Supplementary Information

Synthesis of Platinum Nanoparticles on Strontium Titanate Nanocuboids via Surface Organometallic Grafting for the Catalytic Hydrogenolysis of Plastic Waste

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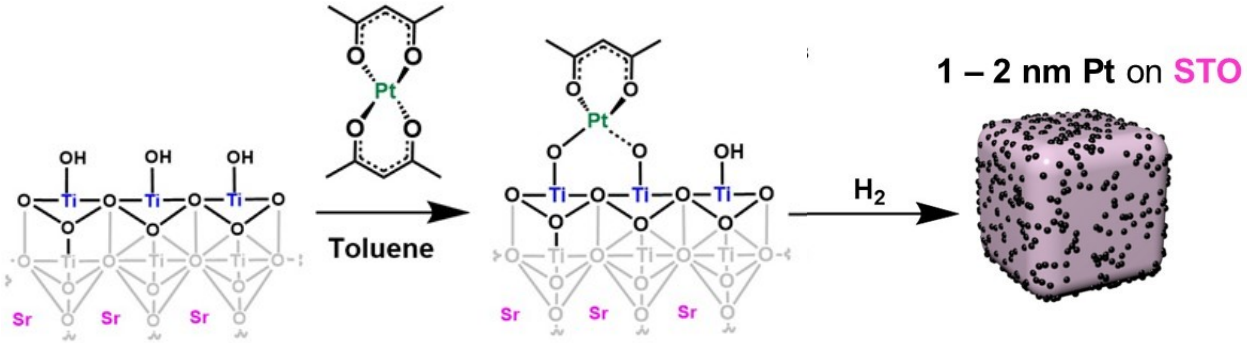


Fig. S1 Stepwise SOMC Synthesis of Pt/STO Catalysts. Pt (green) is deposited onto a STO nanocuboid (surface termination shown) in toluene under heating via platinum(II)acetylacetonate ($Pt(acac)_2$). $Pt(acac)_2$ bonds to hydroxyl groups on the STO surface, at which point the sample is placed in a reducing environment ("H_2") to afford a sample with 1 - 2 nm Pt nanoparticles on the STO nanocuboid support (right).

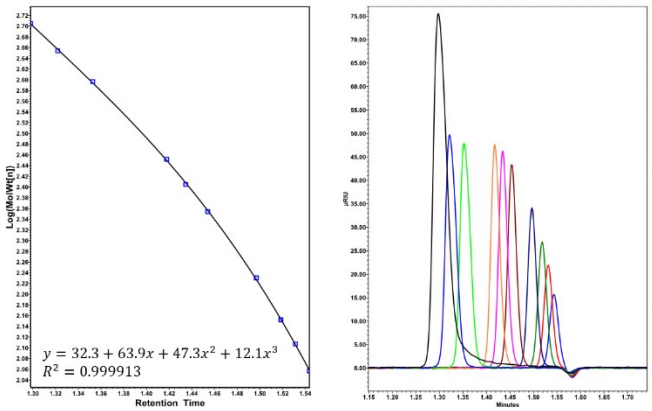


Fig. S2 *iPP*-Derived Liquid Sample Analysis. The calibration curve used to benchmark polymer upcycling products in liquid sample analysis is presented on the left of this figure, and a sample high-pressure liquid chromatography output is presented on the right. A more extensive description of this analytical technique is presented in the Experimental section of the main manuscript under the same title.

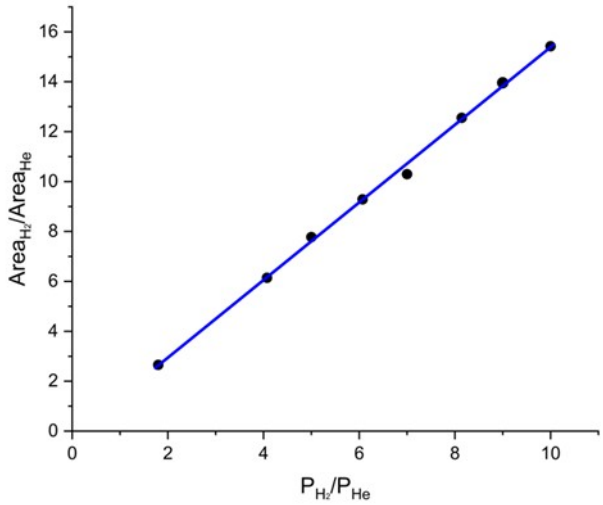


Fig. S3 Gas Species Quantification and H_2 Consumption Analysis. The calibration curve used to quantify gaseous species and hydrogen consumption in this work is presented above. A more extensive description of this analytical technique is presented in The Experimental section of the main manuscript under the same title.

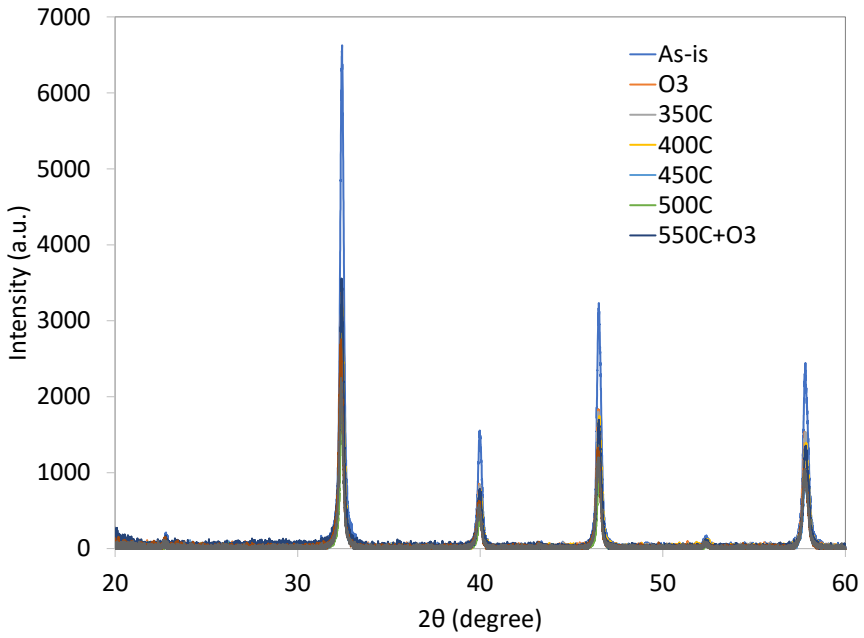


Fig. S4 Diffraction patterns of $SrTiO_3$ after Various Treatments. Patterns were collected by power x-ray diffraction, and all correspond to crystalline strontium titanate.

