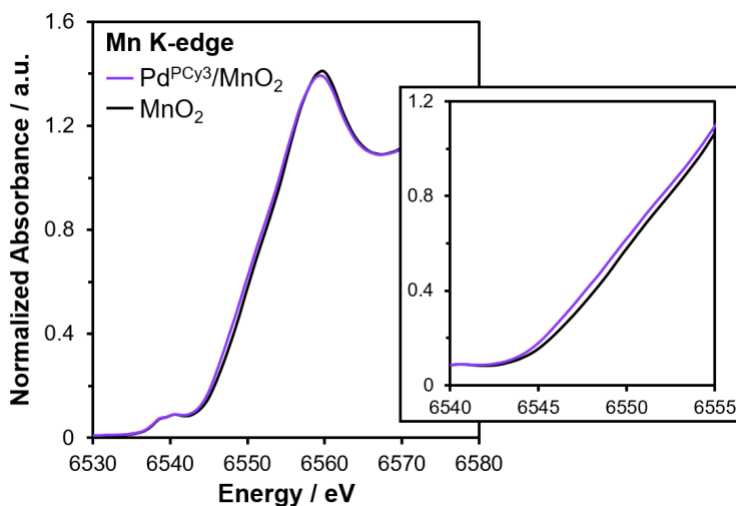


Figure S3. Mn K-edge XANES of the parent MnO_2 support and Pd/ MnO_2 with the inset highlighting the change in the absorption edge energy.

Table S1: Tabulated EXAFS fitting results for the $\text{Pd}(\text{PCy}_3)_2$ precursor and fresh Pd/ MnO_2 (measured air-free) ($\Delta k = 0.1$, $k = 3 - 13.8 \text{ \AA}^{-1}$, $k^N N = 1,2,3$ weighting, $R = 1.1 - 2.4 \text{ \AA}$, $S_0^2 = 0.78$ (set) fit from the Pd reference foil). For Pd/ MnO_2 fit 2, the coordination number (N) refers to the total first shell coordination number and the fraction refers to the fraction of Pd-X bonds which are Pd-O (0.5 ± 0.2) versus Pd-P (0.5 ± 0.2).

Sample	Path	N	Fraction	R (\AA)	σ^2 ($\times 10^{-3} \text{\AA}^2$)	ΔE_0 (eV)	R-factor
$\text{Pd}(\text{PCy}_3)_2$	Pd-P	2.2 ± 0.1	---	2.269 ± 0.005	3.7 ± 0.5	7.1 ± 0.7	0.006
Pd/ MnO_2	Pd-O	1.9 ± 0.9	---	2.041 ± 0.043	5.6 ± 2.6	6.9 ± 5.0	0.004
	(fit 1) Pd-P	1.6 ± 0.4	---	2.294 ± 0.015	3.7		
Pd/ MnO_2	Pd-O	3.5 ± 0.6	0.54 ± 0.18	2.041 ± 0.043	5.6 ± 2.6	6.9 ± 5.0	0.004
	(fit 2) Pd-P		0.46 ± 0.18	2.294 ± 0.015	3.7		

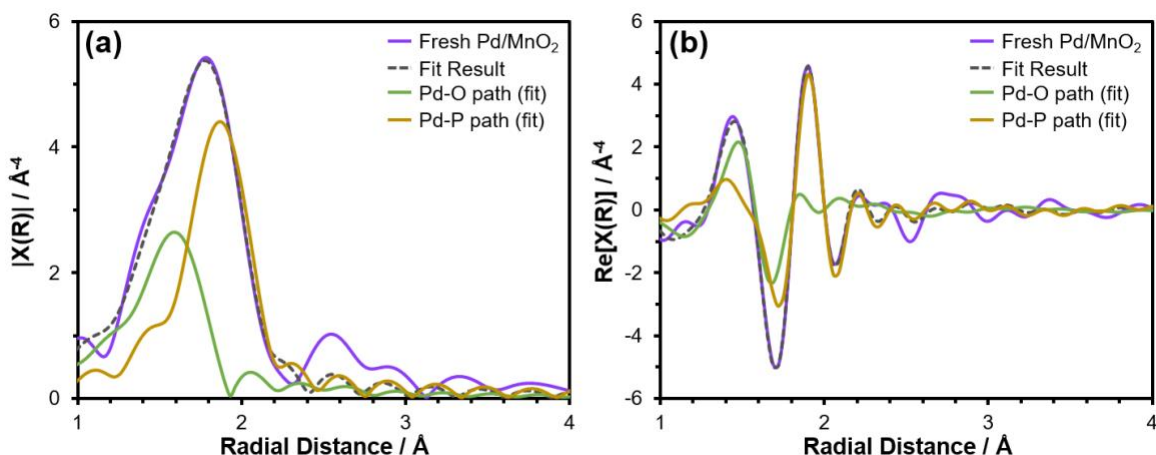


Figure S4. Pd EXAFS fit results (fit 1 in Table S1) showing the (a) magnitude and (b) real component of $\chi(R)$ for fresh Pd/MnO₂ (measured air-free) ($k = 3.0 - 13.8 \text{ \AA}^{-1}$, $\Delta k = 0.1$, k^3 weighting, $R = 1.1 - 2.4 \text{ \AA}$, $S_0^2 = 0.78$ (set) fit from the Pd reference foil).

