Supplementary information

Organic–Inorganic Interface Engineering for Integrated Control of Surface Sites and Hydrogen Dynamics in Chemoselective Hydrogenation

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Table S1. TOF values of Pt-HDTMS(*x*) catalysts in acetophenone hydrogenation.

Sample	TOF (h^{-1})[a]
Pt-HDTMS(0)	59
Pt-HDTMS(0.3)	87
Pt-HDTMS(3)	727
Pt-HDTMS(30)	876

[a] TOF values determined using the total number of surface Pt atoms calculated from the theoretical Pt NP model based on their average particle size.[1]

Table S2. TOF values and chemoselectivity of Pt-HDTMS(*x*) catalysts in cinnamaldehyde hydrogenation.

Sample	TOF_{CO} (h^{-1})[a]	TOF_{model} (h^{-1})[b]	Chemoselectivity (%)[c]
Pt-HDTMS(0)	26	30	34.5
Pt-HDTMS(0.3)	180	59	49.0
Pt-HDTMS(3)	2965	385	60.2
Pt-HDTMS(30)	7039	620	68.8

[a] TOF values determined using the number of exposed Pt sites measured by CO chemisorption.

[b] TOF values determined using the total number of surface Pt atoms calculated from the theoretical Pt NP model based on their average particle size.

[c] Chemoselectivity measured at full conversion.

Table S3. Pt and carbon contents of Pt-HDTMS(30) before and after ten consecutive reaction cycles.

Sample	Pt (wt.%)[a]	C (wt.%)[b]
Fresh Pt-HDTMS(30)	0.3	8.5
Spent Pt-HDTMS(30)	0.3	8.3

[a] Pt loadings measured by ICP-OES.

[b] Carbon content determined by elemental analysis.

Table S4. Fitting parameters used for deconvolution of CO-DRIFTS peaks corresponding to WC and UC Pt sites.

Peak designation	Peak position (cm^{-1})	Full width at half maximum (FWHM, cm^{-1})	Shape
CO-UC (1)	2033	38	
CO-UC (2)	2056–2060	20	
CO-UC (3)	2065–2071	15	Gaussian
CO-WC (1)	2082–2087	15	
CO-WC (2)	2087–2095	8	

Table S5. Pt physicochemical properties and catalytic performance of the Pt-HDTMS(0), Pt-HDTMS(0.3) and HDTMS(0.3)-Pt catalysts

Sample	Pt_{avail}[a]	d_{CO} (nm)[a]	Conversion (%)[b]	Chemoselectivity (%)[c]
Pt-HDTMS(0)	0.53	2.2	34.7	46.3
Pt-HDTMS(0.3)	0.12	7.0	65.6	55.2
HDTMS(0.3)-Pt	0.05	19.8	32.6	54.6

[a] Pt_{avail} and d_{CO} obtained from CO chemisorption measurements.

[b] Conversion measured at 3 h of reaction time.

[c] Chemoselectivity measured at full conversion.

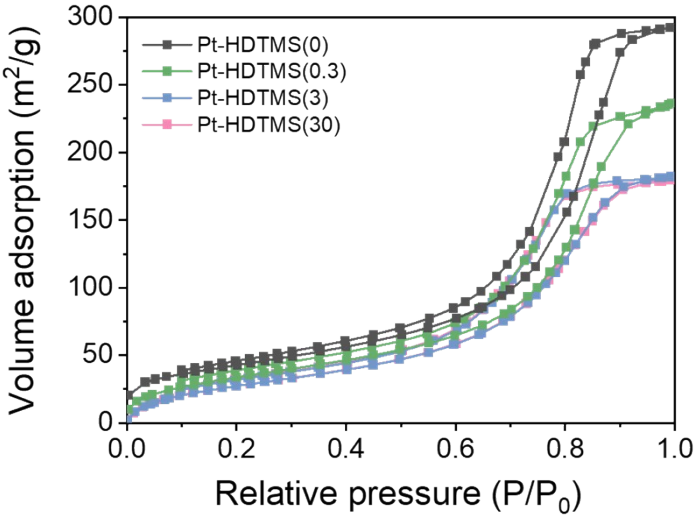

Figure S1. N_2 adsorption–desorption isotherms of Pt-HDTMS(*x*) catalysts.

