

Supporting Information

Structural Dynamics of PtSn/SiO₂ for Propane Dehydrogenation

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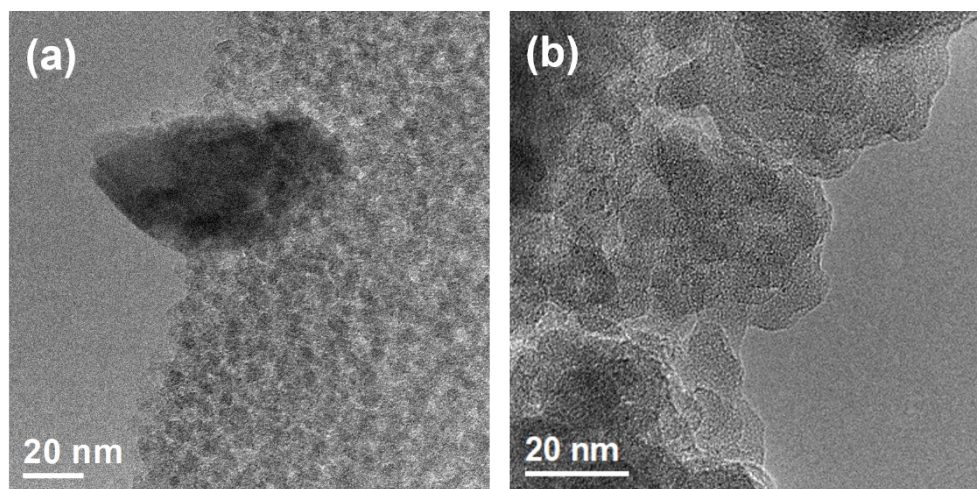


Figure S1. HRTEM images of Sn/SiO₂. (a) HRTEM of Sn/SiO₂-500C; (b) HRTEM of Sn/SiO₂-500C-600R.

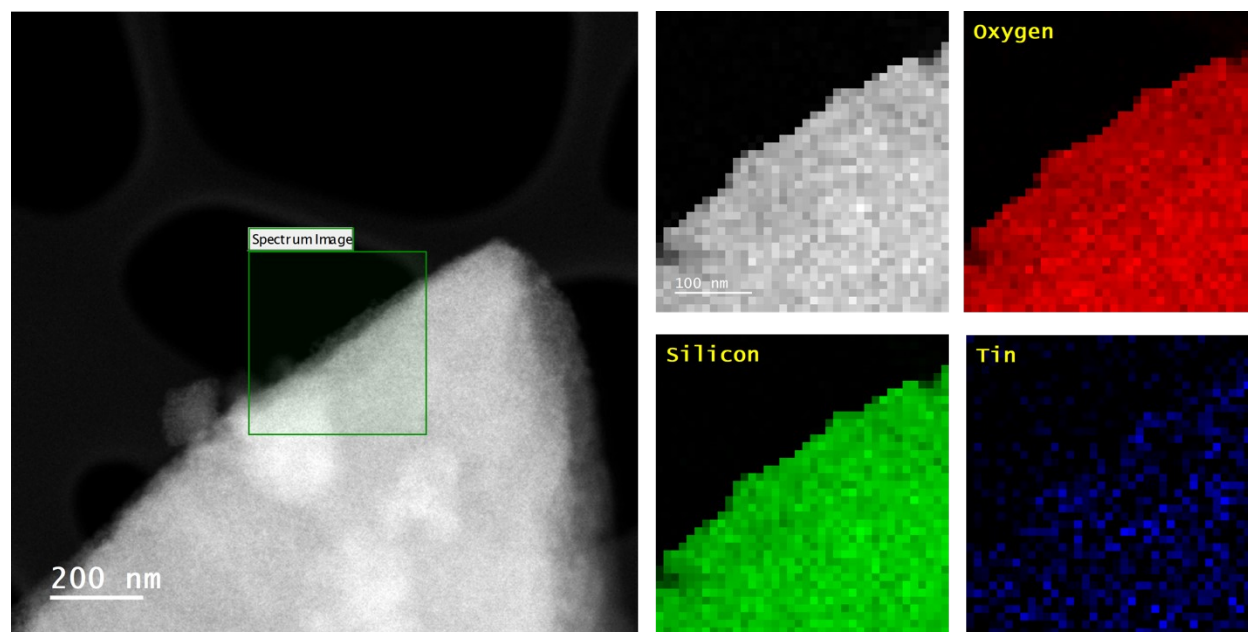


Figure S2. EDS mapping images of Sn/SiO₂. Sn species are uniformly distributed on the SiO₂ support.

