

Electronic Supplementary Information

Reactivity of Pd-MO encapsulated catalytic systems for CO oxidation

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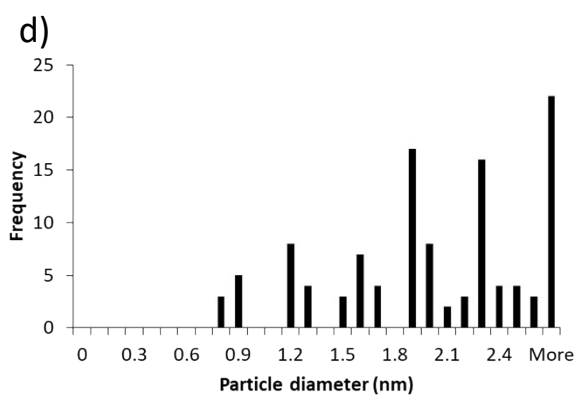
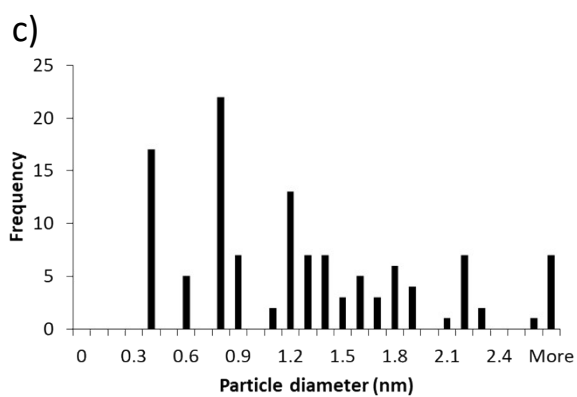
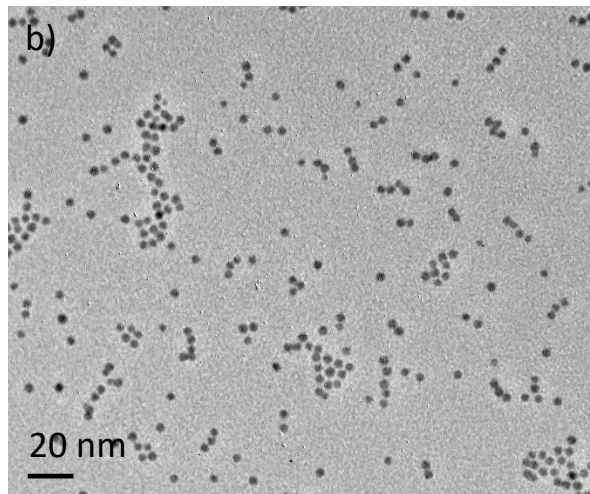
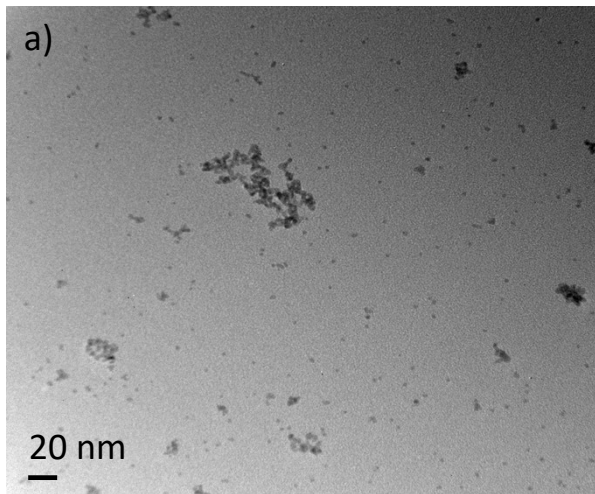


Figure S1: Transmission electron micrographs (TEM) of (a) Pd_{PEG} NPs and (b) Pd_{TOP} NPs in solution along with the histograms of the corresponding particle size distribution (panels (c), and (d), respectively).