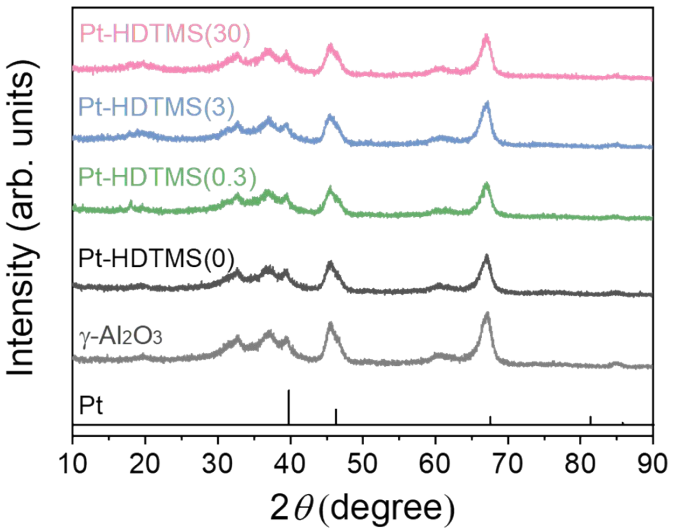

Figure S2. XRD patterns of Pt reference, γ-Al_2O_3, and Pt-HDTMS(*x*) catalysts.

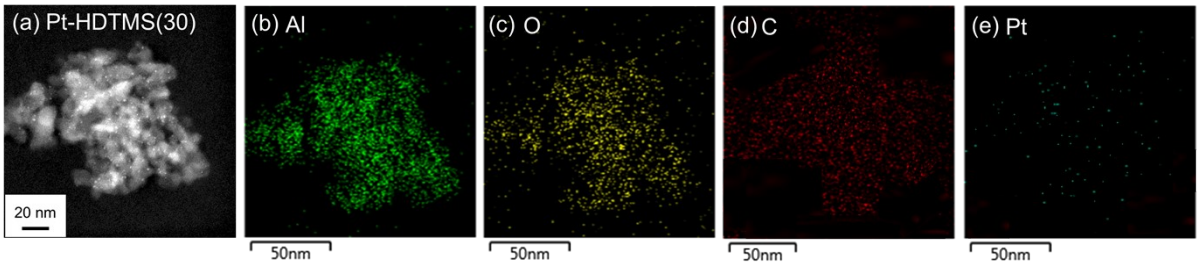

Figure S3. STEM and EDS elemental mapping images of Pt-HDTMS(30).

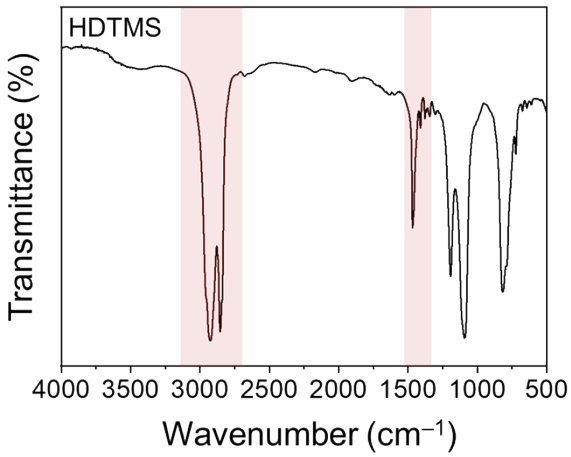

Figure S4. FTIR transmittance spectrum of HDTMS over the region of 4000–500 cm^{-1}.

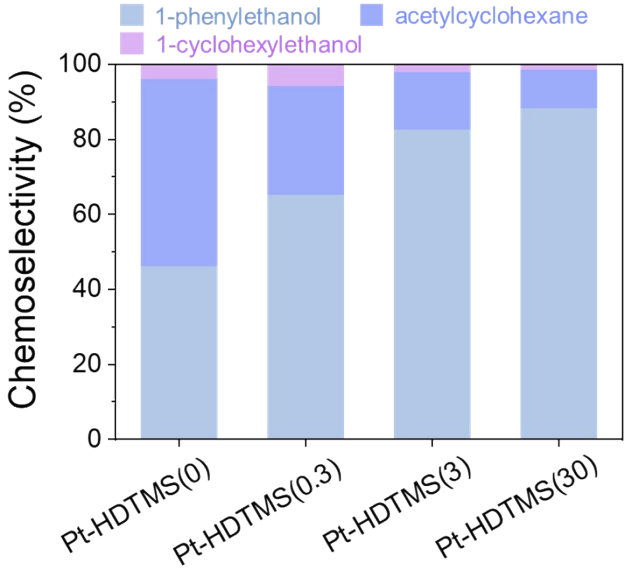

Figure S5. Product distribution in the hydrogenation of acetophenone over Pt-HDTMS(*x*) catalysts.

