Supplemental Information:

Controlled site coverage of strong metal-support interaction (SMSI)

on Pd NP catalysts

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Supplemental Results

Figures S1-S3 show the Fourier transform of $k^2\chi(k)$ EXAFS scans of the 0.1, 0.5, and 1.0 wt% Ti containing catalysts after 450 °C calcination and 250/400/500/550 °C reduction. All have similar peak shapes characteristic of Pd. They also show similar trends where increasing the reduction tempearture increases the height of the peak which corresponds to increasing Pd-Pd coordination and particle size.



Figure S1: Pd K edge EXAFS spectra for the 0.1 wt% Ti containing catalyst reduced at 250 (red, dash), 400 (blue, dot), 500 (green, solid), 550 (black, dash)



Figure S2: Pd K edge EXAFS spectra for the 0.5 wt% Ti containing catalyst reduced at 250 (red, dash), 400 (blue, dot), 500 (green, solid), 550 (black, dash)



Figure S3: Pd K edge EXAFS spectra for the 1.0 wt% Ti containing catalyst reduced at 250 (red, dash), 400 (blue, dot), 500 (green, solid), 550 (black, dash)

Table S1 includes the fitting parameters of all samples after calcination at 450 °C and reduction at 200/400/500/550 °C. All samples show similar trends where increasing reduction temperature increased the Pd-Pd coordination and particle size most notably after 500 and 550 °C.

Sample / Ti Loading (wt%)	Reduction Temperature (°C)	CN _{Pd-Pd}	R (Å)	$\Delta\sigma^2$ (Å ²)	E _o Shift (eV)	Surface Fraction Pd	Est. Size (nm)
Pd Foil	-	12	2.75	0	0	-	-
0	250	5.1	2.74	0.0045	-3.4	0.83	1.2
	400	5.4	2.74	0.0045	-2.8	0.76	1.3
	500	5.9	2.73	0.0040	-2.6	0.65	1.5
	550	6.0	2.73	0.0040	-2.7	0.63	1.6
0.1	250	4.9	2.73	0.0045	-2.7	0.88	1.1
	400	4.8	2.72	0.0045	-3.4	0.90	1.1
	500	5.1	2.73	0.0045	-2.2	0.83	1.2
	550	6.1	2.72	0.0040	-3.6	0.61	1.6
0.5	250	6.1	2.73	0.0040	-3.9	0.61	1.6
	400	5.9	2.73	0.0040	-3.6	0.65	1.5
	500	6.5	2.73	0.0040	-4.1	0.54	1.8
	550	7.1	2.73	0.0040	-3.6	0.45	2.2
1.0	250	5.6	2.74	0.0040	-2.4	0.71	1.4
	400	5.7	2.73	0.0040	-3.4	0.69	1.4
	500	6.6	2.73	0.0040	-3.3	0.53	1.9
	550	7.2	2.74	0.0040	-3.6	0.44	2.3

Table S1: EXAFS fitting parameters for Pd foil and all catalysts calcined at 450 °C and reduced at different temperatures

Figures S4-S9 show the STEM images and the particle size distributions for all catalysts after 450 °C calcination and 550 °C reduction and after subsequent oxidation at 350 °C and rereduction at 200 C for the 0.1-1.0 wt% Ti containing catalysts. All catalysts had similar average particle sizes with the majority of nanoparticles being 1-3 nm. There were small amounts of larger nanoparticles (4-6.5 nm) present in all catalysts.



Figures S4: STEM image and particle size distribution of the 0 wt% Ti containing catalyst after 550 °C reduction



Figures S5: STEM image and particle size distribution of the 0.1 wt% Ti containing catalyst after 550 °C reduction



Figures S6: STEM image and particle size distribution of the 1.0 wt% Ti containing catalyst after 550 °C reduction





Figures S7: STEM image and particle size distribution of the 0.1 wt% Ti containing catalyst after 550 °C reduction, 350 °C oxidation, and 200 °C re-reduction



Figures S8: STEM image and particle size distribution of the 0.5 wt% Ti containing catalyst after 550 °C reduction, 350 °C oxidation, and 200 °C re-reduction



Figures S9: STEM image and particle size distribution of the 1.0 wt% Ti containing catalyst after 550 °C reduction, 350 °C oxidation, and 200 °C re-reduction

Table S2 includes the data used to calculate the estimated TORs in Figure 4.