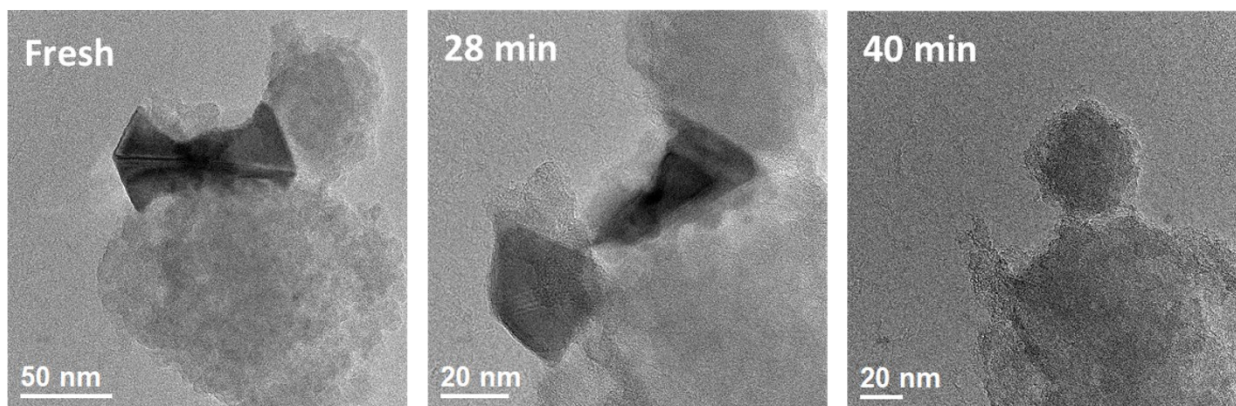


Figure S3. In situ heating HRTEM images of Sn/SiO₂ in vacuum at 600 °C. Images are from a sample region with a large SnO₂ cluster, after the indicated duration of heating time. The SnO₂ cluster (a darker region in the first image) disappeared after heating for 40 min. Electrons from the TEM act as the reducing agent.