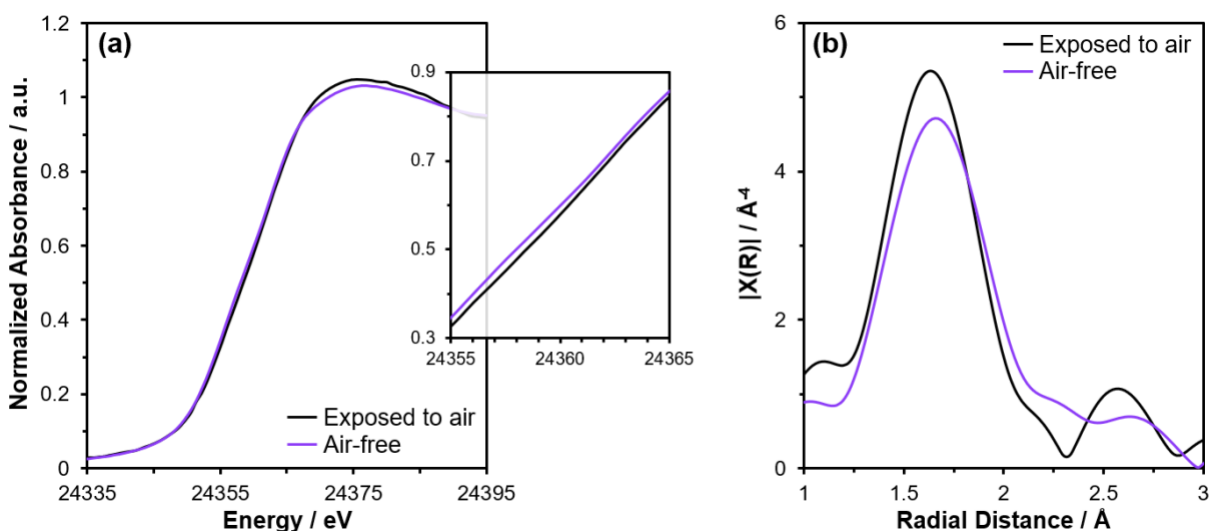


Figure S5. Pd K-edge (a) XANES and (b) EXAFS for Pd/MnO₂ measured air-free and following exposure to air. $k = 3.0 - 11.1 \text{ \AA}^{-1}$.

Table S2. Results of the linear combination fitting (LCF) of the ex-situ Pd/MnO₂ post-catalysis (7 h, 323 K, 7.7 kPa O₂, 2.6 kPa CO) using the fresh Pd/MnO₂ and Pd foil as standards. The fitting ranges were 24314 – 24464 eV and 3 – 11 \AA^{-1} for the XANES and EXAFS, respectively.

XANES LCF		EXAFS LCF	
Fresh Pd/MnO ₂	Pd Foil	Fresh Pd/MnO ₂	Pd Foil
0.822 ± 0.003	0.178 ± 0.003	0.778 ± 0.011	0.222 ± 0.011

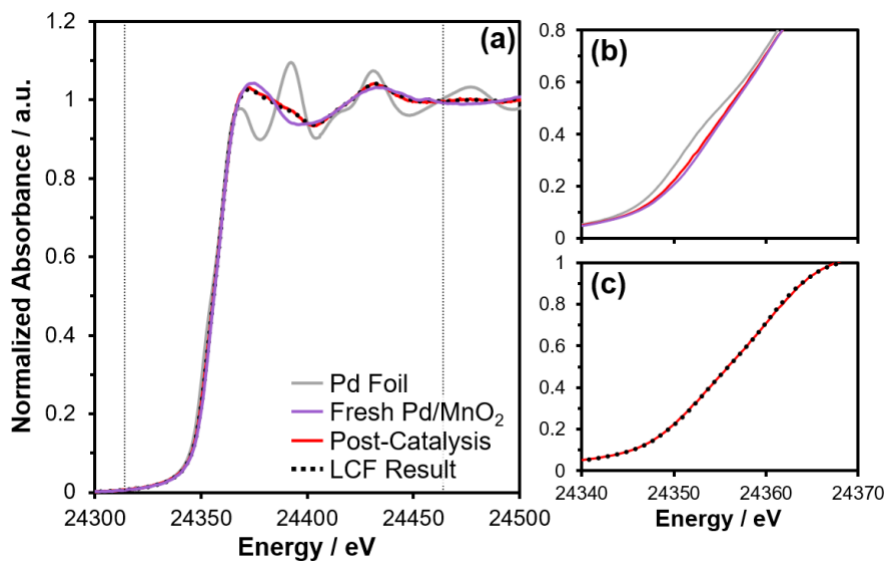


Figure S6. (a) Pd K edge XANES of the ex-situ Pd/MnO₂ post-catalysis sample (7 h, 323 K, 7.7 kPa O₂, 2.6 kPa CO) showing the linear combination fitting (LCF) result of using the Pd foil and the fresh Pd/MnO₂ sample as references and the fitting range. (b) and (c) show magnification on the rising edge.

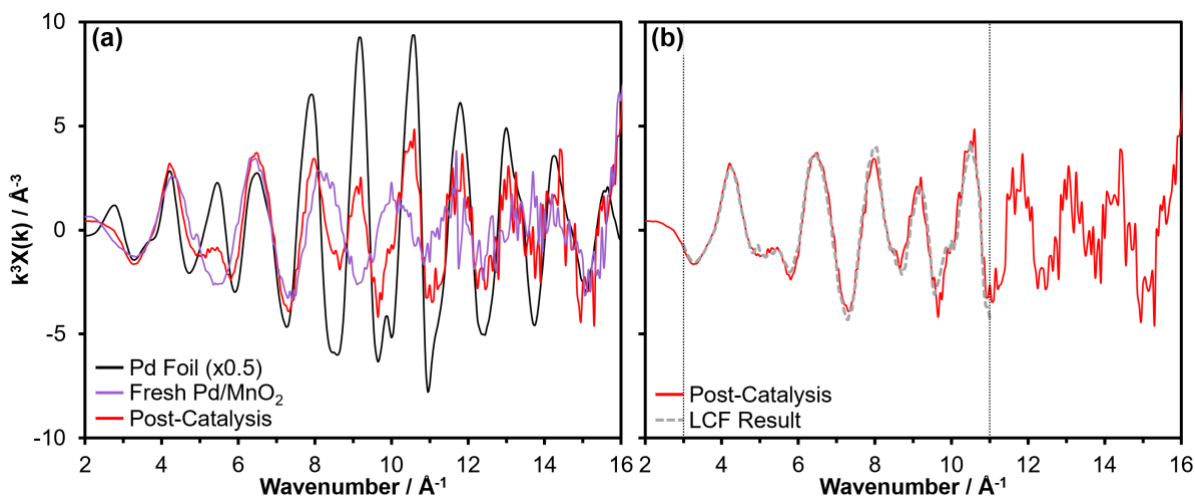


Figure S7. Pd K edge X(k) spectra of the ex-situ Pd/MnO₂ post-catalysis sample (7 h, 323 K, 7.7 kPa O₂, 2.6 kPa CO) (a) compared with Pd foil (multiplied by 0.5) and fresh Pd/MnO₂ and (b) showing the results of the linear combination fitting from 3 – 11 Å⁻¹.

