Supporting Information

Surface Engineering of Pt Nanocatalysts with Metal Oleates for Selective Catalysis: A Case Study on the Hydrogenation of α,β-Unsaturated Aldehydes

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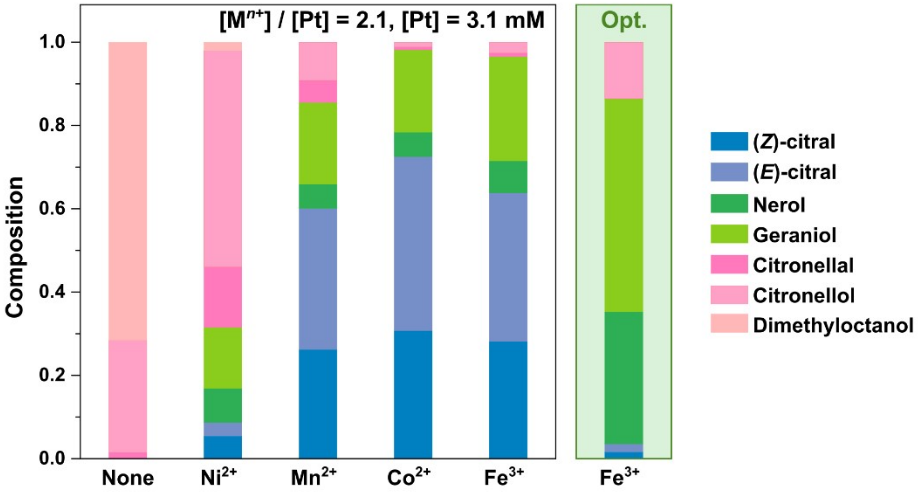
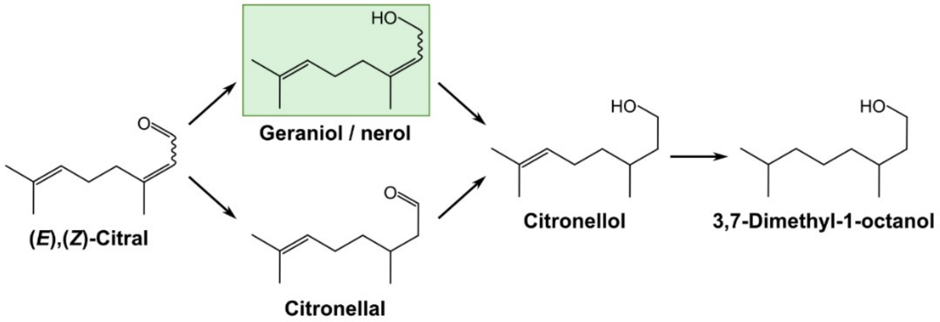


Figure S1. Compositional data for citral hydrogenation reactions corresponding to Figure 1b in the main text. Blueish colors indicate the substrates, greenish the target products, and reddish the byproducts.



Scheme S1. Hydrogenation reaction pathways of citral.

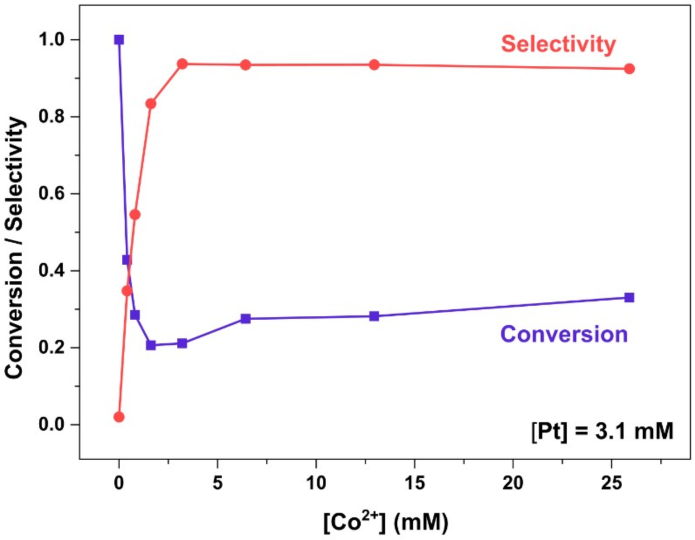


Figure S2. Plots for conversion and selectivity in citral hydrogenation as functions of Co(oleate)$_2$ with Pt concentration fixed as indicated in the panel.