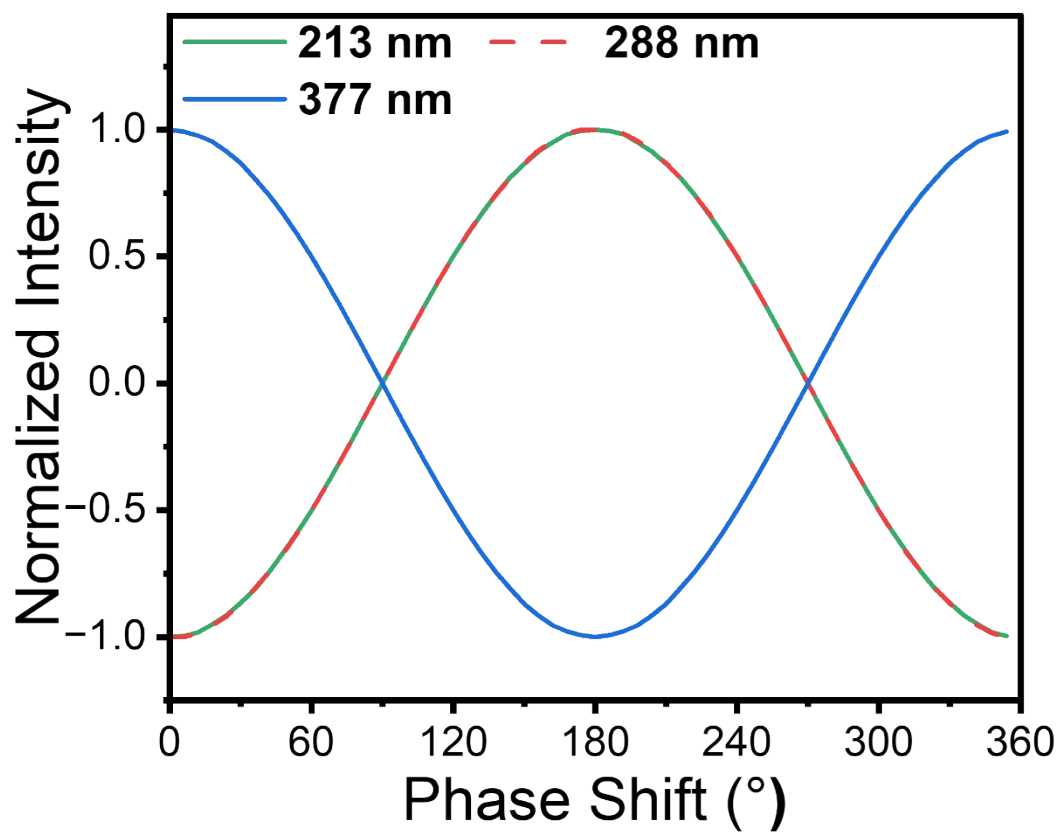


Figure S4. *Phase plot for MES-UV-vis spectra. Same phase for 213 nm and 288 nm bands, which are in opposite phase with 377 nm band.*