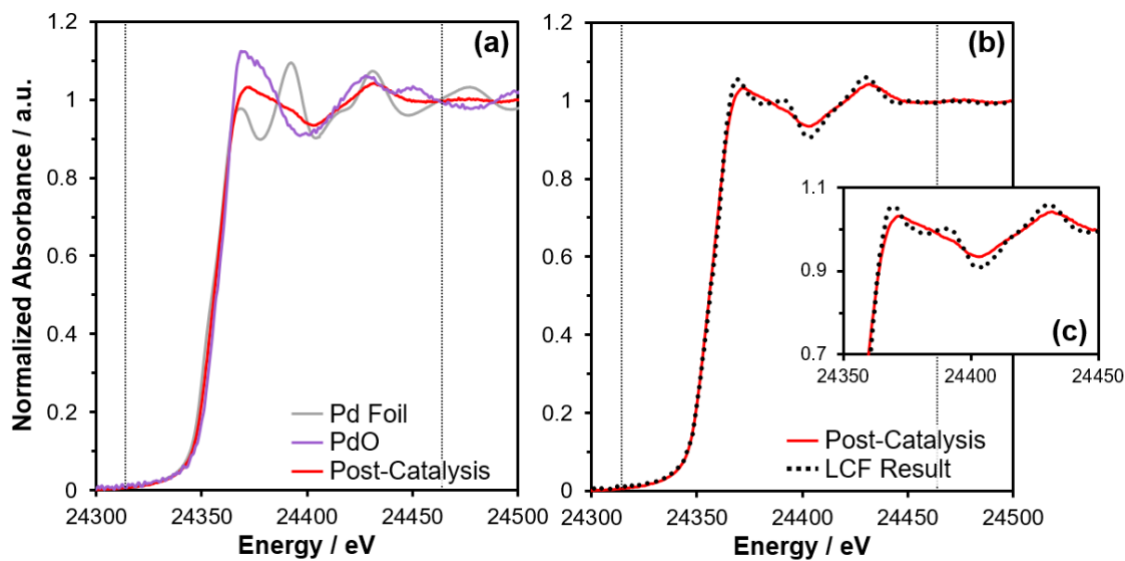


Figure S8. (a) Pd K edge XANES of the ex-situ Pd/MnO₂ post-catalysis sample (7 h, 323 K, 7.7 kPa O₂, 2.6 kPa CO) compared with Pd foil and PdO. (b) LCF result using the Pd foil and PdO as references for Pd/MnO₂ post-catalysis samples and (c) magnification of differences in the structure past the absorption edge.

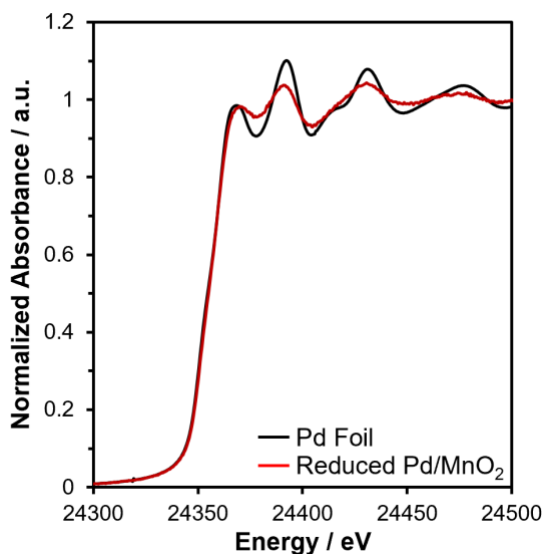


Figure S9. Comparison of the Pd K edge XANES of Pd/MnO₂ reduced in 10% CO/He for 1.5 hours at 423 K and the reference Pd foil.

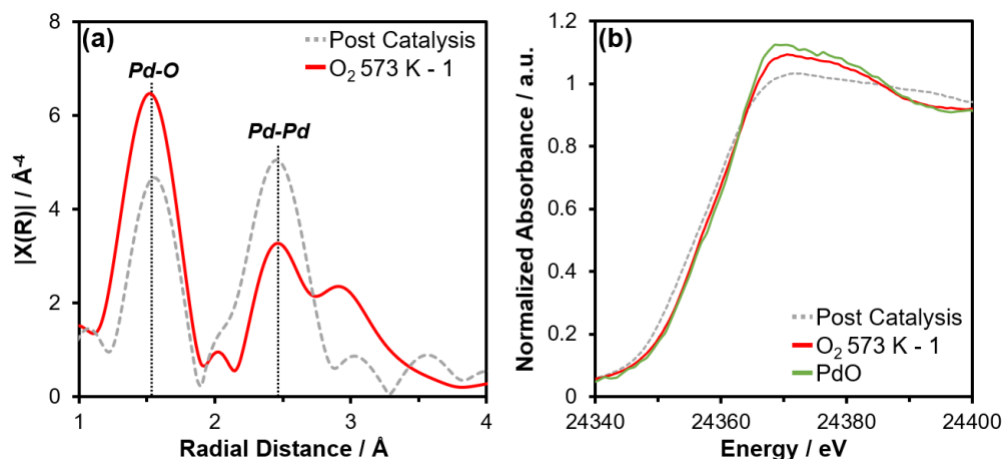


Figure S10. Pd K edge (a) EXAFS and (b) XANES for Pd/MnO₂ following reaction for 7 hours at 323 K (Post Catalysis and following 1 cycle of reaction and O₂ regeneration at 323 K and 573 K, respectively. $k = 3.0 - 11.1 \text{ \AA}^{-1}$. A PdO standard is also added for comparison of the XANES to show the material is reoxidized upon treatment in O₂ at 573 K, following reaction at 323 K.