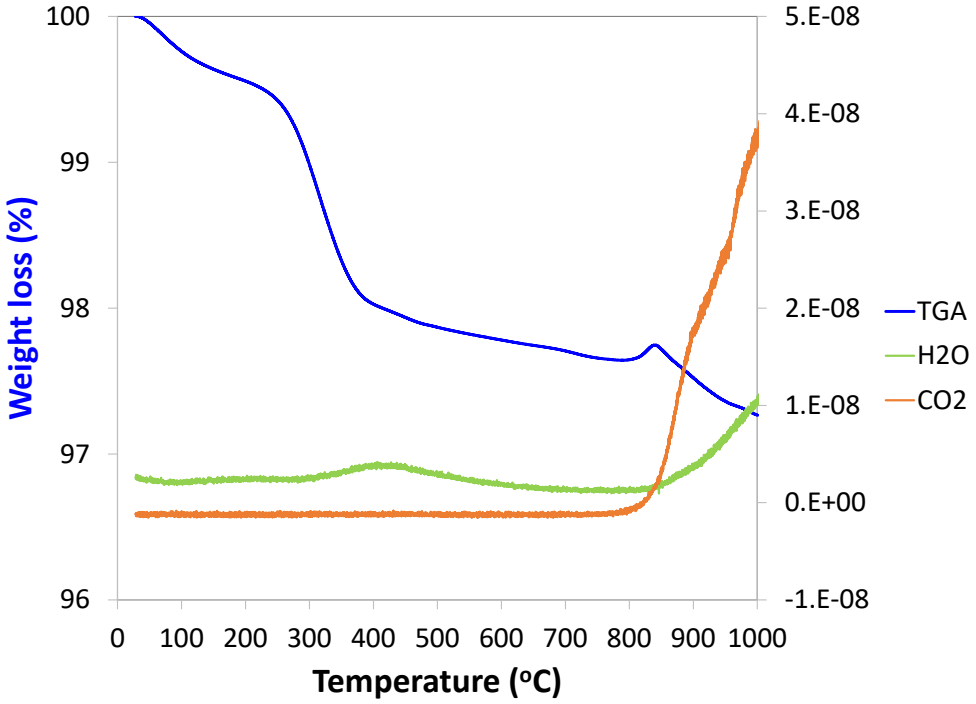


Fig. S5 Thermogravimetric analysis (TGA) of as-prepared STO supports. The data show 0.5 % by mass of carbonate desorption above 800 °C, which would indicate a minority surface species (e.g. $SrCO_3$) present after synthesis that does not significantly affect the STO surface. This is consistent with previous observations about $SrCO_3$ formation in Peczak et al.[13a]

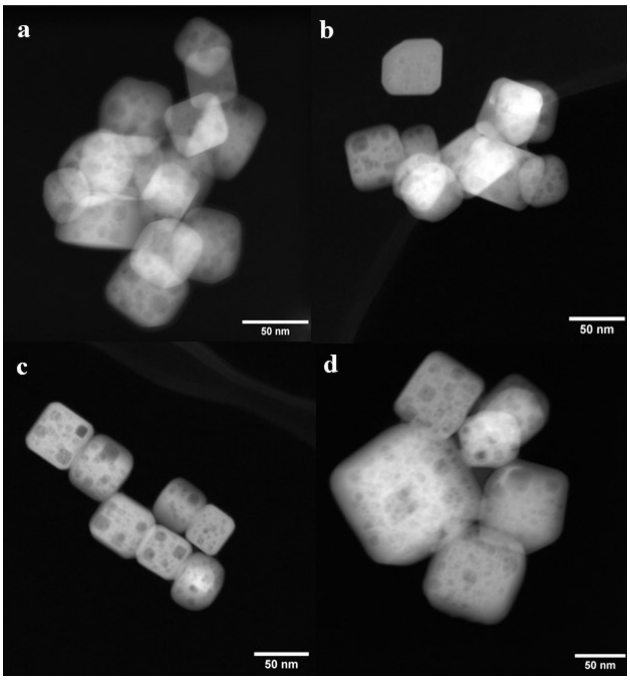


Fig. S6 TEM images of as-prepared STO (a) and STO after calcination at 350 °C (b), 450 °C (c), and 550 °C (d). All samples, regardless of calcination conditions or lack thereof, appear to have average sizes of around 45.0 ± 10.0 nm and contain between 70 – 75 % nanocuboid particles per sample. Measurements of these two parameters corresponding to each sample are presented in the supplementary information.

Table S1. Average size of STO nanocuboids and average amount of nanocuboid particles per sample analyzed for an as-synthesized support sample, and samples that had been calcined at 350 °C, 450 °C, and 550 °C.

Calcination Temperature (°C)	Average STO Particle Size (nm)	% Cubes
As-prepared (no calcination)	45.9 ± 9.7	74.2
350	45.7 ± 11.1	71.4
450	42.1 ± 9.9	72.1
550	42.6 ± 9.1	73.5

Table S2. BET Surface Area of STO supports After Calcination at Various Temperatures. Catalyst surface area was determined by N_2 adsorption. Prior to surface area measurements, each sample was degassed by heating under vacuum at 150°C. Five data points were collected to ensure accuracy.