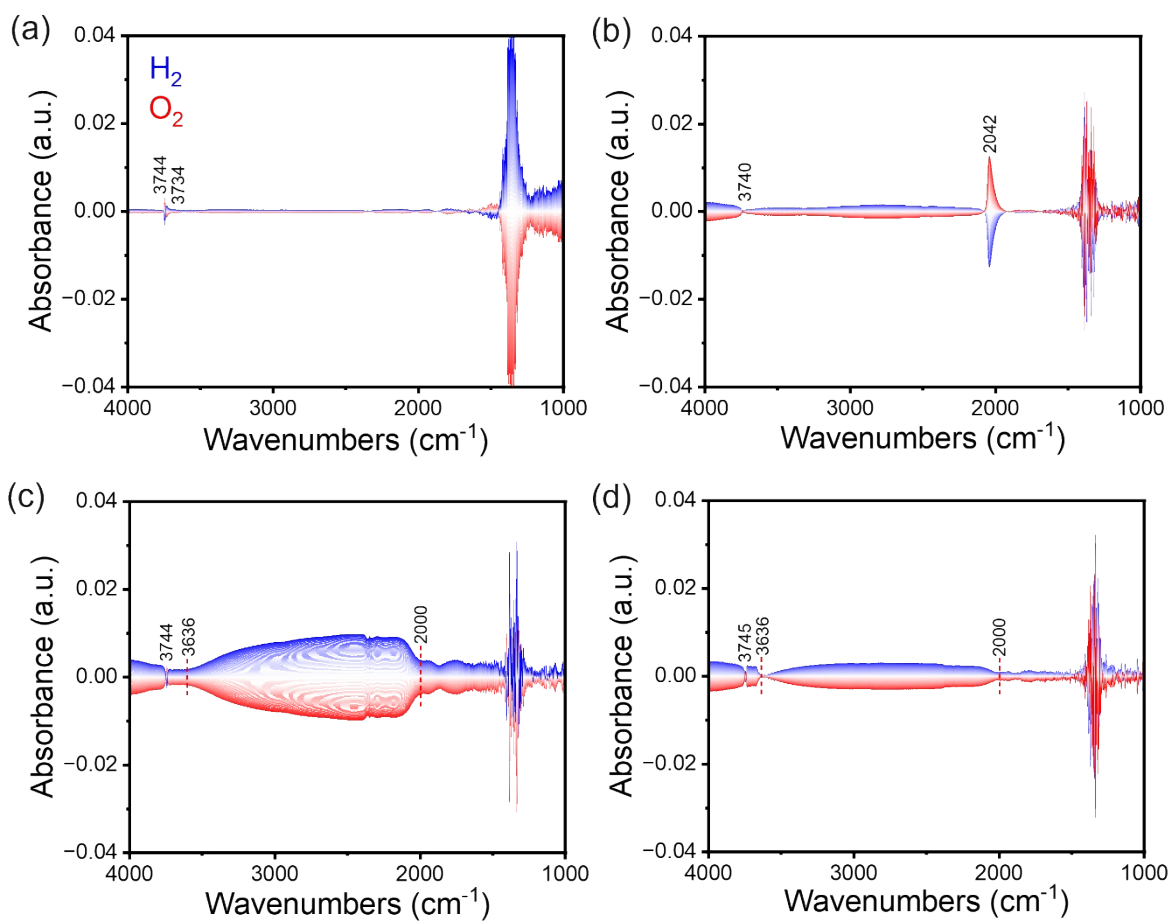


Figure S5. Phase domain MES-DRIFTS-FTIR in full range for: (a) SiO_2 ; (b) Pt/SiO_2 ; (c) Sn/SiO_2 ; and (d) $1\text{Pt}3\text{Sn}/\text{SiO}_2\text{-seq}$. Gas feed: $10\% \text{O}_2/\text{Ar}$ or $10\% \text{H}_2/\text{Ar}$, total 50 sccm gas flow. Modulation frequency = $1/120 \text{ Hz}$ (period = 120 s). Temperature = $400 \text{ }^\circ\text{C}$.

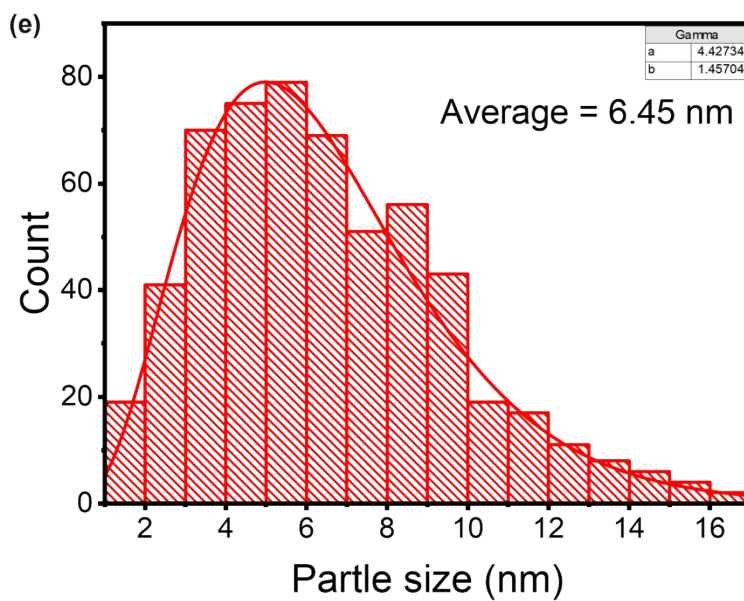
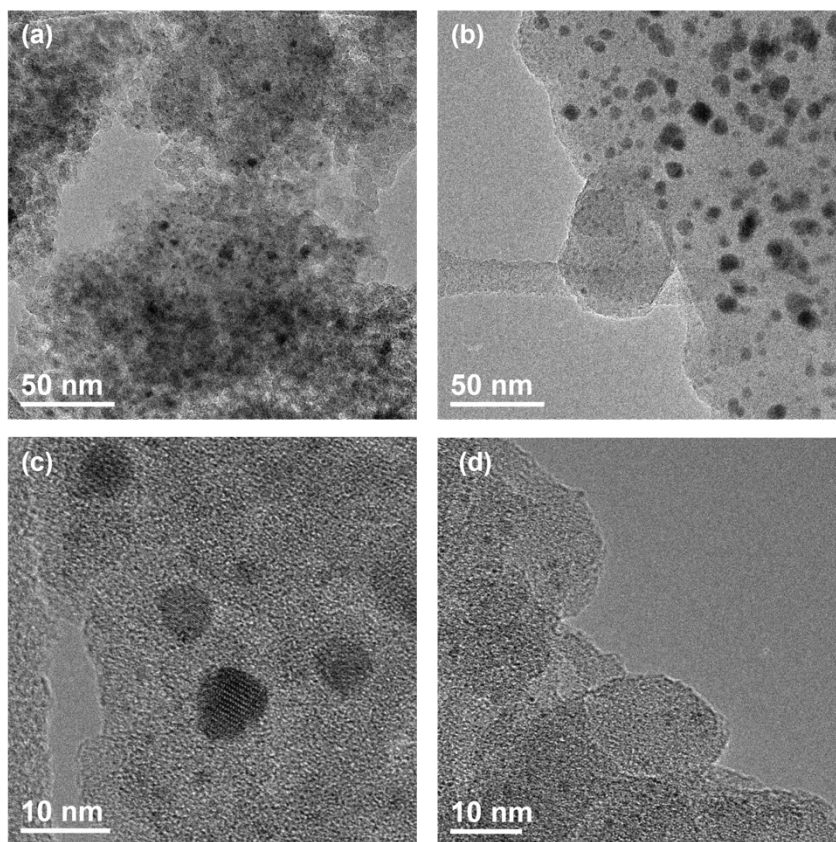