Table S3. Tabulated EXAFS fitting results for Pd/MnO₂ following reaction for 7 hours at 323 K (post catalysis, 323 K), post reduction in CO at 423 K for 1.5 hours (reduced, CO, 423 K), and following 1 cycle of catalysis at 323 K and O₂ regeneration at 573 K (O₂-Regenerated). $S_0^2 = 0.78$ fit from the Pd reference foil and set for all other samples. Italicized values indicate the value was set during fitting.

Sample	k range \AA^{-1}	R range \AA	Path	N	R (\AA)	σ^2 ($\times 10^{-3} \text{\AA}^2$)	ΔE_0 (eV)	R-factor
Reduced	3 - 12.3	1.8 - 2.4	Pd-Pd	6.4 ± 0.9	2.744 ± 0.005	7.1 ± 1.0	-9.3	0.016
Post Catalysis	3 - 11	1 - 3	Pd-O	1.9 ± 0.4	2.044 ± 0.018	0.4 ± 2.1	1.6 ± 2.8	0.013
			Pd-Pd	3.1 ± 0.9	2.737 ± 0.007	6.4 ± 2.2	-9.3	
O ₂ Regenerated	3 - 11.3	1 - 2.7	Pd-O	3.4 ± 0.5	2.009 ± 0.012	1.2 ± 1.3	-2.3 ± 2.0	0.008
			Pd-Pd	1.5 ± 1.0	2.706 ± 0.015	6.1 ± 4.9	-9.3	
Pd (foil)	3 - 12.3	1.8 - 4.9	Pd-Pd	12 (set)	2.740 ± 0.004	5.3 ± 0.6	-9.3 ± 0.8	0.021

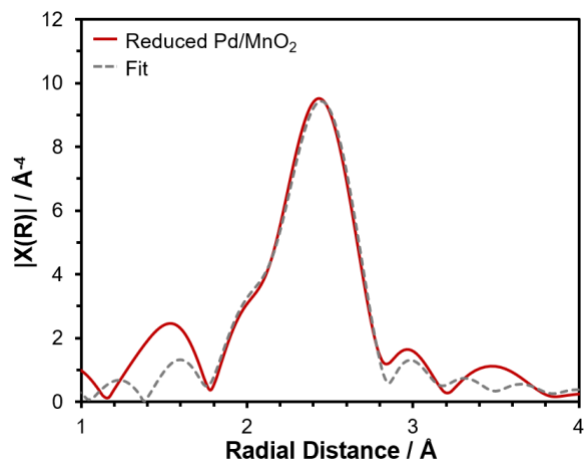


Figure S11. Pd EXAFS fit results for Pd/MnO₂ reduced at 423 K in 10% CO/He for 1.5 hours. Spectra of the sample was measured ex-situ ($k = 3.0 - 12.3 \text{ \AA}^{-1}$, $\Delta k = 0.1$, k^3 weighting, $R = 1.75 - 2.4 \text{ \AA}$, $S_0^2 = 0.78$ (set) fit from the Pd reference foil).

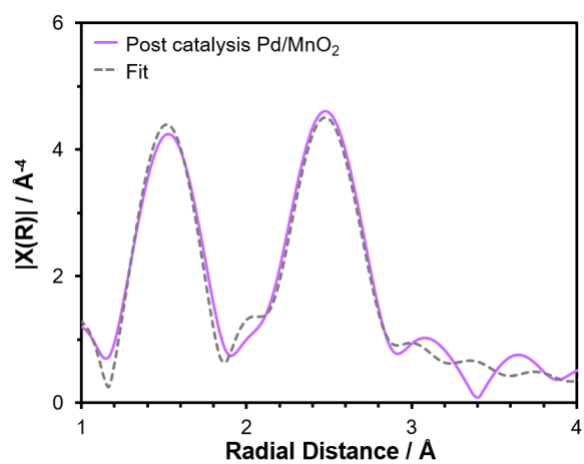


Figure S12. Pd EXAFS fit results for Pd/MnO₂ post-catalysis (7 h, 323 K, 7.7 kPa O₂, 2.6 kPa CO) measured ex-situ ($k = 3 - 11 \text{ \AA}^{-1}$, $\Delta k = 0.1$, k^3 weighting, $R = 1 - 3 \text{ \AA}$, $S_0^2 = 0.78$ (set) fit from the Pd reference foil).

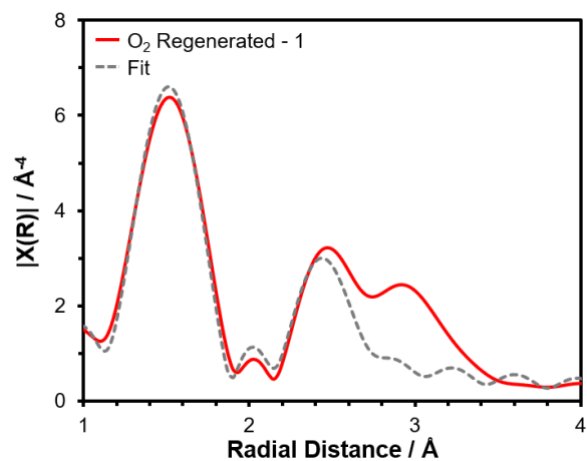


Figure S13. Pd EXAFS fit results for Pd/MnO₂ following one cycle of O₂ regeneration (573 K, 1.5 h, 10% O₂) following catalysis (7 h, 323 K, 7.7 kPa O₂, 2.6 kPa CO). Spectra were measured ex-situ ($k = 3.0 - 11.3 \text{ \AA}^{-1}$, $\Delta k = 0.1, k^3$, $R = 1 - 2.7 \text{ \AA}$, $S_0^2 = 0.78$ (set) fit from the Pd reference foil).