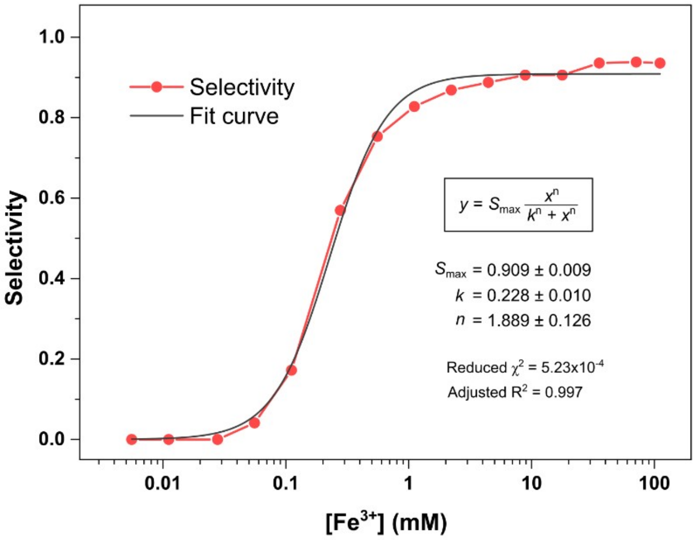


Figure S3. Selectivity plot from Figure 1c in the main text and its fit result using the Hill–Langmuir equation as fitting function.

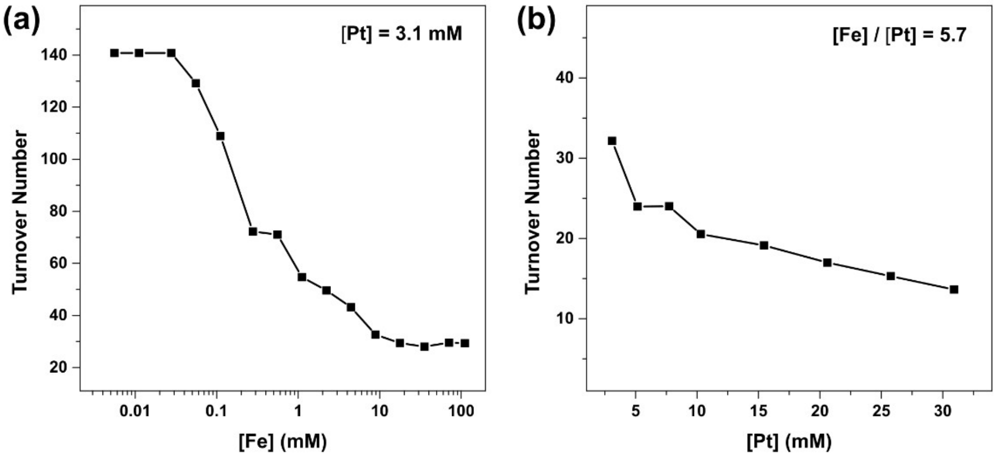


Figure S4. Turnover number for 3.5 nm Pt NPs in citral hydrogenation reaction as a function of Fe(oleate)$_3$ concentration (a) and Pt NPs concentration when the concentration ratio of Fe(oleate)$_3$ to Pt NPs was kept as 5.7 that provided high selectivity. TON calculations were performed using the formular shown below:

$$\mathrm{TON} = \frac{[\mathrm{citral}] \times \mathrm{conversion}}{[\mathrm{Pt}]_{\mathrm{surf}}}$$

where $[\mathrm{Pt}]_{\mathrm{surf}}$ is the concentration of Pt atoms at the surface of Pt nanoparticles (NPs). The conversion values were taken from Figure 1d and Figure 1c. Assuming the spherical shape of Pt with the diameter is 3.5 nm, we obtain $[\mathrm{Pt}]_{\mathrm{surf}} / [\mathrm{Pt}] = 0.424$. Under the standard reaction condition, [citral] = 185 mM and [Pt] = 3.1 mM.