Figure S6. HRTEM images of 1Pt2Sn/SiO₂-co. (a)-(d) TEM images. (e) Particle size distribution. Images indicate a wide particle size distribution, ranging from subnanometer clusters to particles larger than 10 nm.

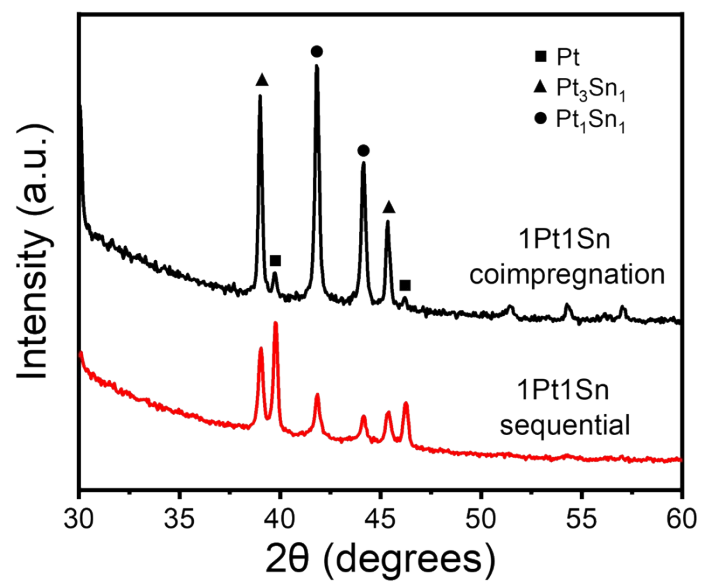


Figure S7. XRD of PtSn/SiO₂ catalysts synthesized through calcination-reduction. 500 °C calcination in air, 600 °C reduction in 10% H₂.