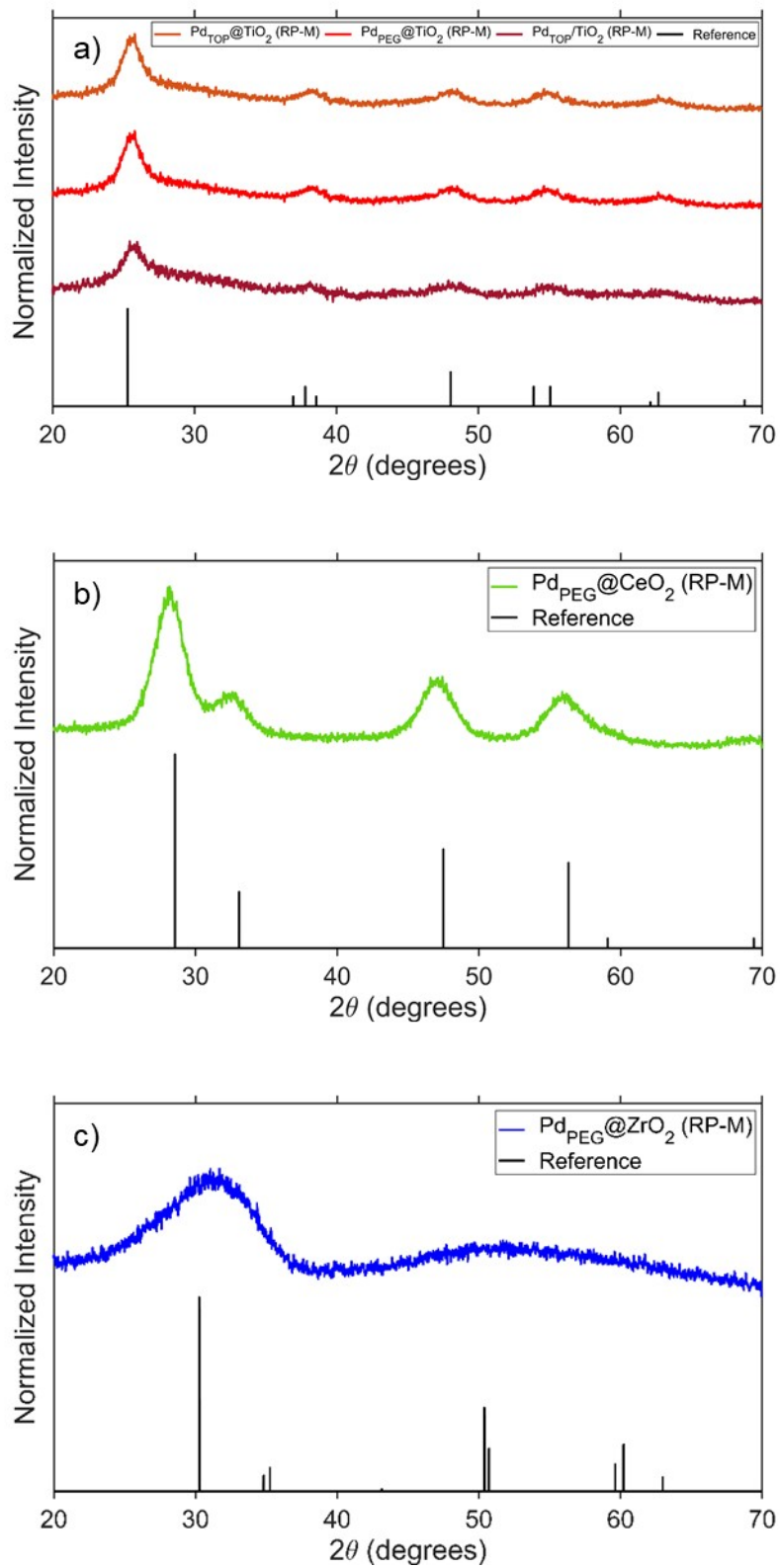


Figure S2: XRD spectra of (a) TiO₂-based catalysts, (b) Pd_{PEG}@CeO₂, and (c) Pd_{PEG}@ZrO₂ using an RP-M pretreatment within tetragonal anatase TiO₂, cubic cerianite CeO₂, and tetragonal ZrO₂ as a reference, respectively.