Calcination Temperature (°C)	BET Surface Area (m^2 / g)
As-prepared (no calcination)	26.5
350	22.9
450	17.0
550	16.7

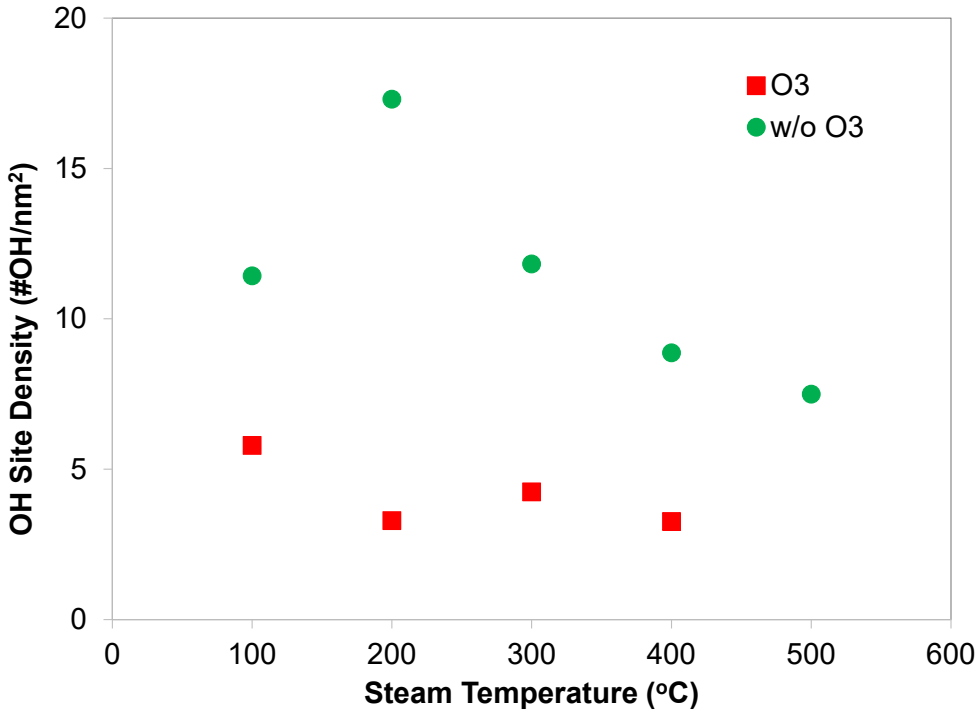


Fig. S7 NMR titration of surface hydroxyls per nm^2 on STO with $Bn_2Mg(THF)_2$ in C_6D_6 and cyclohexane. The STO was calcined at 550 °C followed by steam for 2 h ranging from 100 °C to 500 °C (green dots). The STO was calcined at 550 °C followed O_3 treatment at 200 °C for 2 h and by steam for 2 h ranging from 100 °C to 400 °C (red square).

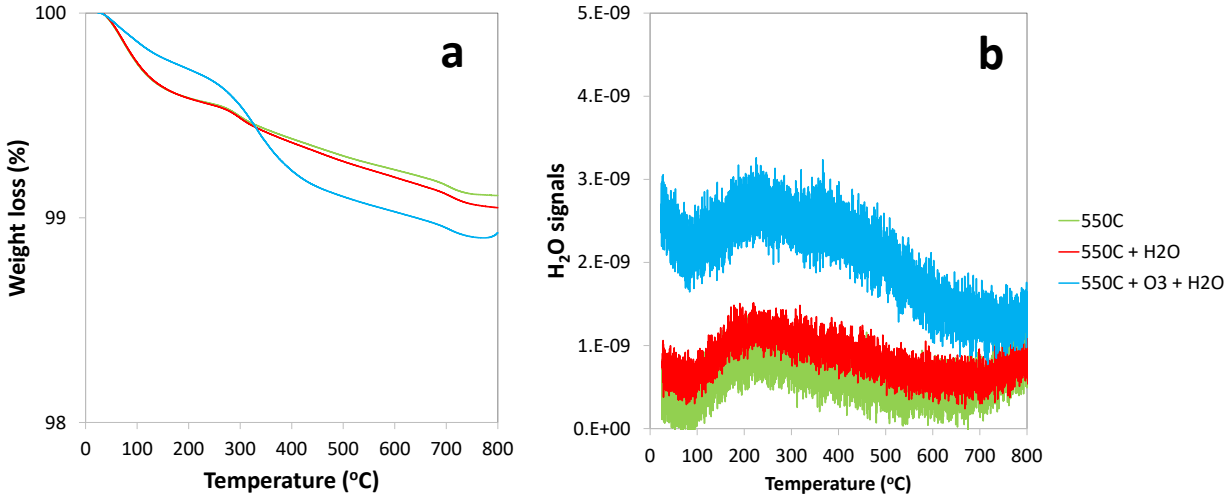


Fig. S8 TGA curve (a) and H_2O signals (b) of STO at various treatments.

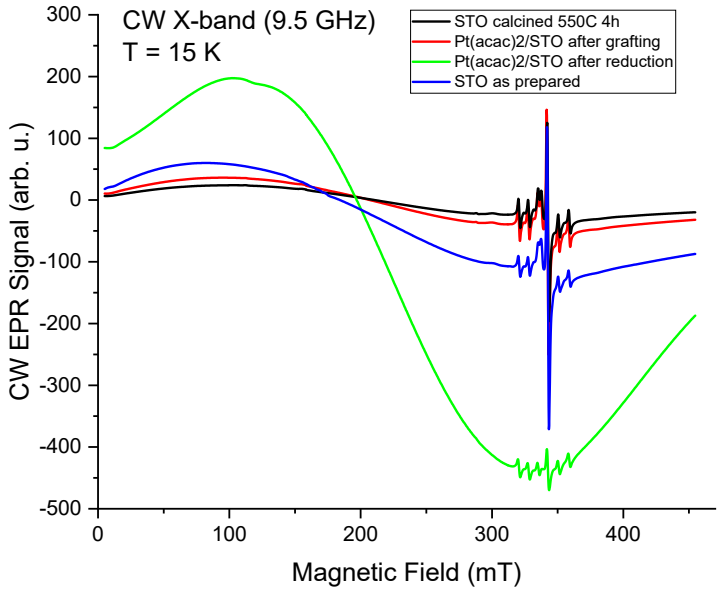


Fig. S9 Continuous wave (CW) X-band EPR Spectra of Calcined STO, $Pt(acac)_2$ on STO after grafting, $Pt(acac)_2$ on STO after reduction, and as prepared STO (black, red, green, and blue respectively) at cryogenic temperatures (T = 15 K). The intense broad EPR signal centered around 220 mT is due to ferromagnetically coupled electron spins, which we assign to Ti(III) ions in the STO support.