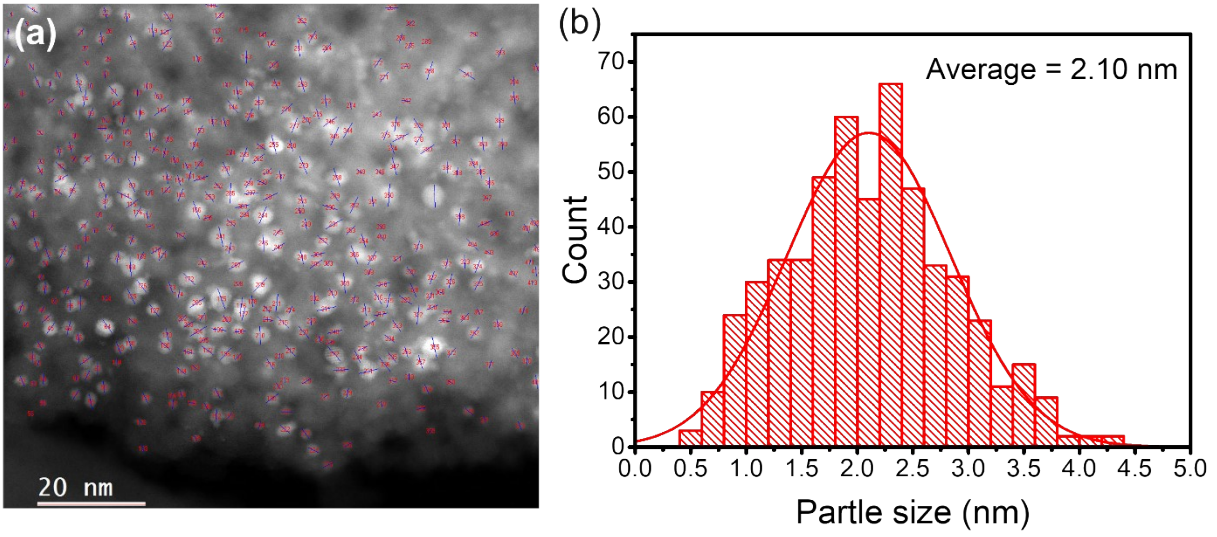


Figure S8. HAADF-STEM imaging of 1Pt3Sn/SiO₂-seq. (a) STEM image; (b) particle size distribution and average particle size.

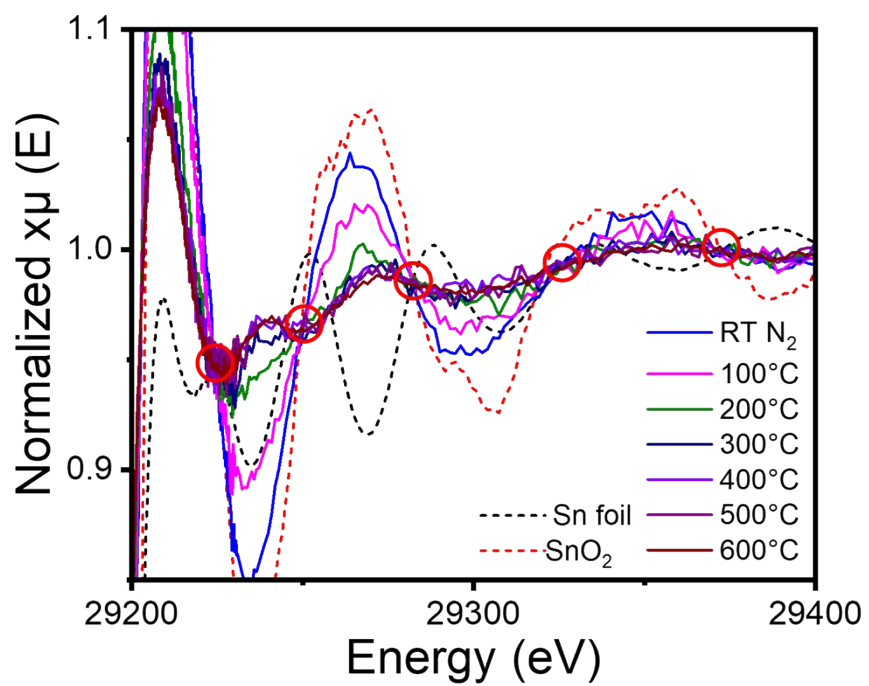


Figure S9. Sn K-edge XANES spectra of 1Pt3Sn/SiO₂-seq (zoom in view). Isosbestic points indicated by the circles.