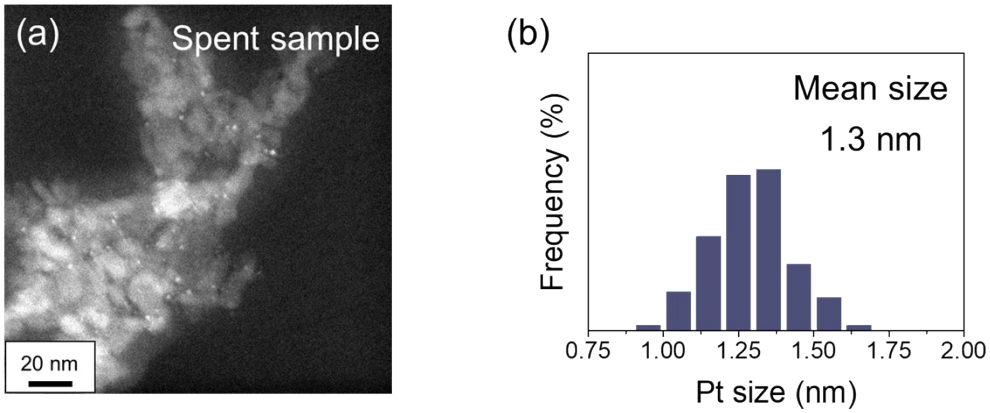

Figure S6. (a) STEM images and (b) size distribution of Pt NPs for spent Pt-HDTMS(30).

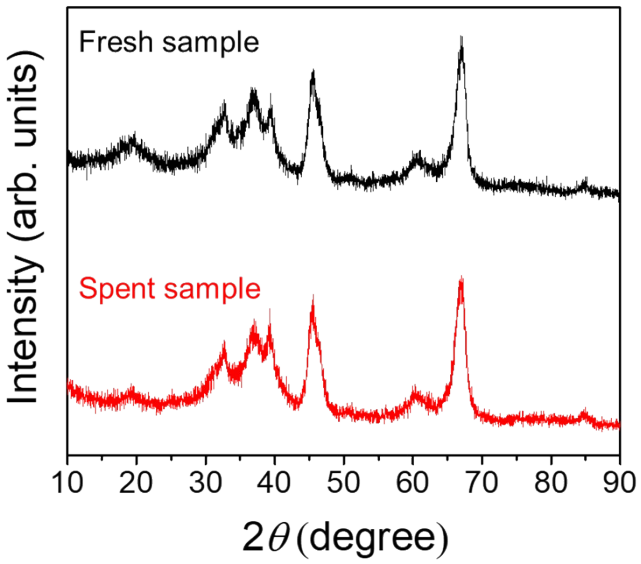

Figure S7. XRD patterns of fresh and spent Pt-HDTMS(30) catalysts.

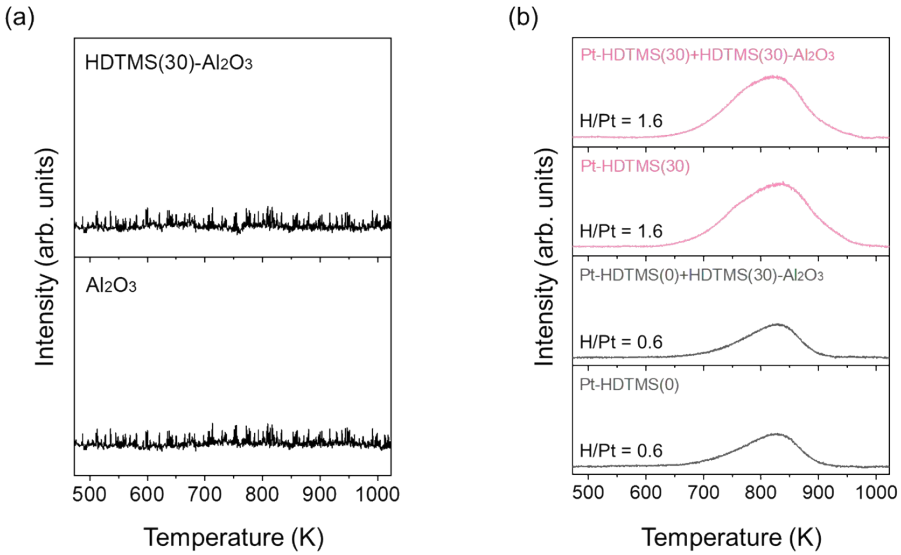

Figure S8. H_2-TPD profiles of (a) Al_2O_3 and HDTMS(30)-Al_2O_3 supports, and (b) Pt-HDTMS(0), Pt-HDTMS(30), and their corresponding physical mixtures with HDTMS(30)-Al_2O_3.