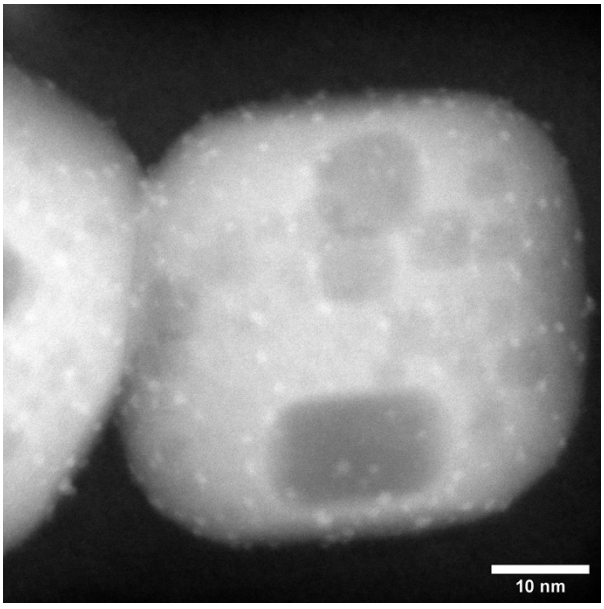


Fig. S10 STEM HAADF micrographs of SOMC 1cPt/STO calcined at 550 °C, followed by O_3 and steam treatment at 200 °C, made at 90 °C (1.5 ± 0.4 nm).

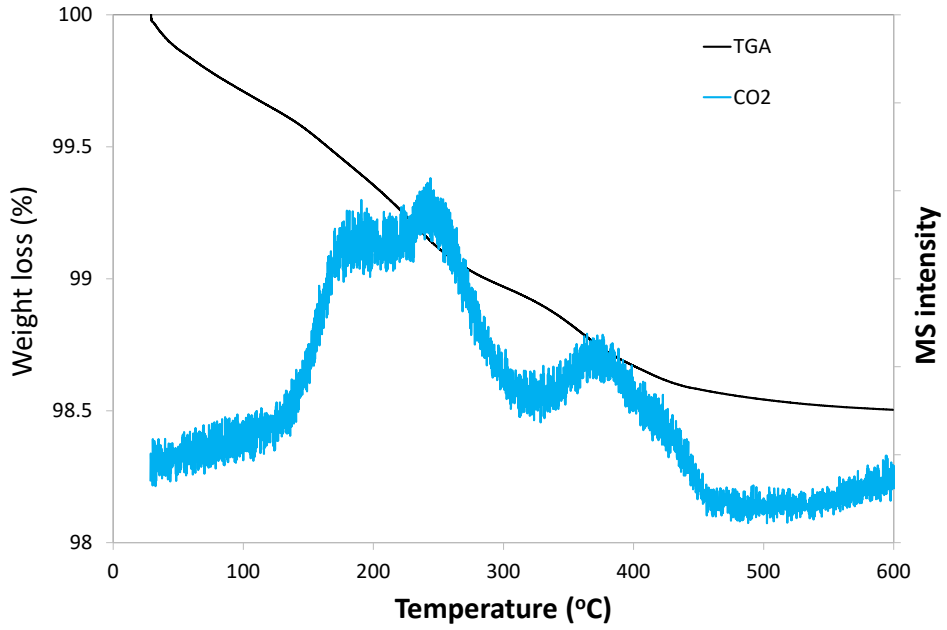


Fig. S11 TGA of 2cPt/STO with the second deposition of $(Pt(acac)_2$ is only dried.