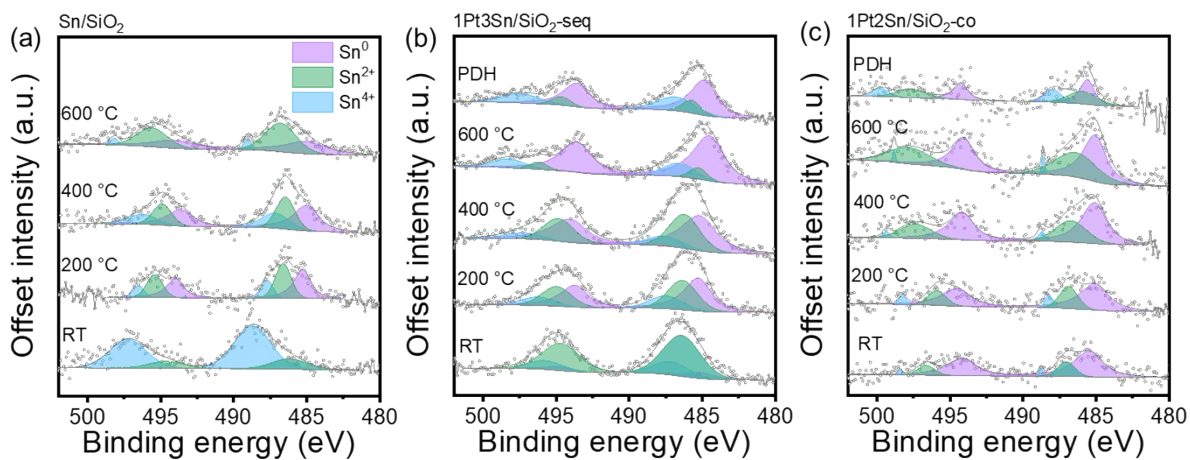


Figure S10. **NAP-XPS Sn 3d spectra.** (a) Sn/SiO₂; (b) 1Pt3Sn/SiO₂-seq; (c) 1Pt2Sn/SiO₂-co. Spectra taken during reduction at indicated temperatures in 1 mbar H₂. PDH spectra taken in 1 mbar C₃H₈ at 600 °C.

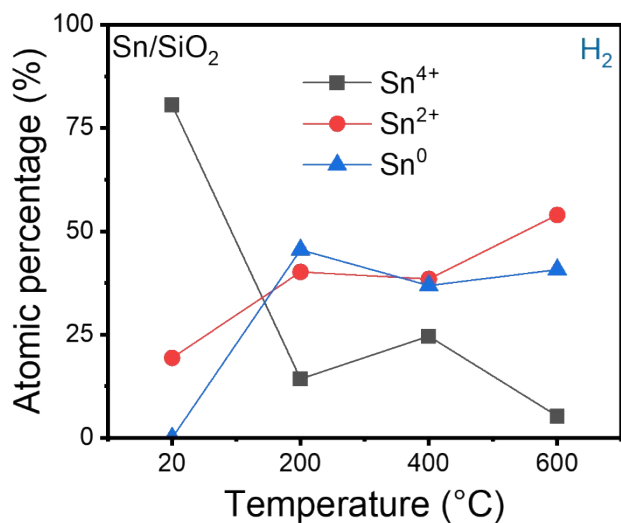


Figure S11. **NAP-XPS surface Sn oxidation states composition evolution with temperature of Sn/SiO₂.**

Table S1. NAP-XPS surface Sn oxidation state percentage. (a) 1Pt3Sn/SiO₂-seq; (b) Sn/SiO₂; (c) 1Pt2Sn/SiO₂-co. Measurement conducted 1 mbar H₂ or C₃H₈ at indicated temperatures.

	Sn ⁴⁺ (%)	Sn ²⁺ (%)	Sn ⁰ (%)
1Pt3Sn/SiO ₂ -seq 1 mbar H ₂ 20 °C	21.021	69.20615	9.77285
1Pt3Sn/SiO ₂ -seq 1 mbar H ₂ 200 °C	17.55581	35.61	46.8342
1Pt3Sn/SiO ₂ -seq 1 mbar H ₂ 400 °C	11.54706	35.14118	53.31176
1Pt3Sn/SiO ₂ -seq 1 mbar H ₂ 600 °C	17.71299	7.93077	74.35625
1Pt3Sn/SiO ₂ -seq 1 mbar C ₃ H ₈ 600 °C	27.07032	12.14468	60.785
Sn/SiO ₂ 1 mbar H ₂ RT	80.60708	19.39292	0
Sn/SiO ₂ 1 mbar H ₂ 200 °C	14.25745	40.19437	45.54818
Sn/SiO ₂ 1 mbar H ₂ 400 °C	24.60946	38.48766	36.90288
Sn/SiO ₂ 1 mbar H ₂ 600 °C	5.2814	53.9833	40.73531
1Pt2Sn/SiO ₂ -co 1 mbar H ₂ 20 °C	2.42285	20.34371	77.23343
1Pt2Sn/SiO ₂ -co 1 mbar H ₂ 200 °C	6.47813	27.19262	66.32925
1Pt2Sn/SiO ₂ -co 1 mbar H ₂ 400 °C	3.27675	32.7611	63.96215
1Pt2Sn/SiO ₂ -co 1 mbar H ₂ 600 °C	2.01534	41.82163	56.16304