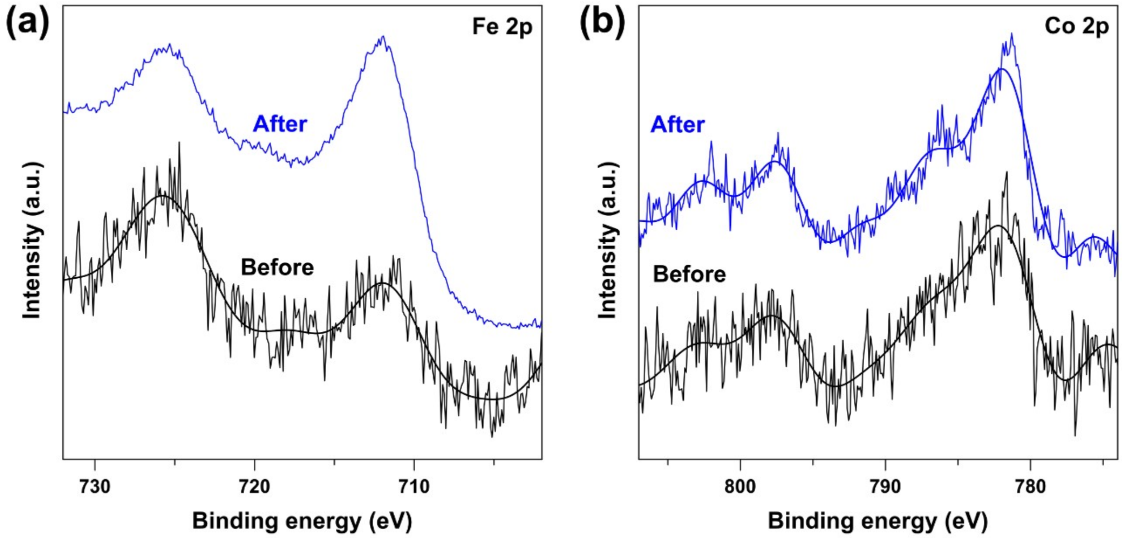


Figure S5. (a) Fe 2p and (b) Co 2p X-ray photoelectron spectroscopy spectra of the solution using the corresponding metal oleate additives before and after hydrogenation reaction. The samples were prepared from the solution containing 3.1 mM Pt. The concentration ratio of oleic acid or Me(oleate)$_n$ to Pt was ~10.

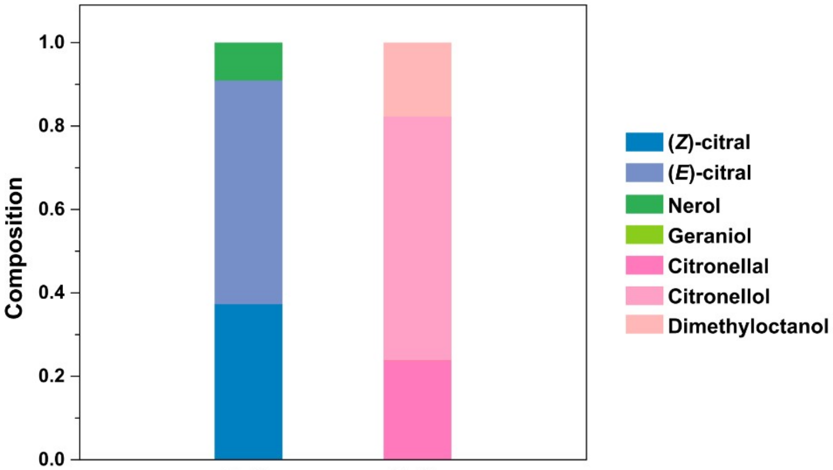
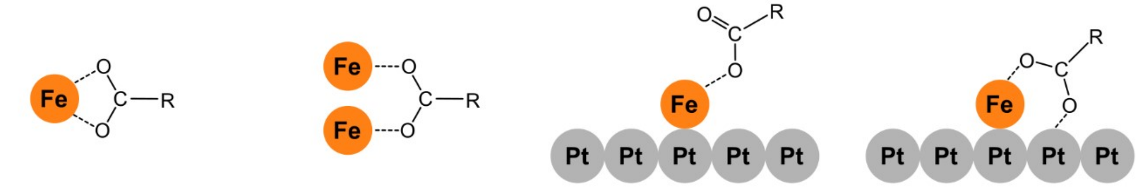