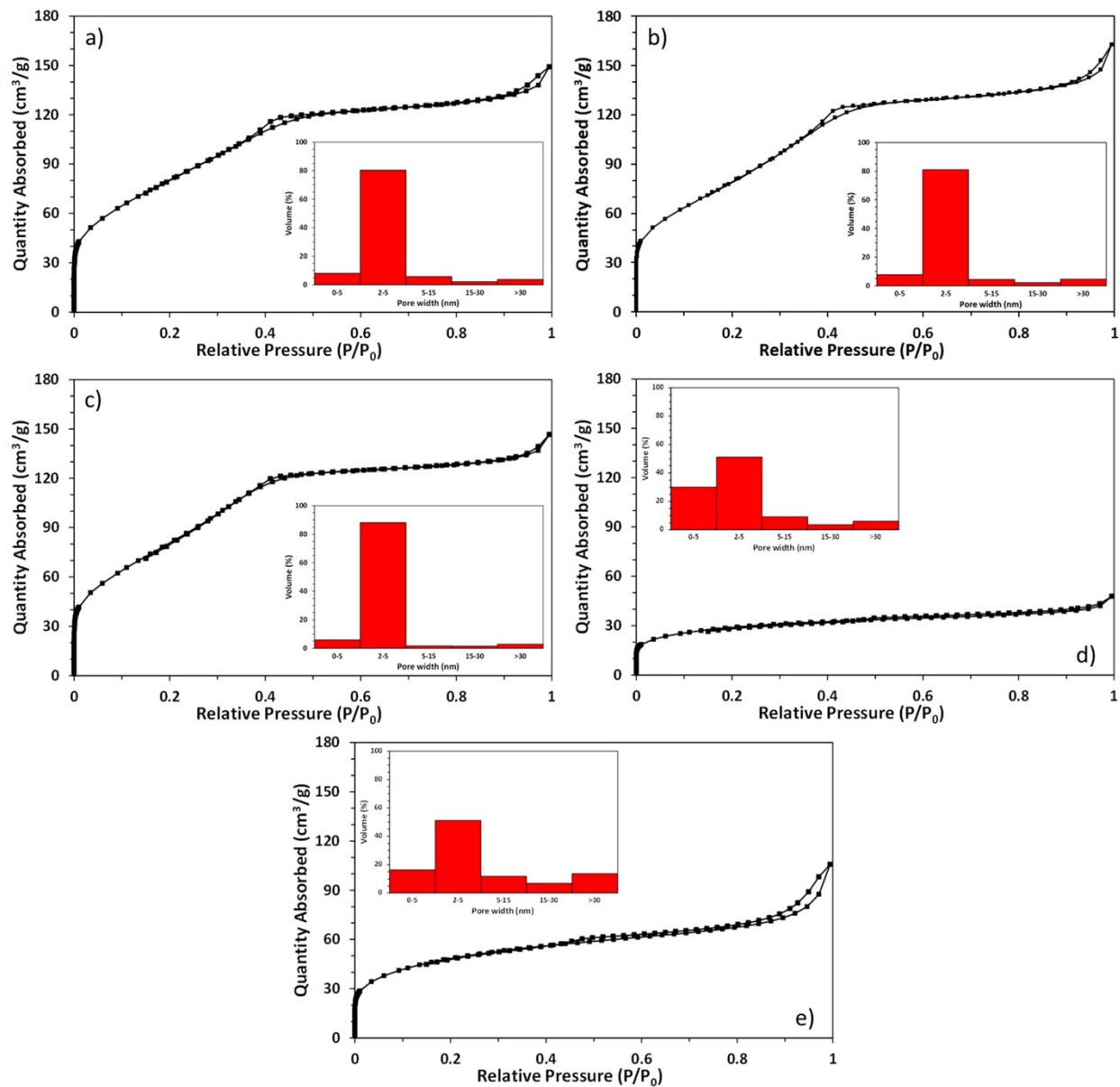


Figure S3: N_2 physisorption isotherms and pore size distribution plots of TiO_2 films on Pd NPs a) $Pd_{TOP}@TiO_2$, b) $Pd_{PEG}@TiO_2$, c) Pd_{TOP}/TiO_2 , d) $Pd_{PEG}@CeO_2$, and e) $Pd_{PEG}@ZrO_2$ using an RP-M pretreatment.

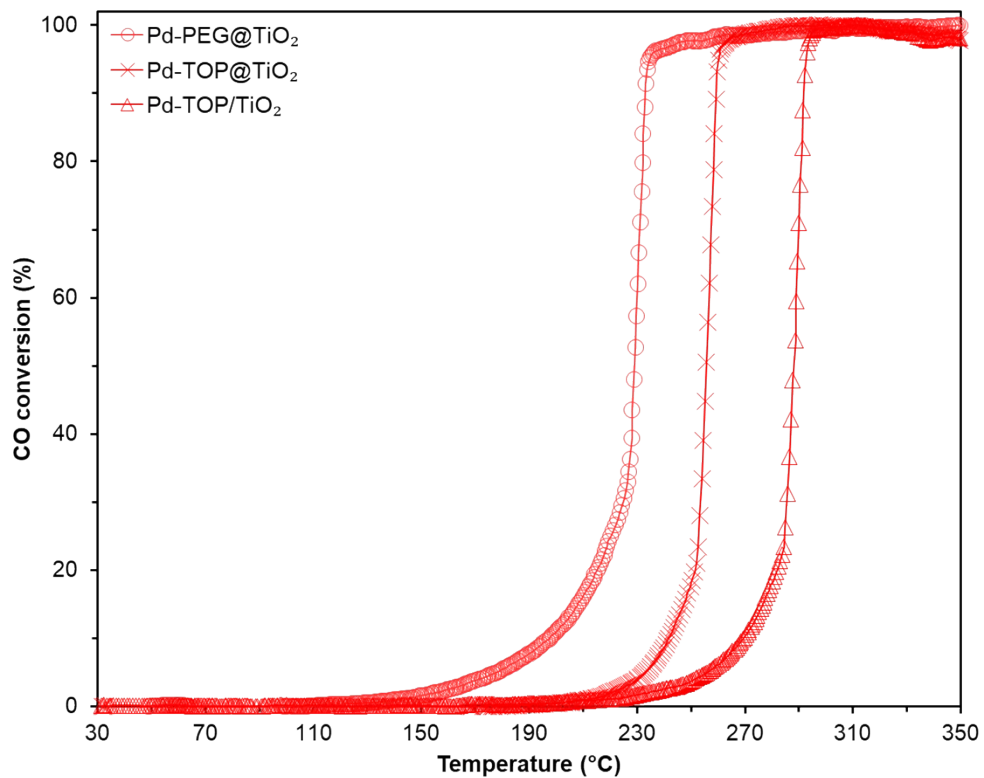


Figure S4: Light-off curves for CO oxidation reaction on encapsulated ($\text{Pd}_{\text{PEG}}@\text{TiO}_2$, $\text{Pd}_{\text{TOP}}@\text{TiO}_2$) and supported catalysts ($\text{Pd}_{\text{TOP}}/\text{TiO}_2$), performed in gas-phase reactor. Before reaction, the catalysts underwent RP-M pretreatment.