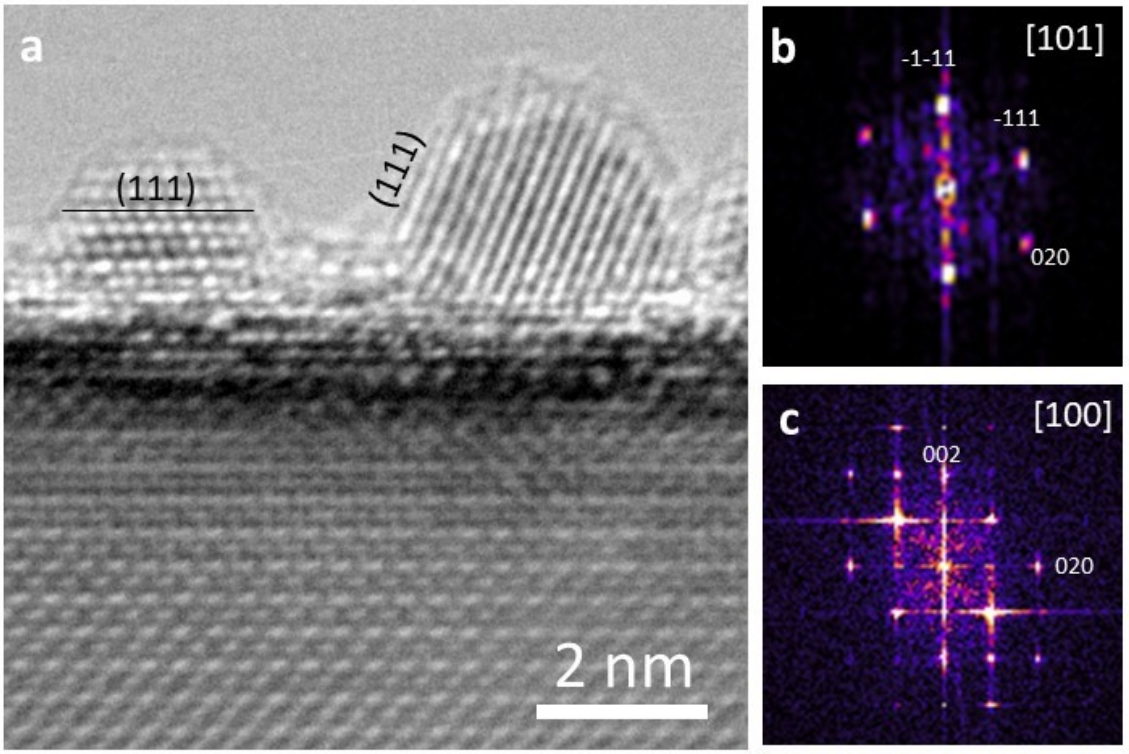
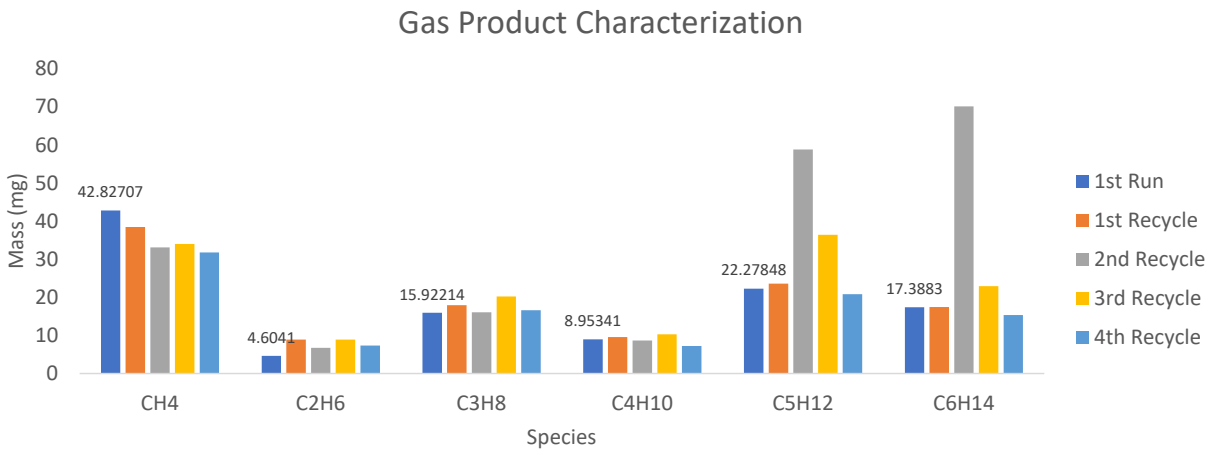
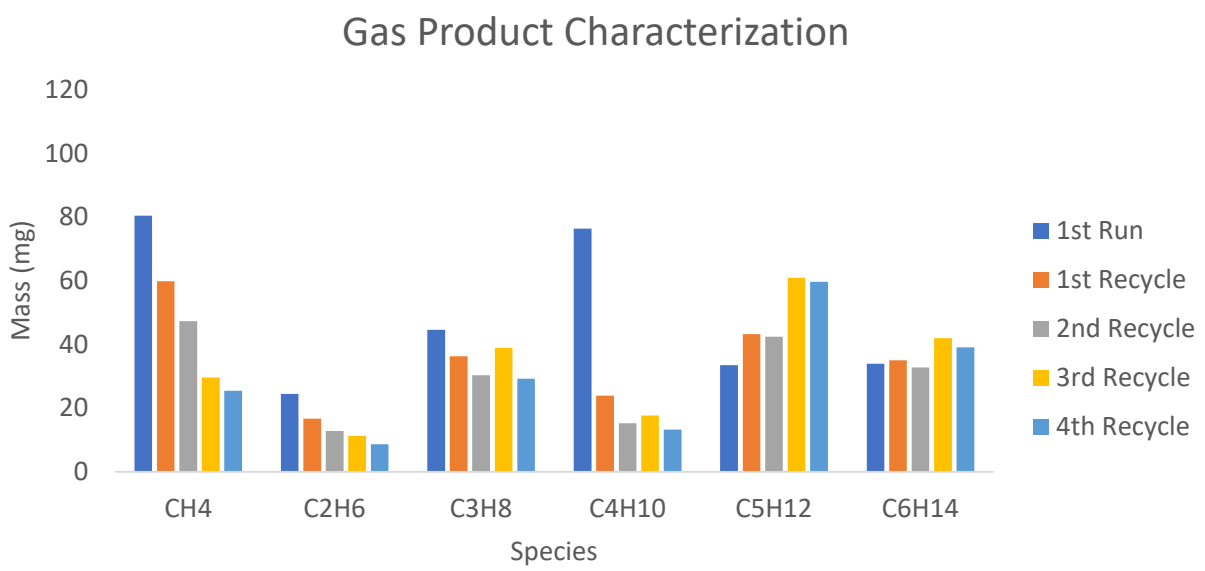


Fig. S12 (a) Aberration corrected HAADF of platinum nanoparticles grafted onto STO with two different exposed orientations. Fourier transform of the (b) leftmost platinum nanoparticle and (c) STO indicating the orientation of the nanoparticle on STO



	Gas (%)	**H_2 Consumption (%)**
1st Run	0.149 g (4.9%)	4.1 mmol (12.2%)
1st Recycle	0.128 g (4.2%)	5.6 mmol (16.9%)
2nd Recycle	0.255 g (8.5%)	5.9 mmol (17.9%)
3rd Recycle	0.185 g (6.2%)	5.6 mmol (16.9%)
4th Recycle	0.129 g (4.2%)	5.9 mmol (17.8%)

Fig. S13 Characterization of Gas Products Formed Via *i*PP Hydrogenolysis of 2cPt_red/STO.



	Gas (%)	**H_2 Consumption (%)**
1st Run	0.374 g (12.3%)	8.0 mmol (23.9%)
1st Recycle	0.248 g (8.2%)	6.2 mmol (18.6%)
2nd Recycle	0.212 g (7.0%)	5.2 mmol (15.6%)
3rd Recycle	0.224 g (7.4%)	7.3 mmol (22.0%)
4th Recycle	0.207 g (6.9%)	6.8 mmol (20.3%)

Fig. S14 Characterization of Gas Products Formed Via *i*PP Hydrogenolysis of 2cPt_cal+red/STO.