Figure S6. Compositional data for citral hydrogenations using 4 nm FePt and 4.5 nm CoPt$_3$ NPs as catalysts. The concentration of Pt is adjusted to be 3.1 mM for both types of nanocatalysts.

Samples	Bond	N	R (Å)	σ^2(Å^2)
Fe(oleate)$_3$	Fe-O	5.3±0.2	2.04 ±0.02	0.006
[Fe^{3+}]:[Pt] = 1:4	Fe-O	5.0±0.5	1.98±0.02	0.005±0.002
	Fe-Fe	0.4±0.3	2.62±0.05	0.006
	Fe-Pt	2.7±0.9	3.08±0.02	0.006
[Fe^{3+}]:[Pt] = 1:20	Fe-O	3.6±0.9	2.00±0.07	0.004±0.002
	Fe-Fe	0.8±0.7	2.66±0.06	0.006
	Fe-Pt	3.1±1.9	3.07±0.04	0.006

Table S1. EXAFS fitting result for Fe *K*-edge data in Figure 3b in the main text.



Chelating-bidentate **Bridging-bidentate** **Monodentate** **Bridging-bidentate**

Scheme S2. Coordination geometries of carboxylate ligand for free- and Pt-adsorbed Fe(oleate)$_3$.

Samples	Curve	Centroid	Amp	Width	R factor	χ^2
Pt NPs	arctan	11564.593	1.017	1.783	.00037	.03515
	Gaussian	11565.633	**4.214**	**3.205**		
[Fe^{3+}]:[Pt] = 10:1	arctan	11564.593	1.012	1.880	.00042	.03945
	Gaussian	11565.633	**4.157**	**3.218**		

Table S2. Curve fitting result for the white line of Pt L_3-edge XANES spectra in Figure 3c in the main text.

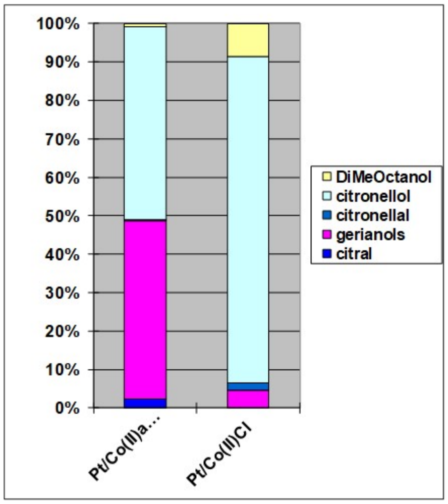


Figure S7. Compositional data for citral hydrogenation reactions for 3.5 nm Pt NPs in the presence of cobalt (II) acecylacetonate and cobalt (II) chloride. Pt concentration was fixed at 3.1 mM. Molar ratio of cobalt cation to Pt was fixed at 5.7. The hydrogenation reaction was carried out under H_2 atmosphere (200 psig) at room temperature for 3 hr.