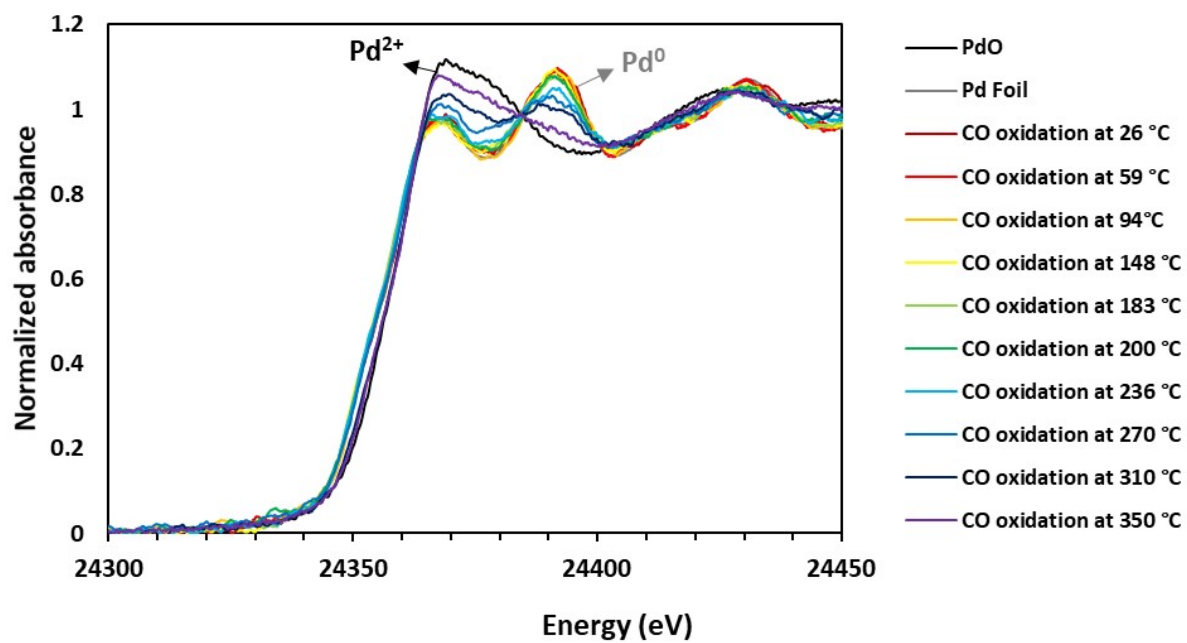


Figure S5: Pd K-edge XANES spectra for CO oxidation recorded during heating processes.

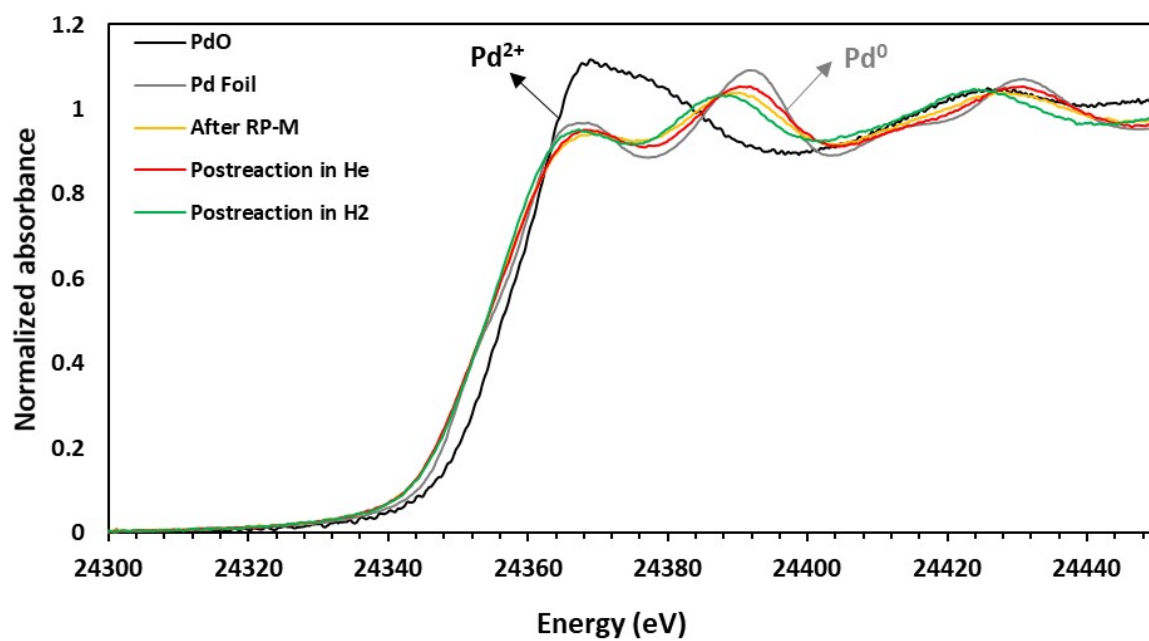


Figure S6: XANES spectra of Pd_{TOP}@TiO₂ before and after CO oxidation.

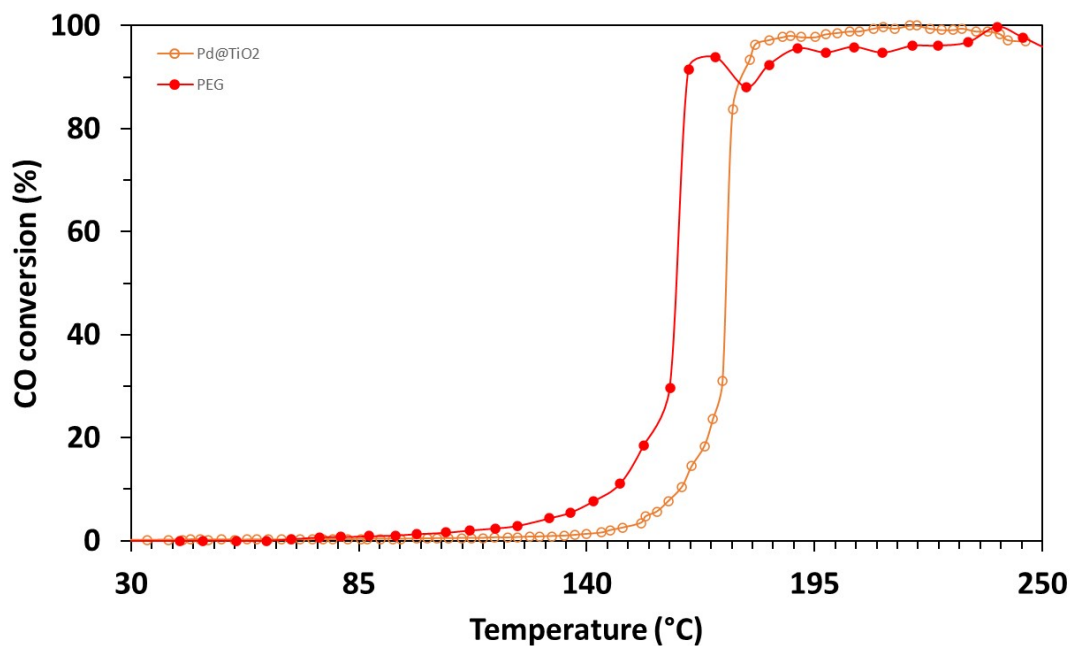


Figure S7: CO conversion during CO oxidation over Pd_{TOP}@TiO₂ and Pd_{PEG}@TiO₂, as measured by MS during XAS experiments.