S2.3. CO Oxidation Reaction Data

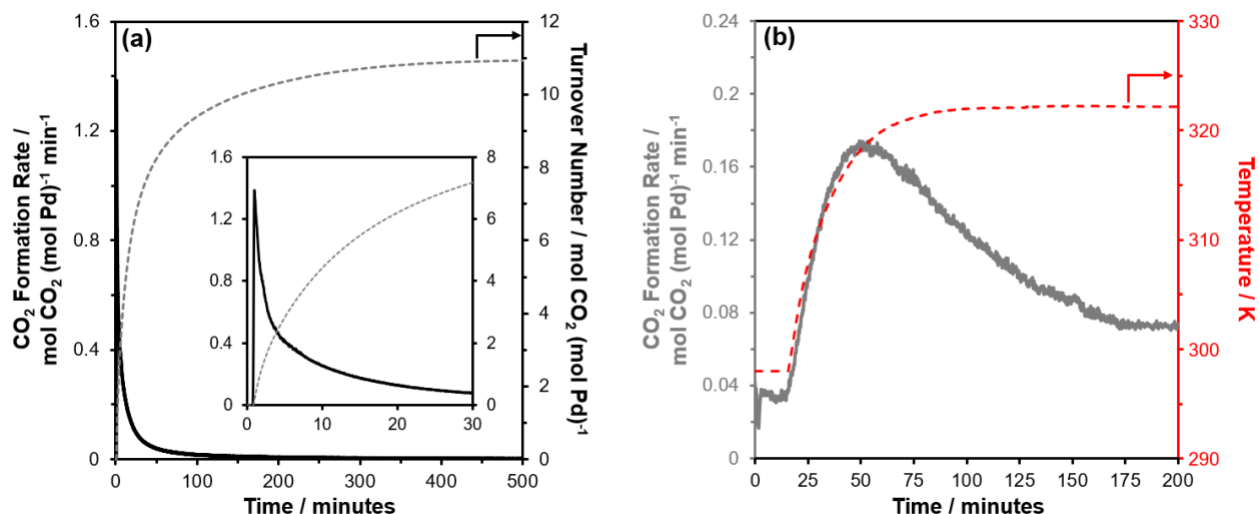


Figure S14. (a) CO oxidation at 295 K over Pd/MnO₂. (b) Temperature-programmed reaction from room temperature to 323 K over Pd/MnO₂ during CO oxidation. Reaction conditions: 7.71 kPa O₂, 2.56 kPa CO, 50 mL min⁻¹, 20 mg catalyst.

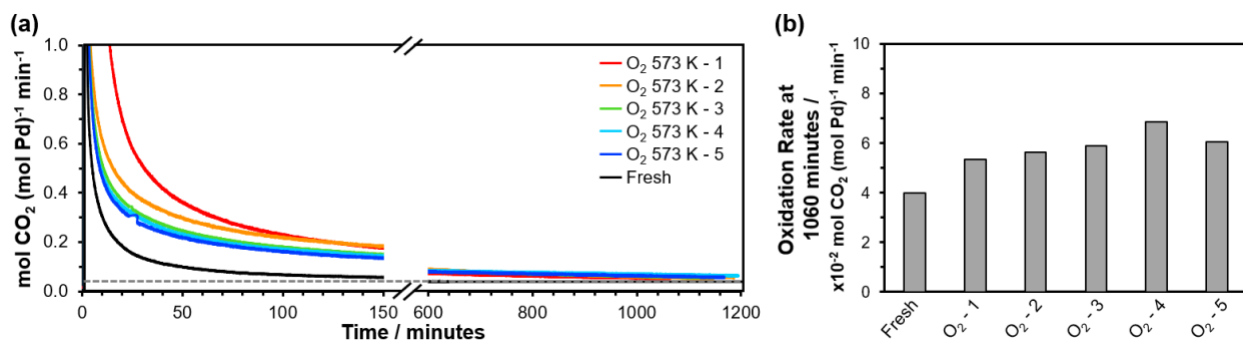


Figure S15. CO oxidation at 323 K for fresh Pd/MnO₂ or following O₂ regeneration for 1 – 5 cycles (regenerated at 573 K in 10% O₂/He for 1.5 hours) (a) showing the CO oxidation rate as a function of time and (b) the rate at 1060 minutes of reaction. Reaction conditions: 7.71 kPa O₂, 2.56 kPa CO, 50 mL min⁻¹, 20 mg catalyst.

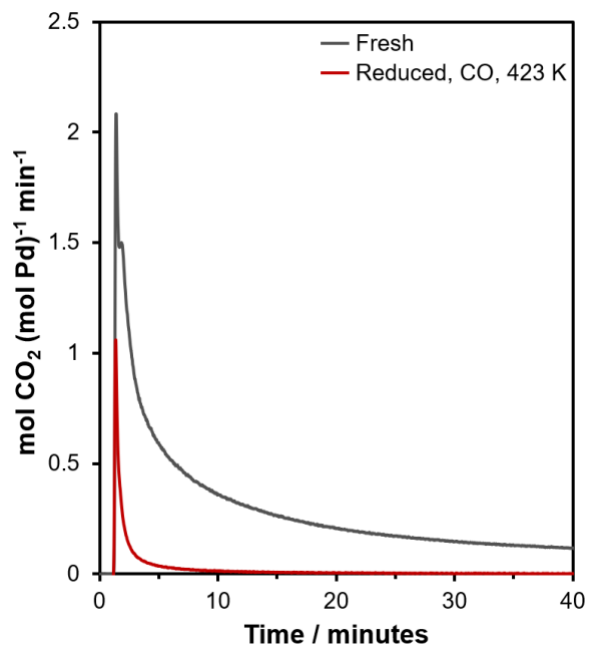


Figure S16. CO oxidation at 323 K for fresh Pd/MnO₂ and Pd/MnO₂ pre-reduced at 423 K in 5% CO for 1.5 hours (reaction conditions: 7.71 kPa O₂, 2.56 kPa CO, 50 mL min⁻¹, 20 mg catalyst).