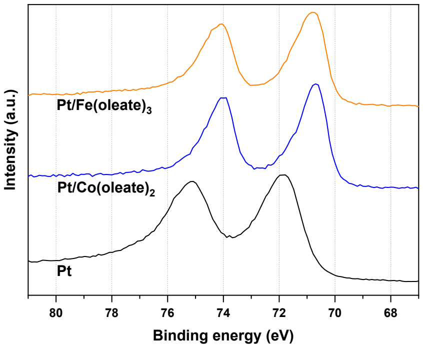


Figure S8. Pt 4f XPS spectra of 3.5 nm Pt NPs as synthetized and purified by 3 rounds of solvent/nonsolvent treatment (black spectrum) (toluene and isopropanol were used as solvent and nonsolvent), 3.5 nm Pt NPs modified with $Co(oleate)_2$ (blue spectrum) and $Fe(oleate)_3$ (orange spectrum), respectively. To prepare the samples Pt concentration was kept at 3.1 mM. The concentration ratio of oleic acid or $Me(oleate)_n$ to Pt was ~10.

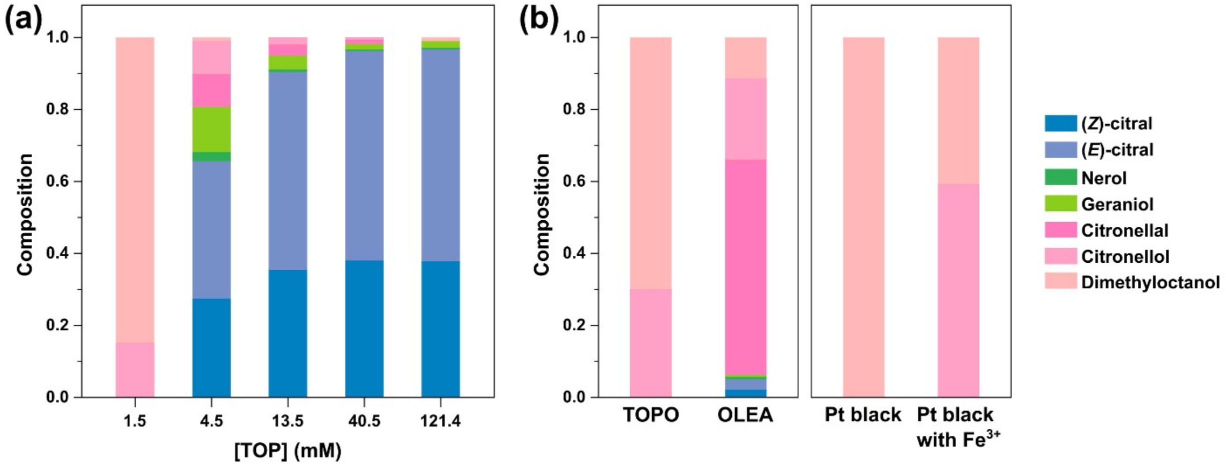


Figure S9. Compositional data for citral hydrogenation reactions corresponding to Figure 5 in the main text for 3.5 nm Pt NPs modified with strongly and weakly bound organic ligands and results of catalytic tests when Pt black was used as catalyst.

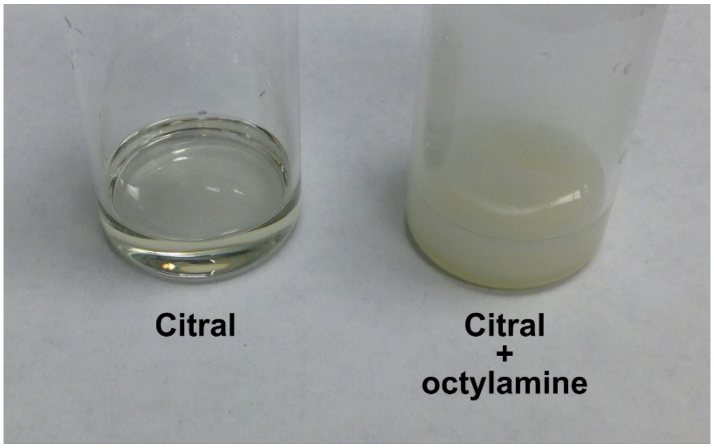


Figure S10. Pure citral (left) and a mixture of 2.0 g citral and 1.0 g n-octylamine (right). Upon mixing, the mixture immediately forms a white emulsion accompanied by vigorous water vapor formation, presumably due to a chemical reaction R–C=C–C=O + H_2N–R → R–C=C–C=N–R + H_2O.