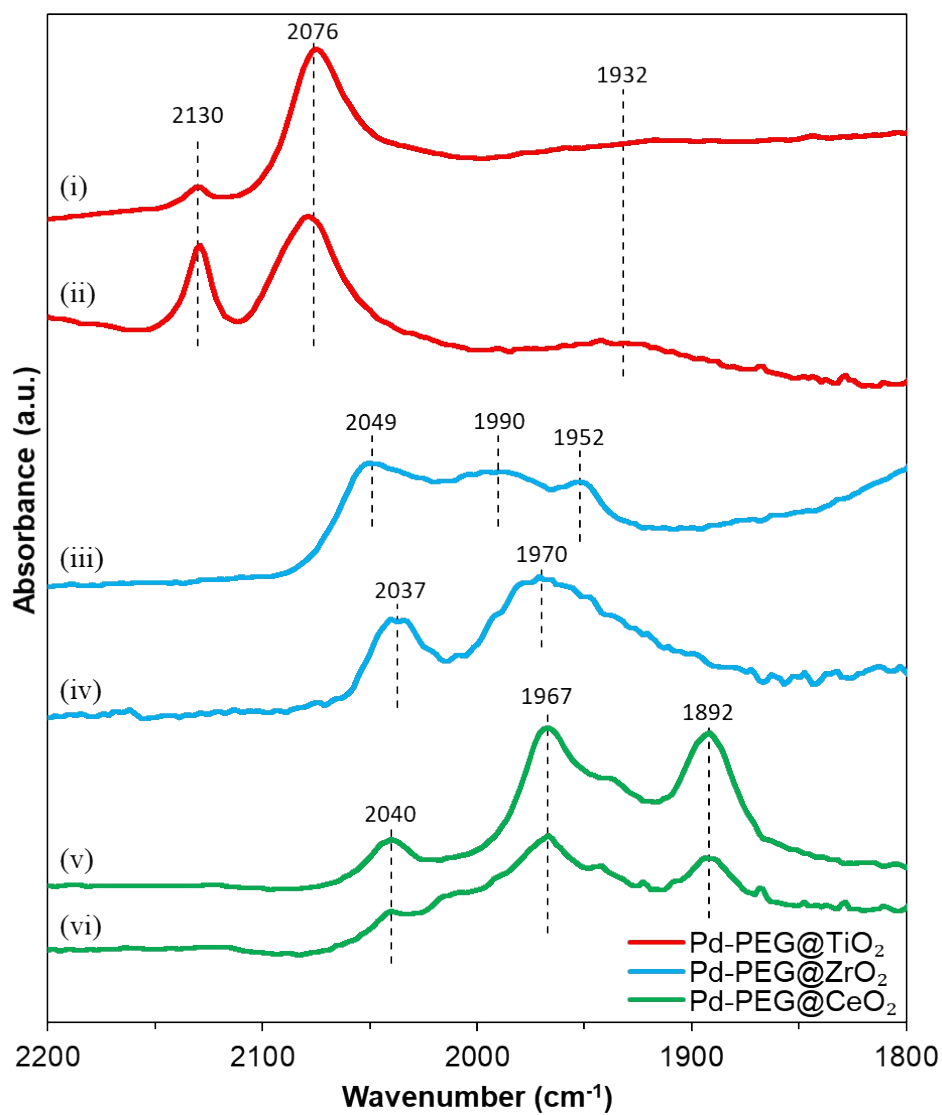


Figure S8: CO DRIFTS spectra of the carbonyl stretch region ($1800 - 2200 \text{ cm}^{-1}$) obtained during minute 5 of CO purge in Ar of (i) $\text{Pd}_{\text{PEG}}@\text{TiO}_2$ before in-situ CO oxidation reaction, (ii) $\text{Pd}_{\text{PEG}}@\text{TiO}_2$ after reaction, (iii) $\text{Pd}_{\text{PEG}}@\text{ZrO}_2$ before in-situ CO oxidation reaction, (iv) $\text{Pd}_{\text{PEG}}@\text{ZrO}_2$ after reaction, (v) $\text{Pd}_{\text{PEG}}@\text{CeO}_2$ before in-situ CO oxidation reaction, and (vi) $\text{Pd}_{\text{PEG}}@\text{CeO}_2$ after reaction.