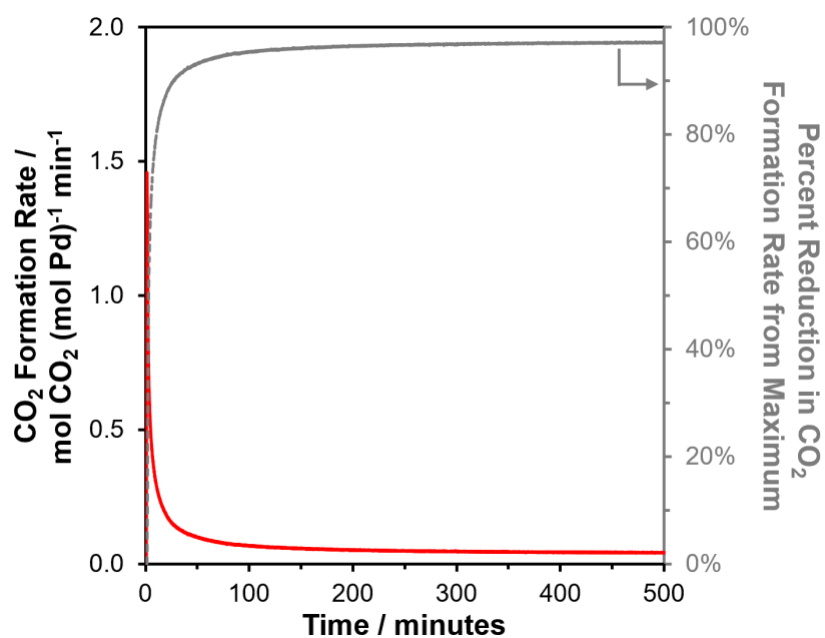


Figure S17. CO oxidation at 323 K over fresh Pd/MnO₂ at short reaction times indicating the percent reduction in the CO₂ formation rate from the maximum value as a function of time (reaction conditions: 7.71 kPa O₂, 2.56 kPa CO, 50 mL min⁻¹, 20 mg catalyst).

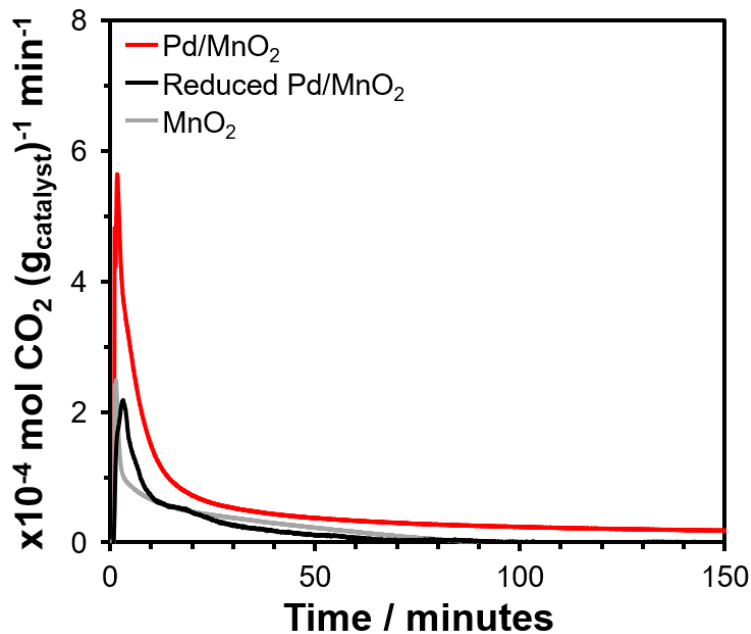


Figure S18. CO oxidation at 323 K for Pd/MnO₂, reduced Pd/MnO₂, and MnO₂ following O₂ regeneration at 573 K. Reduced Pd/MnO₂ was reduced at 423 K in 5% CO for 1.5 hours prior to O₂ regeneration. Reaction conditions: 7.71 kPa O₂, 2.56 kPa CO; regeneration conditions: 10% O₂/He, 573 K, 1.5 hours.

Table S4. Cumulative moles of CO₂ formed (per gram of catalyst) over 100 minutes of reaction for Pd/MnO₂, reduced Pd/MnO₂, and MnO₂ following O₂ regeneration at 573 K. Reduced Pd/MnO₂ was reduced at 423 K in 5% CO for 1.5 hours prior to O₂ regeneration. Reaction conditions: 7.71 kPa O₂, 2.56 kPa CO; regeneration conditions: 10% O₂/He, 573 K, 1.5 hours. The corresponding plot of CO₂ formation with time is provided in Figure S18.

Sample	Cumulative CO ₂ formed / mol CO ₂ (g _{catalyst}) ⁻¹	Cumulative CO ₂ formed / mol CO ₂ (mol Pd) ⁻¹
MnO ₂	2.9 x 10 ⁻³	---
Pd/MnO ₂	6.6 x 10 ⁻³	64
Reduced Pd/MnO ₂	2.7 x 10 ⁻³	26

S2.4. Supplementary Operando XAFS Results

Table S5. Tabulated EXAFS fitting results for Pd/MnO₂ measured during in-situ CO oxidation while holding at 323 K for 0 – 120 minutes ($k = 3.0 - 11 \text{ \AA}^{-1}$, $\Delta k = 0.1$, $k^N N = 1,2,3$ weighting, $R = 1 - 3 \text{ \AA}$, $S_0^2 = 0.78$ (set) and ΔE_0 (set) from the Pd reference foil). Italicized values indicate the value was set during fitting.