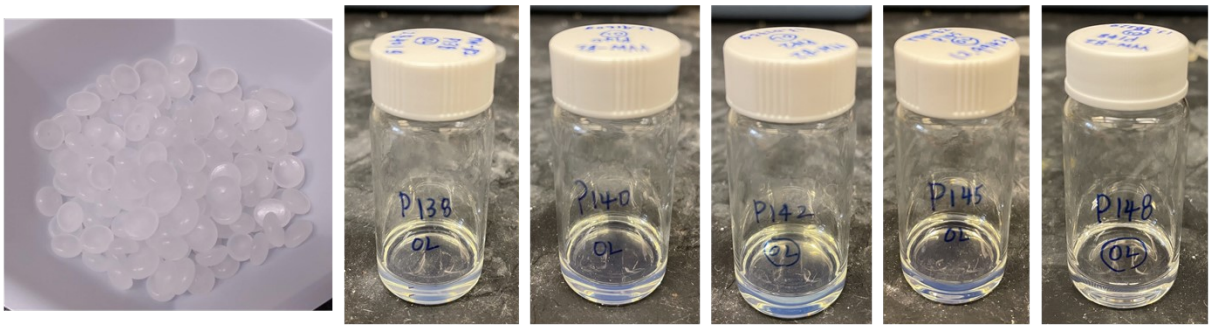


Fig. S15 Images of the initial polymer and after the 5 successive hydrogenolyses using 2cPt_cal+red /STO.

Table S3. Upcycling Data for Supported Pt Upcycling Catalysts Comparable to SOMC-derived Catalysts Reported in This Work.

Sample	Starting Sample	$M_{n,i}$ (Da)	Time (h)	$M_{n,f}$ (Da)	Đ	Yield (%)
ALD Pt/STO[a]	*i*PP	6000	24	250	1.4	83
1c-ALD Pt/STO[b]	HDPE	8150	24	1250	4.7	91
Pt/Al_2O_3[b]	HDPE	8150	18	1850	5.8	-

a R.A. Hackler, J.V. Lamb, I.L. Peczak, R.M. Kennedy, A.M. LaPointe, K.R. Poeppelmeier, A.D. Sadow, M. Delferro. *Macromolecules,* 2022, **55**, 15, 6801-6810.

b G. Celik, R.M. Kennedy, R.A. Hackler, M. Ferrandon, A. Tennakoon, S. Patnaik, A.M. LaPointe, S.C. Ammal, A. Heyden, F.A. Perras, M. Pruski, S.L. Scott, K.R. Poeppelmeier, A.D. Sadow, M. Delferro. *ACS Cent. Sci.*, 2019, **5**, 1795-1803.

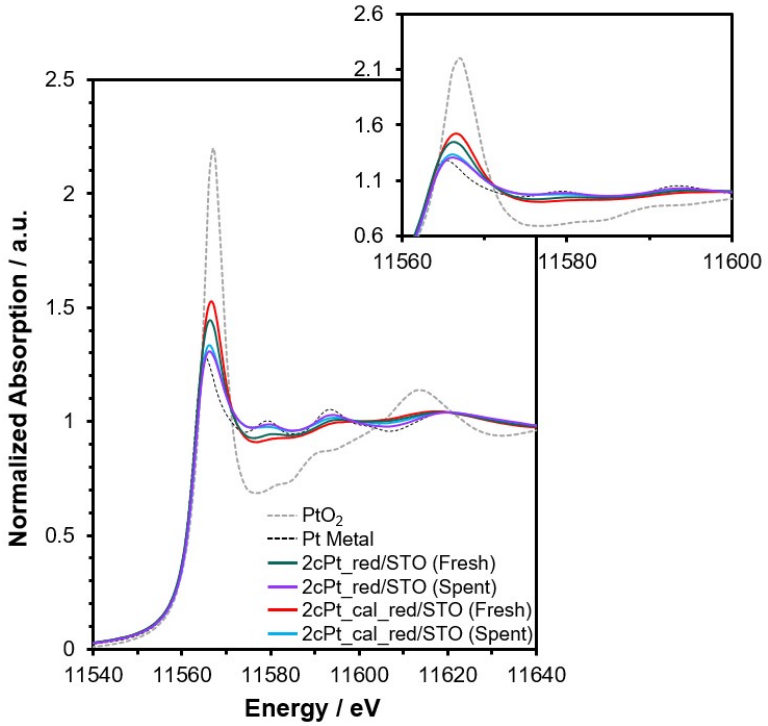


Fig. S16 XANES region for 2cPt_red/STO and 2cPt_cal+red/STO before and after reaction. All materials were measured without treatment at room temperature under inert flow.

Table S4. Linear combination fitting results for the as-received Pt/STO samples using PtO_2 and Pt as references. Fit in XANES from 11553 to 11603 eV.

Sample	**Condition**	**PtO_2**	**Pt**
2cPt_red/STO	Fresh	0.212 ± 0.009	0.788 ± 0.009
2cPt_cal+red/STO	Fresh	0.299 ± 0.009	0.701 ± 0.009

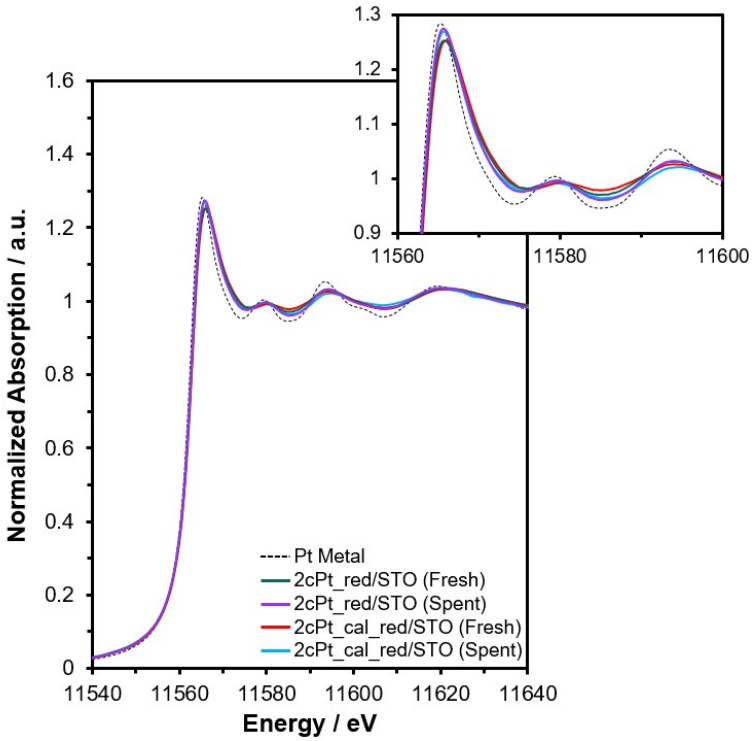


Fig. S17 XANES region for 2cPt_red/STO and 2cPt_cal+red/STO before and after reaction. All materials were reduced in-situ at 250 °C, 3.5% H_2 prior to measurement at room temperature under inert flow.