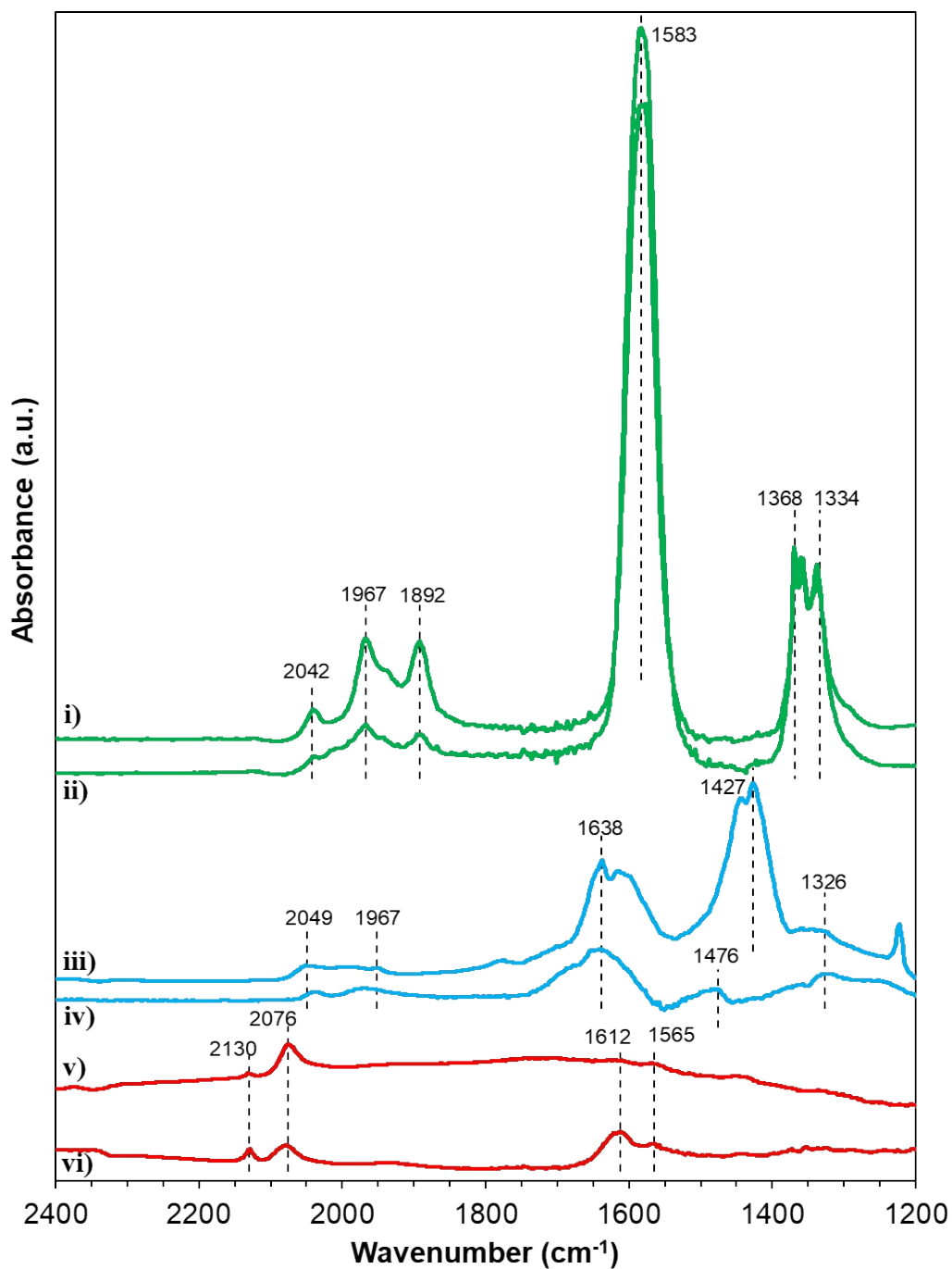


Figure S9: CO DRIFTS full spectra obtained during minute 5 of CO purge in Ar of (i) Pd_{PEG}@CeO₂ before in-situ CO oxidation reaction, (ii) Pd_{PEG}@CeO₂ after reaction, (iii) Pd_{PEG}@ZrO₂ before in-situ CO oxidation reaction, (iv) Pd_{PEG}@ZrO₂ after reaction, (v) Pd_{PEG}@TiO₂ before in-situ CO oxidation reaction, and (vi) Pd_{PEG}@TiO₂ after reaction.