Sample	Path	N	R (\AA)	σ^2 ($\times 10^{-3} \text{ \AA}^2$)	ΔE_0 (eV)	R-factor
323 K – 0 min.	Pd-O	2.6 ± 0.4	2.055 ± 0.015	1.1 ± 1.9	5.4 ± 2.3	0.018
	Pd-Pd	0.6 ± 0.9	2.675 ± 0.036	5.8 ± 10.5	<i>(-9.3)</i>	
323 K – 30 min.	Pd-O	2.4 ± 0.3	2.039 ± 0.011	0.9 ± 1.3	3.9 ± 1.7	0.008
	Pd-Pd	1.1 ± 0.7	2.706 ± 0.025	10.2 ± 6.7	<i>(-9.3)</i>	
323 K – 60 min.	Pd-O	2.5 ± 0.3	2.041 ± 0.011	1.2 ± 1.3	4.2 ± 1.7	0.008
	Pd-Pd	1.1 ± 0.7	2.696 ± 0.018	8.2 ± 4.9	<i>(-9.3)</i>	
323 K – 90 min.	Pd-O	2.5 ± 0.3	2.039 ± 0.013	0.7 ± 1.3	4.1 ± 1.7	0.008
	Pd-Pd	1.3 ± 0.8	2.703 ± 0.018	8.8 ± 4.9	<i>(-9.3)</i>	
323 K – 120 min.	Pd-O	2.4 ± 0.3	2.039 ± 0.012	1.1 ± 1.5	4.1 ± 1.9	0.010
	Pd-Pd	1.6 ± 0.9	2.713 ± 0.017	9.4 ± 4.7	<i>(-9.3)</i>	

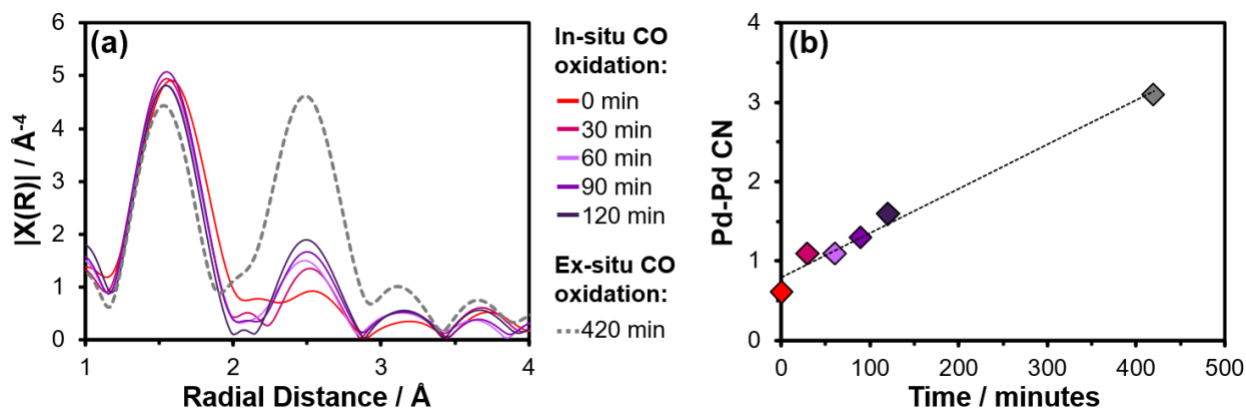


Figure S19. (a) $|X(R)|$ for Pd/MnO₂ during in-situ CO oxidation experiments while holding at 323 K for 0 – 120 minutes and the Pd/MnO₂ prepared and measured ex-situ following 420 minutes of reaction at 323 K under the same conditions (7.7 kPa O₂, 2.6 kPa CO). (b) Pd-Pd coordination number determined from fitting the EXAFS for each sample measured as a function of time in-situ (0 – 120 minutes) and ex-situ (420 minutes).

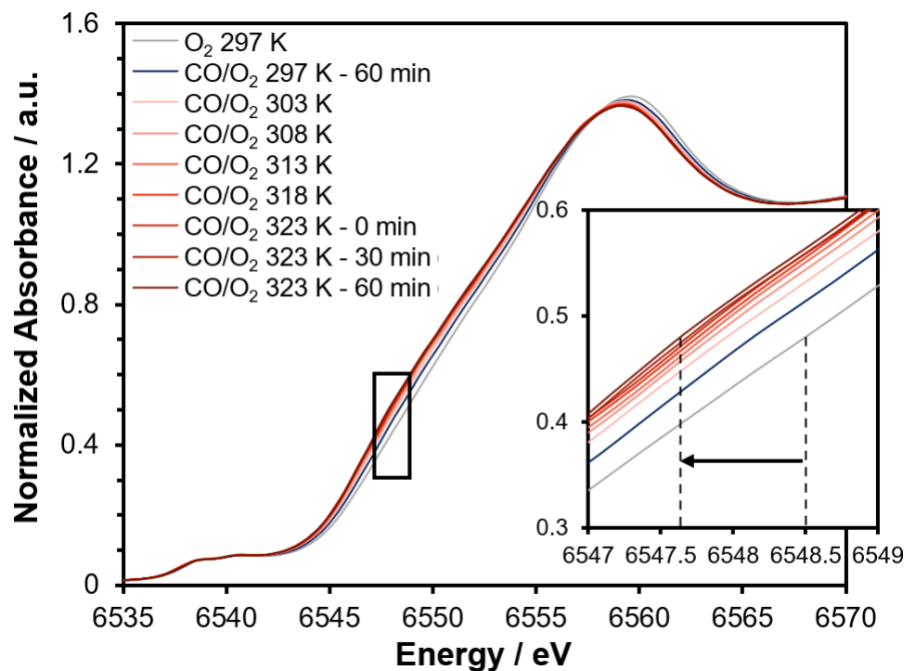


Figure S20. Mn K edge XANES of Pd-MnO₂ during in-situ CO oxidation temperature-programmed reaction experiments between 297 and 323 K (7.7 kPa O₂, 2.6 kPa CO, ramp rate = 0.24 K min⁻¹). Results show a shift in the absorption edge to lower energy with time.