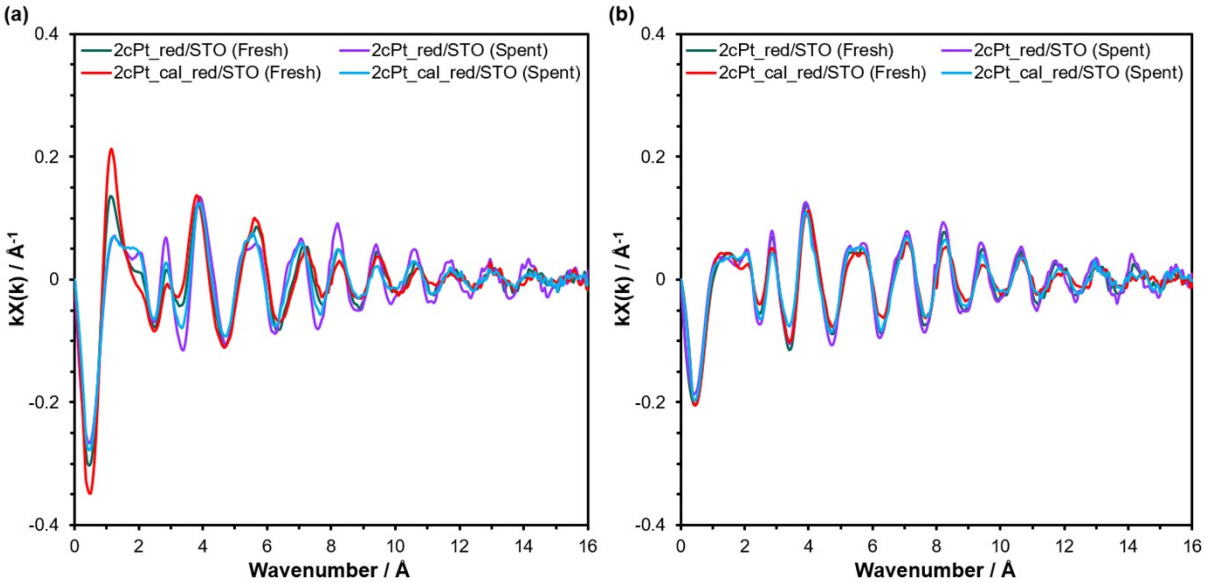


Fig. S18 X(k), k^1-weighted, spectra for 2cPt_red/STO and 2cPt_cal+red/STO before and after reaction measured at room temperature under He flow (a) before and (b) after in-situ reduction at 250 °C in 3.5% H_2.

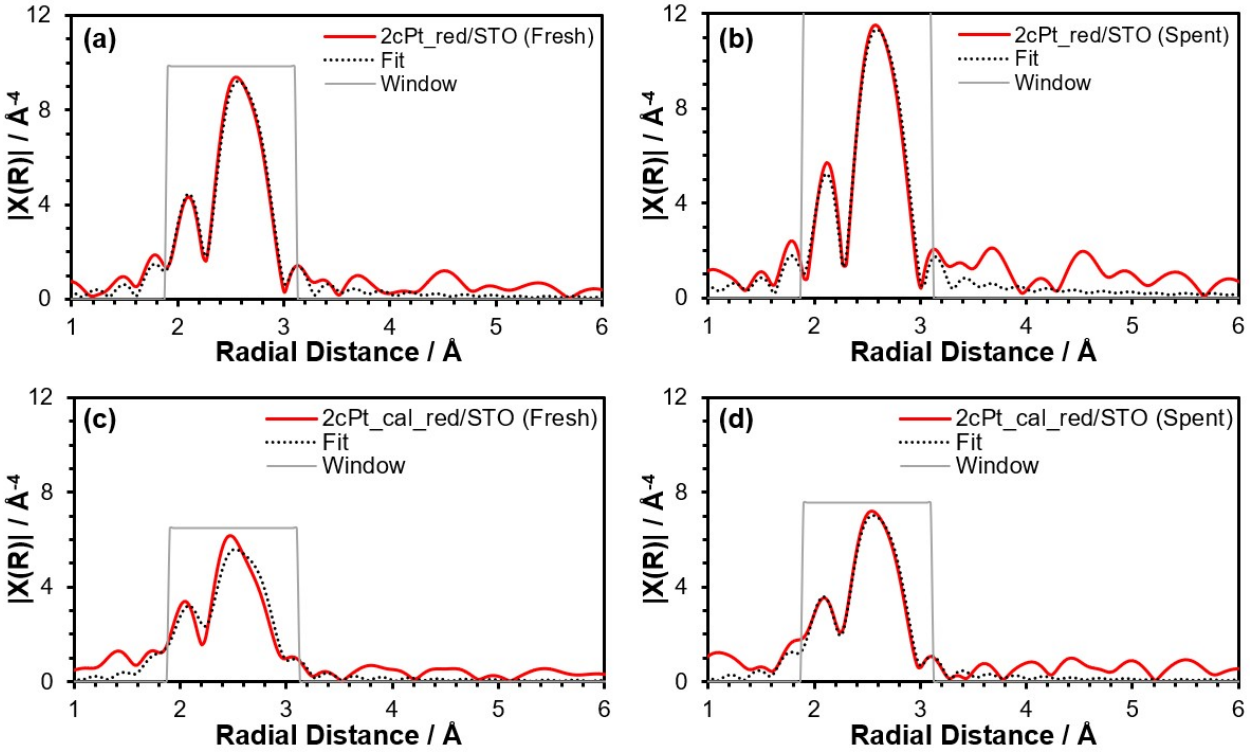


Fig. S19 EXAFS fitting results for (a) fresh 2cPt_red/STO, (b) spent 2cPt_red/STO, (c) fresh 2cPt_cal+red/STO, and (d) spent 2cPt_cal+red/STO for samples measured after reduction at 250 °C in 3.5% H_2. Results and fitting parameters are summarized in Table 2 of the main text.