Ti Loading (wt%)	Rate (mol C ₃ H ₈ *mol _{metal} ⁻¹ *s ⁻¹)	Surface Fraction Pd	Estimated TOR (s ⁻¹)
0	2.6	0.64	4.0
0.1	1.6	0.57	2.5
0.5	0.8	0.44	1.8
1.0	0.4	0.44	0.9

Table S2: Estimated TOR of catalysts after reduction at 550 °C

Table S3 includes the catalytic rates that were used to calculate the coverages in Figure 6. All coverages were determined as follows: $Coverage = (1 - \frac{SMSI Rate}{Non - SMSI Rate}) * 100\%$

Ti Loading (wt%)	SMSI Rate (mol C ₃ H ₈ *mol _{metal} ^{-1*} s ⁻¹)	Non-SMSI Rate (mol C ₃ H ₈ *mol _{metal} ^{-1*} s ⁻¹)	Coverage (%)
0.1	1.6	2.7	40
0.5	0.8	3.1	75
1	0.4	2.7	84
6	0.3	2.5	87

Table S3: Coverage of SMSI catalysts after reduction at 550 °C

Table S4 includes the EXAFS fits of all catalysts after 550 °C reduction (550R), 350° C oxidation, and 200 °C re-reduction (200RR). All had similar peaks characteristic of Pd. All coordination numbers were consistent within \pm 0.3 which is within the 10% error commonly used for EXAFS fittings.

Table S4: EXAFS fitting results for catalysts reduced at 550 °C (550R), oxidized at 350 °C, and re-reduced at 200 °C (200RR)

Ti Loading	Treatment Step &	CN _{Pd-Pd}	R (Å)	Δ σ^2 (Å ²)	E _o Shift	Dispersion	Est. Size
(wt%)	Scan Conditions				(eV)		(nm)

0	550R, He	6.0	2.73	0.0040	-2.8	0.63	1.6
	550R, H ₂	6.1	2.75	0.0040	-2.3	0.61	1.6
	200RR, He	5.8	2.72	0.0040	-1.1	0.67	1.5
0.1	550R, He	6.1	2.72	0.0040	-3.6	0.61	1.6
	550R, H ₂	6.4	2.75	0.0040	-1.5	0.56	1.8
	200RR, H ₂	6.6	2.73	0.0040	-1.9	0.53	1.9
0.5	550R, He	7.1	2.73	0.0040	-1.3	0.45	2.2
	550R, H ₂	7.2	2.75	0.0040	-0.7	0.44	2.3
	200RR, H ₂	7.3	2.73	0.0040	-1.9	0.43	2.3
1.0	550R, He	7.2	2.74	0.0040	-3.6	0.44	2.3
	550R, H ₂	7.1	2.75	0.0040	-2.4	0.45	2.2
	200RR, H ₂	7.2	2.73	0.0040	-3.1	0.44	2.3

Figures S10-S12 show the Fourier transform of $k^2\chi(k)$ from EXAFS scans of the 0.1, 0.5, and 1.0 wt% Ti containing catalysts after 550 °C reduction and 30° C oxidation. All have similar peaks characteristic of Pd and PdO. There is increasing peak height and area of the PdO peak as Ti loading is decreased which indicates increasing PdO coordination.



Figure S10: k²-weighthed Fourier transform of the Pd K edge EXAFS spectra of the 0.1 wt% Ti containing catalyst reduced at 550 °C (black, solid) then oxidized at 30 °C (purple, dash)



Figure S11: k²-weighthed Fourier transform of the Pd K edge EXAFS spectra of the 0.5 wt% Ti containing catalyst reduced at 550 °C (black, solid) then oxidized at 30 °C (purple, dash)



Figure S12: k²-weighthed Fourier transform of the Pd K edge EXAFS spectra of the 1.0 wt% Ti containing catalyst reduced at 550 °C (black, solid) then oxidized at 30 °C (purple, dash)

Table S5 includes the catalytic rates that were used to calculate the coverages in Figure 8.