S2.5. Supplementary In-Situ DRIFTS Results

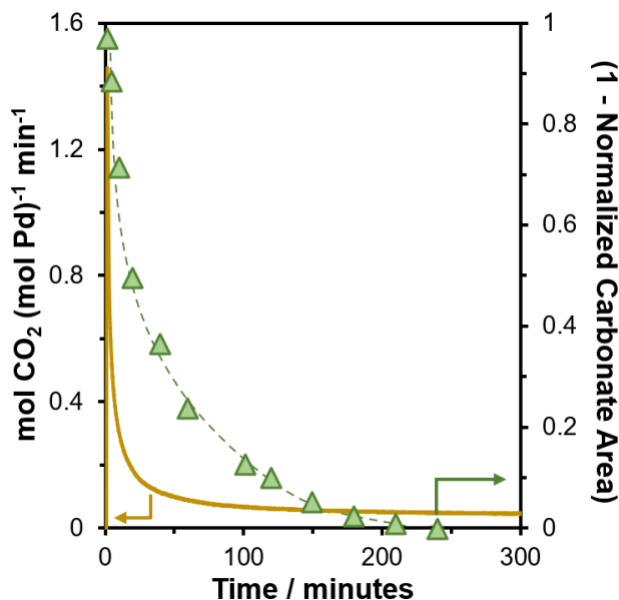


Figure S21. Comparison of the CO₂ formation rate measured over fresh Pd/MnO₂ during CO oxidation at 323 K with the following expression: (1 – Normalized Carbonate Area), where the normalized carbonate area is the area of the infrared spectra from 800 – 1740 cm⁻¹ at a given time divided by the area at 240 minutes measured during CO oxidation at 323 K.

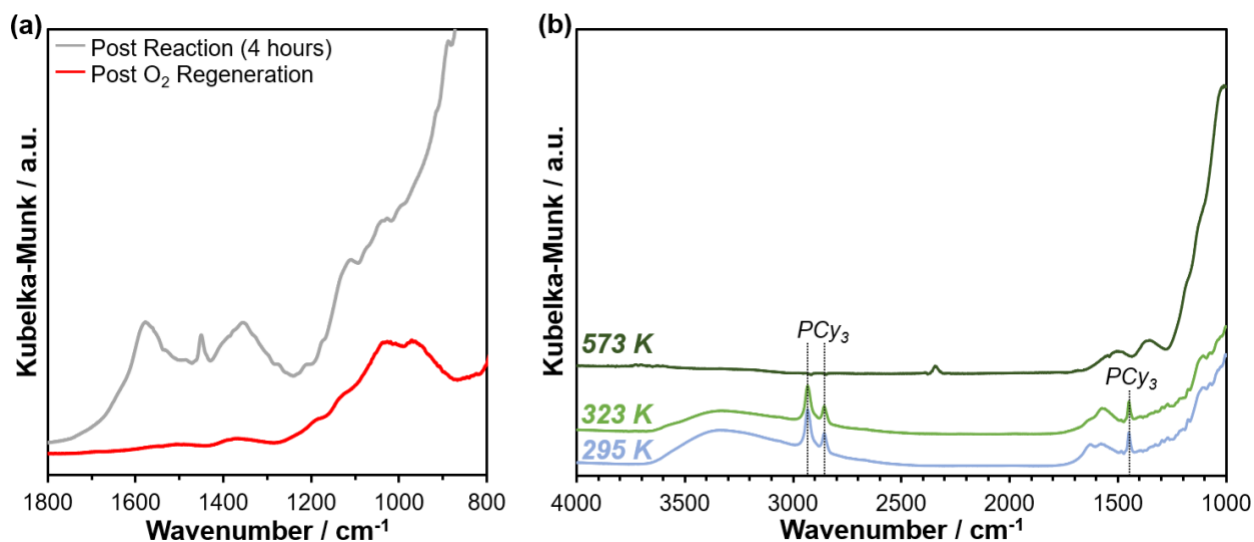


Figure S22. (a) DRIFTS of Pd/MnO₂ measured during in-situ CO oxidation at 323 K for 4 hours and then following an O₂ regeneration step (300 °C, 10% O₂) at 323 K indicating the desorption of carbonates in the region between 1200 – 1800 cm⁻¹. (b) DRIFTS of Pd/MnO₂ under 10% O₂ flow at room temperature (295 K), 323 K, and 573 K, indicating that there is an oxidation of the tricyclohexylphosphine ligands (PCy₃) at or below 573 K.

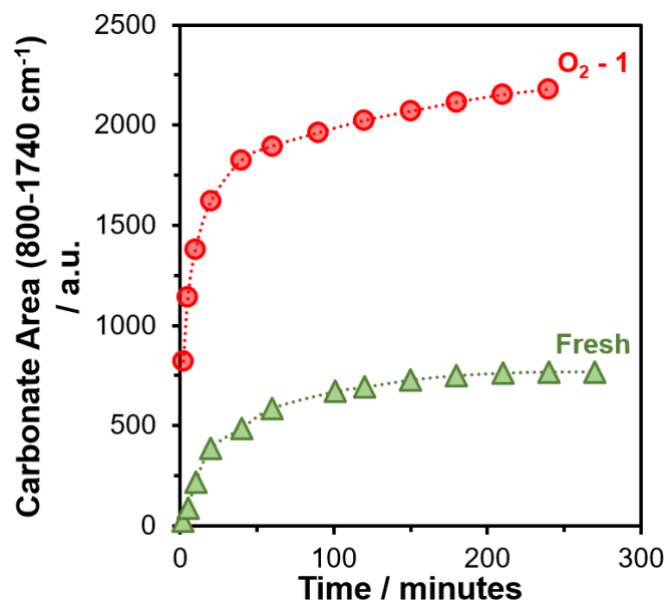


Figure S23. Integrated area of the infrared spectra from 800 to 1740 cm^{-1} during in-situ CO oxidation at 323 K as a function of time for fresh Pd/MnO₂ and following 1 cycle of reaction and regeneration (O₂-1). Reaction conditions: 7.71 kPa O₂, 2.56 kPa CO, 50 mL min⁻¹; regeneration was completed at 573 K in 10% O₂/N₂ for 1.5 hours.

S3. References

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