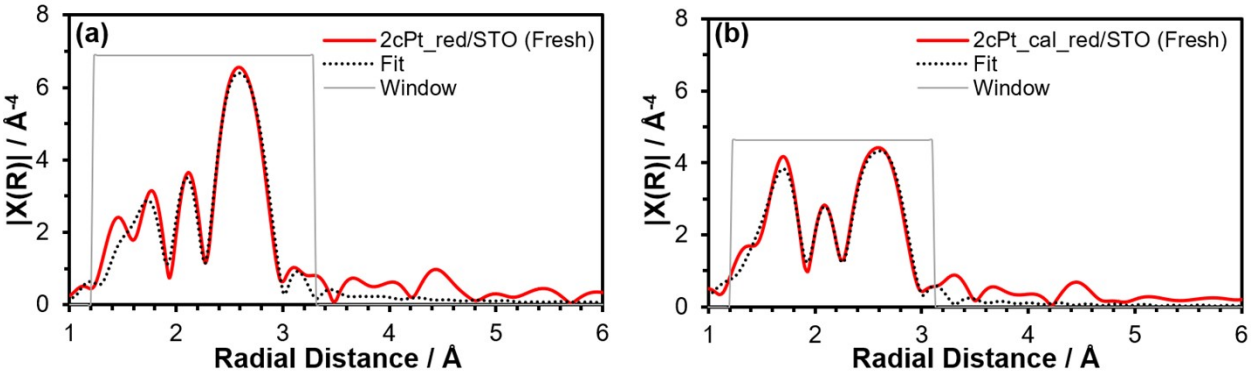


Fig. S20 EXAFS fitting results for (a) fresh 2cPt_red/STO and (b) fresh 2cPt_cal+red/STO for samples measured as received under He flow at room temperature. Results and fitting parameters are summarized in Table S5.

Table S5. Pt L3 edge EXAFS fit results for fresh 2cPt/STO samples measured as received under He flow at room temperature (k = 3.0 – 15 $Å^{-1}$, Δk = 0.5, k^N N = 1,2,3, R = 1.2 – 3.1 Å). S_0^2 set to the value (0.84) fit for the Pt reference foil. The coordination number for the Pt-O scattering path was estimated from the XANES linear combination fitting results (Table S4).

Sample	Path	N	R (Å)	σ^2 (x$10^{-3}Å^2$)	ΔE_0 (eV)	R-factor
2cPt_red/STO	Pt-O	1.3	2.021 ± 0.023	5.3 ± 1.6	14.9 ± 2.4	0.025
	Pt-Pt	5.5 ± 0.7	2.725 ± 0.006	7.0 ± 0.7	6.3 ± 1.0	
2cPt_cal+red/ STO	Pt-O	1.8	2.023 ± 0.012	5.0 ± 0.8	15.4 ± 1.3	0.010
	Pt-Pt	4.4 ± 0.6	2.718 ± 0.007	7.5 ± 0.8	6.8 ± 1.0	

Table S6. Catalytic performance of 2cPt_red/STO with post-synthesis H_2 reduction at 300 °C, 4 h for hydrogenolysis using *i*PP (M_n = 5K Da, M_w = 12K Da, 3 g), 301.0 mg catalyst, 300 °C, 180 psi mixed gas (9:1 ratio of H_2:He) for 24 h. No solid products were observed. Total liquid = OL + IL.

Run	Gas (amt, %)	Liquid (amt, %)	M_n (Da)	M_w (Da)	$Đ$
1st	0.149 g (4.9 %)	OL: 2.78 g (92.1 %) IL: 0.09 g (3.0%)	280	315	1.1
RE_1	0.128 g (4.2 %)	OL: 2.87 g (95.1 %) IL: 0.01 g (0.4%)	270	310	1.1
RE_2	0.255 g (8.5 %)	OL: 1.98 g (66.2 %) IL: 1.01 g (33.5 %)	270	305	1.1
RE_3	0.185 g (6.2 %)	OL: 2.70 g (89.7 %) IL: 0.12 g (4.0 %)	275	310	1.1
RE_4	0.129 g (4.2 %)	OL: 2.15 g (70.7 %) IL: 0.76 g (25.0 %)	270	305	1.1

Table S7. Catalytic performance of 2cPt_cal+red/STO with post-synthesis H_2 reduction and calcination, both at 300 °C, 4 h. Results from hydrogenolysis using *i*PP (M_n = 5K Da, M_w = 12K, 3 g), 301.0 mg catalyst, 300 °C, 180 psi mixed gas (9:1 ratio of H_2:He) for 24 h. No solid products were observed. Total liquid = OL + IL.

Run	Gas (amt, %)	Liquid (amt, %)	M_n (Da)	M_w (Da)	$Đ$
1st	0.374 g (12.3%)	OL: 2.47 g (81.6 %) IL: 0.19 g (6.1%)	180	190	1.1
RE_1	0.248 g (8.2 %)	OL: 2.61 g (86.5 %) IL: 0.16 g (05.3 %)	195	215	1.1
RE_2	0.212 g (7.0%)	OL: 2.73 g (90.2 %) IL: 0.09 g (2.8 %)	200	220	1.1
RE_3	0.224 g (7.4%)	OL: 2.61g (86.3 %) IL: 0.19 g (6.2 %)	210	230	1.1
RE_4	0.207 g (6.9%)	OL: 2.51 g (83.3 %) IL: 0.29 g (9.8 %)	220	245	1.1