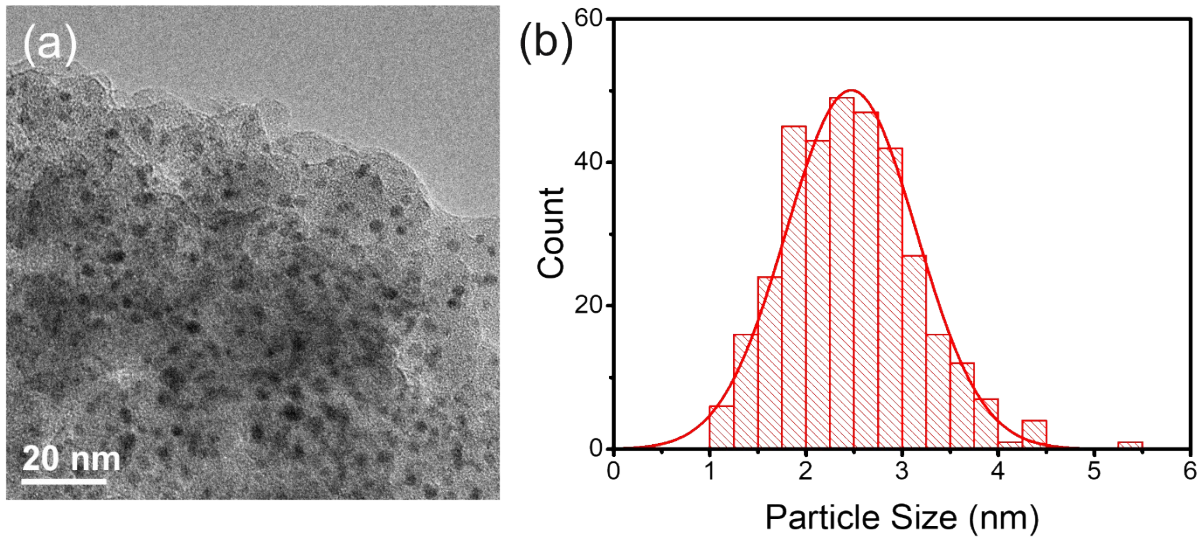


Figure S12. HRTEM of Pt/SiO₂. (a) HRTEM image; (b) Particle size distribution. Average size is 2.47 nm.

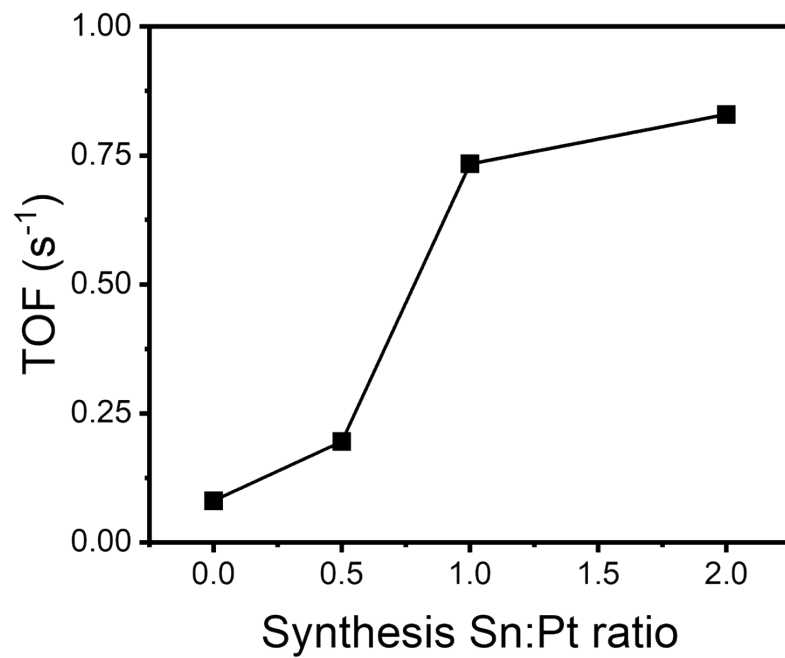


Figure S13. **TOF vs. synthesis Sn:Pt ratio for PtSn/SiO₂-co.** Site densities are estimated based on the CO chemisorption result of Pt/SiO₂ and CO DRIFTS results of Sn-containing samples. PDH reaction rates are based on the initial conversion in the time on stream result in Figure 7.