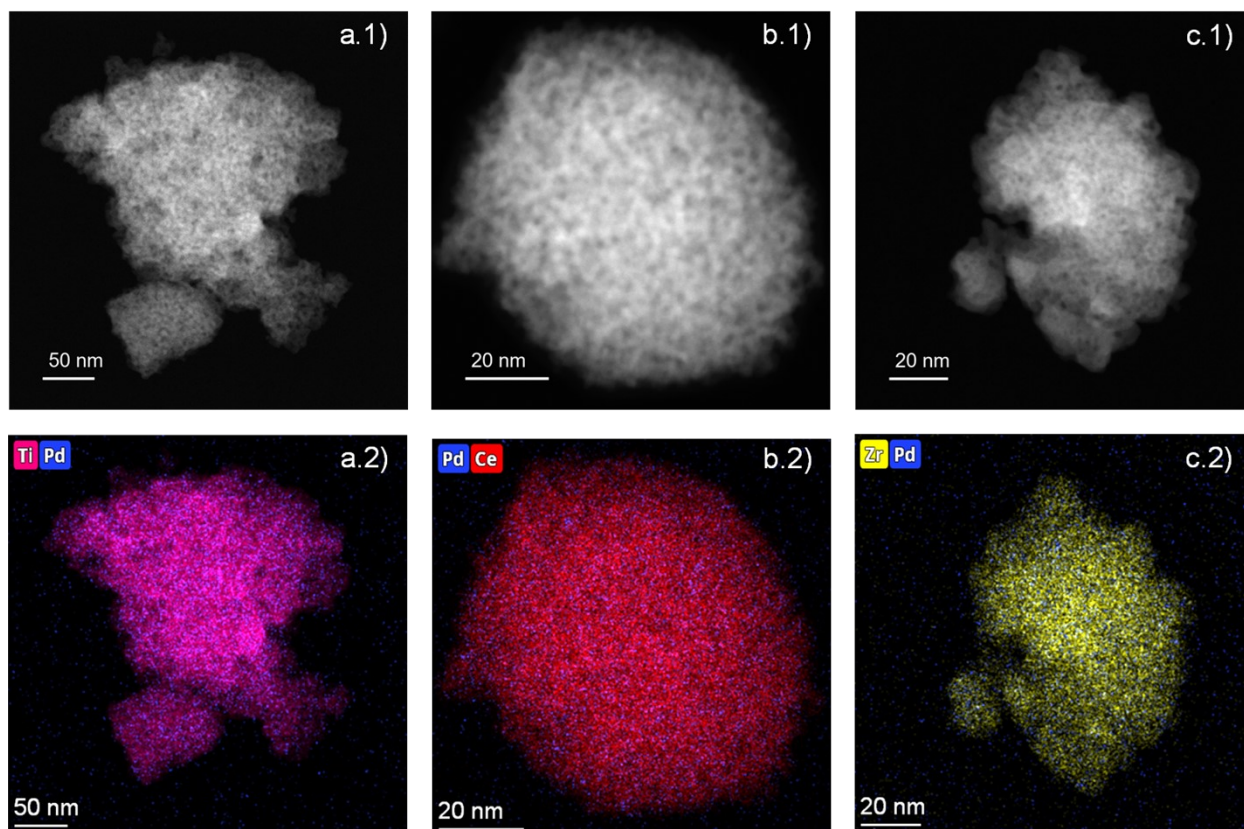


Figure S10: High-resolution scanning transmission electron micrographs (STEM) using high-angle annular dark-field imaging (HAADF) of (a.1) Pd_{PEG}@TiO₂, (b.1) Pd_{PEG}@CeO₂ and (c.1) Pd_{PEG}@ZrO₂. (a.2), (b.2) and (c.2) show the related energy dispersive X-ray spectroscopy (EDS) elemental maps of these HAADF-STEM images (Pd: blue, Ti: magenta, Ce: red and Zr: yellow). A redox pretreatment of 400 °C for the oxidation step and 200 °C for the reduction step was used for all samples prior to analysis.

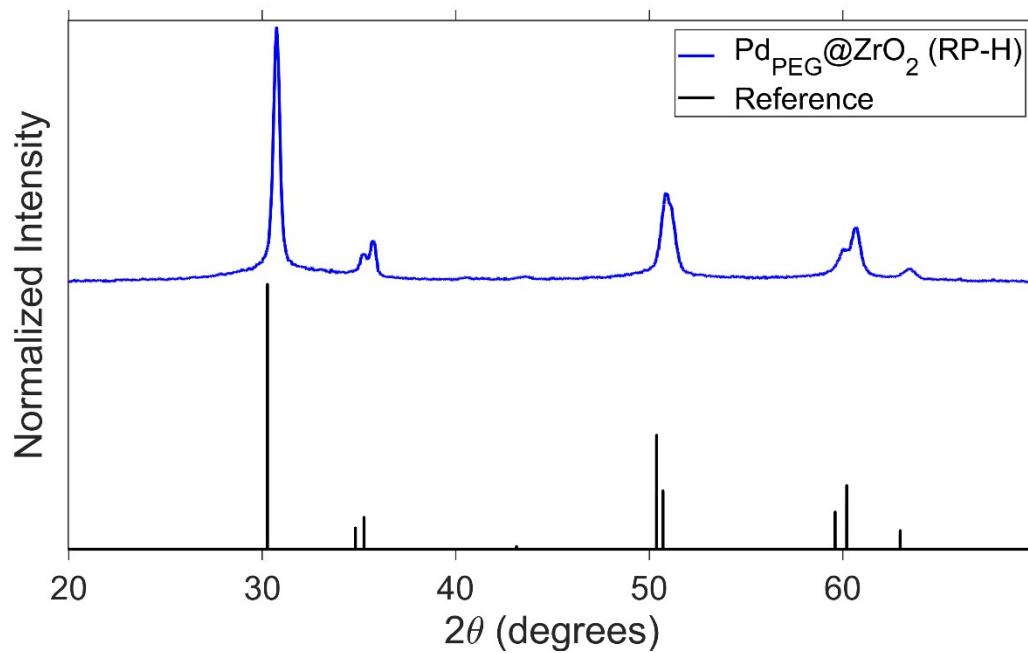


Figure S11: XRD spectrum of Pd_{PEG}@ZrO₂ using a redox pretreatment at 400 °C for the oxidation step and 200 °C for the reduction step within tetragonal ZrO₂ as reference.