Table S5: Coverage of 0.5 wt% Ti containing catalyst after reduction at 550 °C, oxidation at different temperatures, and re-reduction at 200 °C

Oxidation Temperature (°C)	Rate (mol C ₃ H ₈ *mol _{metal} ⁻¹ *s ⁻¹)	Coverage (%)
*	0.8	75
30	1.1	63
200	1.6	48
300	2.0	35
350	3.0	0
400	3.1	0

* Measurement taken after 550 °C reduction (no oxidation)

Table S6 includes the EXAFS fits of all catalysts after 450 °C calcination, 550 °C reduction, and 30/200/300/350° C oxidation. All had similar peaks characteristic of Pd and PdO. There is increasing peak height and area of the PdO peak as oxidation temperature is increased for all catalysts which indicates increasing PdO coordination and an increased fraction of Pd oxidized.

Ti Loading (wt%)	Oxidation Temperature (°C)	Scattering Path	CN	R (Å)	$\Delta\sigma^2$ (Å ²)	E _o Shift (eV)	Fraction Pd Oxidized
0	30	Pd-Pd	4.0	2.72	0.0040	-1.3	0.60
		Pd-O	2.4	2.03	0.0020	2.2	
	200	Pd-Pd	2.5	2.72	0.0040	0.2	0.65
		Pd-O	2.6	2.03	0.0020	2.4	
	300	Pd-Pd	1.9	2.72	0.0040	0.8	0.75
		Pd-O	3.0	2.03	0.0020	1.4	
	350	Pd-Pd	1.0	2.72	0.0040	-1.8	0.80
		Pd-O	3.2	2.02	0.0020	3.1	

0.1	30	Pd-Pd	5.5	2.72	0.0040	-1.4	0.28
		Pd-O	1.1	2.04	0.0020	-1.9	
	200	Pd-Pd	4.7	2.72	0.0040	-0.2	0.35
		Pd-O	1.4	2.03	0.0020	-1.2	
	300	Pd-Pd	3.7	2.72	0.0040	-1.1	0.65
		Pd-O	2.6	2.022	0.0020	1.7	
	350	Pd-Pd	0.9	2.72	0.0040	-2.2	0.75
		Pd-O	3.0	2.04	0.0020	2.1	
0.5	30	Pd-Pd	6.3	2.72	0.0040	-1.3	0.15
		Pd-O	0.5	2.04	0.0020	1.4	
	200	Pd-Pd	5.0	2.73	0.0040	0.4	0.35
		Pd-O	1.4	2.02	0.0020	-0.7	
	300	Pd-Pd	3.6	2.72	0.0040	-0.2	0.53
		Pd-O	2.1	2.03	0.0020	-2.3	
	350	Pd-Pd	2.2	2.72	0.0040	1.4	0.68
		Pd-O	2.7	2.03	0.0020	2.6	
1.0	30	Pd-Pd	6.5	2.73	0.0040	-0.4	0.13
		Pd-O	0.5	2.03	0.0020	2.2	
	200	Pd-Pd	4.2	2.72	0.0040	0.3	0.33
		Pd-O	1.3	2.02	0.0020	-1.6	
	300	Pd-Pd	3.3	2.72	0.0040	-0.4	0.48
		Pd-O	1.9	2.02	0.0020	0.8	
	350	Pd-Pd	2.5	2.72	0.0040	-2.8	0.63
		Pd-O	2.5	2.02	0.0020	-1.6	

Table S7 includes the catalytic rates used to calculate the coverages in Figure 10.

Ti Loading (wt%)	Re-reduction Temperature (°C)	Rate (mol C ₃ H ₈ *mol _{metal} ⁻¹ *s ⁻¹)	Coverage (%)
0.1	200	2.7	0
	300	2.5	7
	400	2.3	16
	500	1.8	34
	550	1.6	40
0.5	200	3.1	0
	300	2.0	27
	400	1.3	55
	500	0.9	70
	550	0.8	73

Table S7: Coverage of SMSI catalysts after calcination at 450 °C, reduction at 550 °C, oxidation at 350 °C, and re-reduction at different temperatures

1.0	200	2.7	0
	300	1.4	47
	400	0.8	72
	500	0.4	87
	550	0.4	84