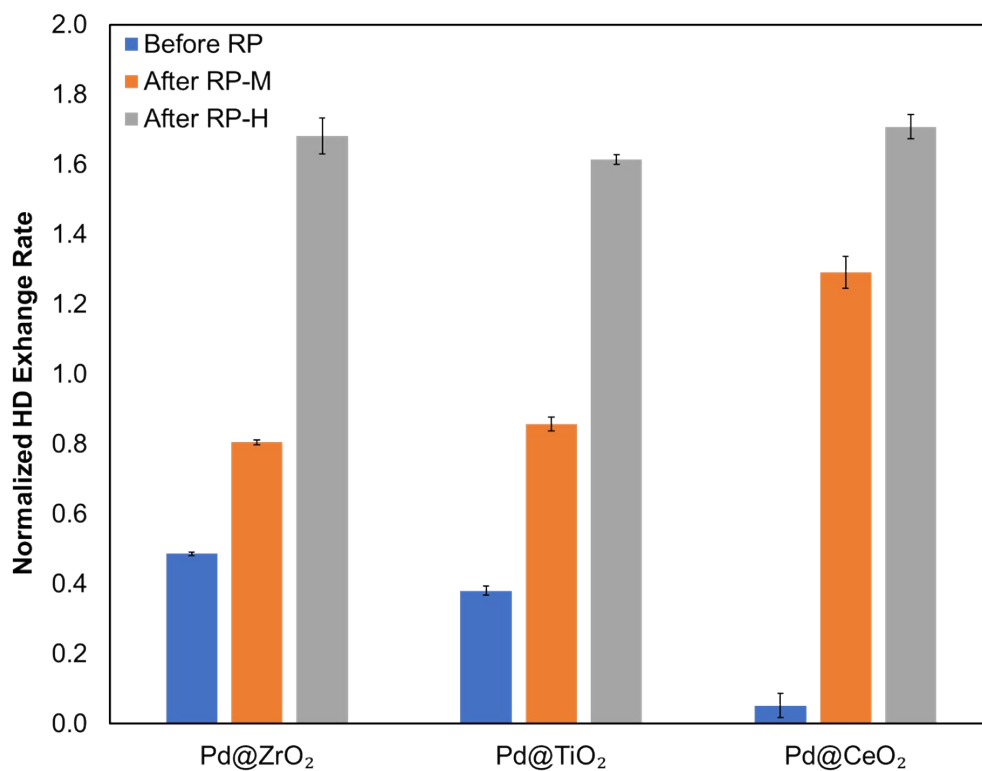


Figure S12: HD exchange rate for Pd_{PEG}@ZrO₂, Pd_{PEG}@TiO₂, and Pd_{PEG}@CeO₂ catalysts before pretreatment, after RP-M (moderate-temperature oxidative-reductive treatment) and after RP-H (high-temperature oxidative-reductive treatment). HD exchange activity is normalized to the scrambling rates obtained with the control catalyst (5 wt.% Pd/Al₂O₃).

Table S1: Summary of linear combination fit (LCF) results of the Pd K-edge XANES spectra of Pd_{TOP}@TiO₂ and Pd_{PEG}@TiO₂.

Sample Name		LCF Results (%)		LCF Parameters		
		Pd foil	PdO	R-factor	χ^2	Reduced χ^2
Pd _{TOP} @TiO ₂	After pretreatment	86	14	0.0031	0.15	0.00050
	Postreaction in He	91	9	0.0017	0.08	0.00027
	Postreaction in H ₂	87	13	0.0067	0.32	0.0011
Pd _{PEG} @TiO ₂	After pretreatment	99	1	0.00042	0.020	0.000072
	Postreaction in He	14	86	0.00068	0.038	0.00012
	Postreaction in H ₂	35	65	0.00064	0.034	0.00011

Table S2: Summary of CO oxidation light-off temperatures and apparent activation energies at moderate temperature (RP-M) and high temperature (RP-H) pretreatments.

Sample Name	Light off at T_{50} , °C (RP-M)	E_a^{app} , kJ mol ⁻¹ (RP-M)	Light off at T_{50} , °C (RP-H)	E_a^{app} , kJ mol ⁻¹ (RP-H)
Pd _{PEG} @ZrO ₂	194 ± 4.64	43.8 ± 0.04	217 ± 0.47	52.0 ± 0.10
Pd _{PEG} @TiO ₂	227 ± 1.89	55.0 ± 0.04	229 ± 5.66	59.8 ± 0.08
Pd _{PEG} @CeO ₂	234 ± 1.25	57.1 ± 0.05	242 ± 1.70	63.7 ± 0.07

Uncertainties indicate standard deviation of T_{50} and E_a^{app} values for three temperature ramps.

Table S3: Summary of H₂/D₂ exchange rates and estimation of metal surface area and dispersion for Pd_{PEG}@ZrO₂, Pd_{PEG}@TiO₂, and Pd_{PEG}@CeO₂ catalysts before pretreatment, after RP-M (moderate-temperature oxidative-reductive treatment) and after RP-H (high-temperature oxidative-reductive treatment).

Sample Name	Treatment	H ₂ /D ₂ scrambling rate [conversion/mg _{Pd}]	Metallic Surface Area [m ² /g _{Pd}]	Apparent Dispersion ^b [%]
Control Pd/Al ₂ O ₃	After treatment ^a	9.8 ± 0.3	187.0	42
Pd _{PEG} @ZrO ₂	Before RP	4.8 ± 0.1	91.2 ± 1.5	20.5 ± 0.2
	After RP-M	7.9 ± 0.1	151.0 ± 0.3	33.9 ± 0.3
	After RP-H	16.5 ± 0.5	315.5 ± 2.2	70.9 ± 2.2
Pd _{PEG} @TiO ₂	Before RP	3.8 ± 0.1	71.5 ± 2.3	16.1 ± 0.5
	After RP-M	8.4 ± 0.2	160.8 ± 0.8	36.1 ± 0.8
	After RP-H	15.9 ± 0.1	302.9 ± 0.6	68.0 ± 0.6
Pd _{PEG} @CeO ₂	Before RP	0.5 ± 0.3	9.8 ± 0.3	2.2 ± 1.5
	After RP-M	12.7 ± 0.5	12.7 ± 0.5	54.4 ± 1.9
	After RP-H	16.8 ± 0.3	16.8 ± 0.3	71.9 ± 1.5

Uncertainties indicate standard deviations of triplicate runs.

^aThe control catalyst was treated at 250 °C in H₂/He for one hour, same treatment used before CO chemisorption to obtain percent dispersion.

^bDispersion is defined as the fraction of exposed metal active sites obtained from H₂/D₂ scrambling activity.