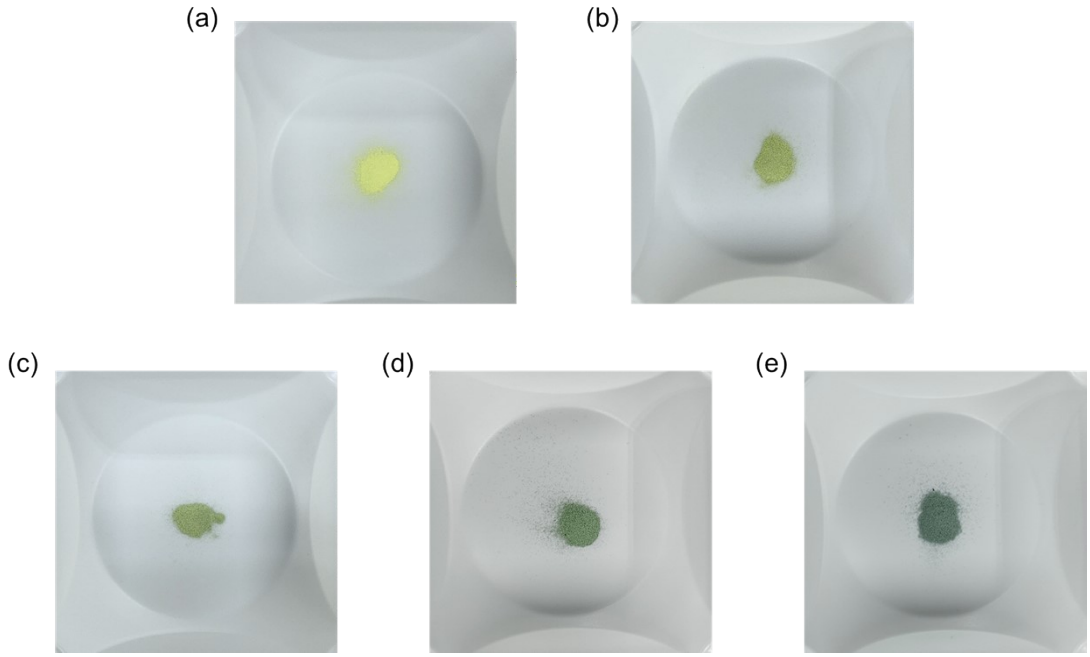

Figure S9. Photographs of (a) WO_3 and WO_3 mixed with (b) Pt-HDTMS(0), (c) Pt-HDTMS(0.3), (d) Pt-HDTMS(3), and (e) Pt-HDTMS(30) after treatment with H_2 at 473 K for 2 h.

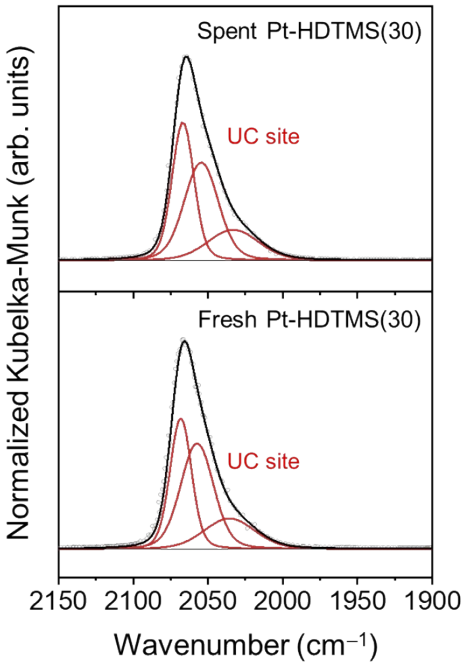

Figure S10. CO-DRIFTS spectra and corresponding deconvoluted peak profiles for the fresh and spent Pt-HDTMS(30) catalysts.

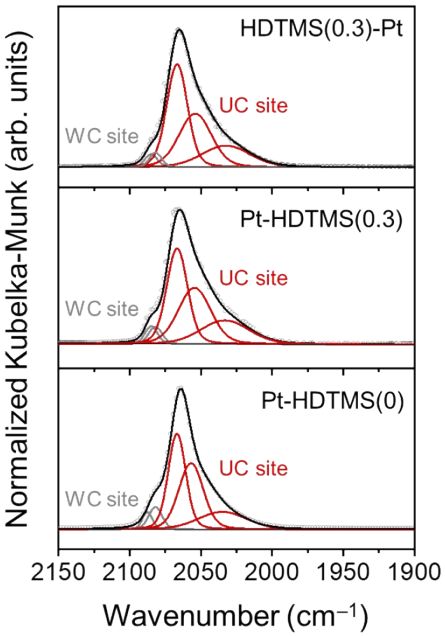

Figure S11. CO-DRIFTS spectra and corresponding deconvoluted peak profiles for the Pt-HDTMS(0), Pt-HDTMS(0.3) and HDTMS(0.3)-Pt catalysts.

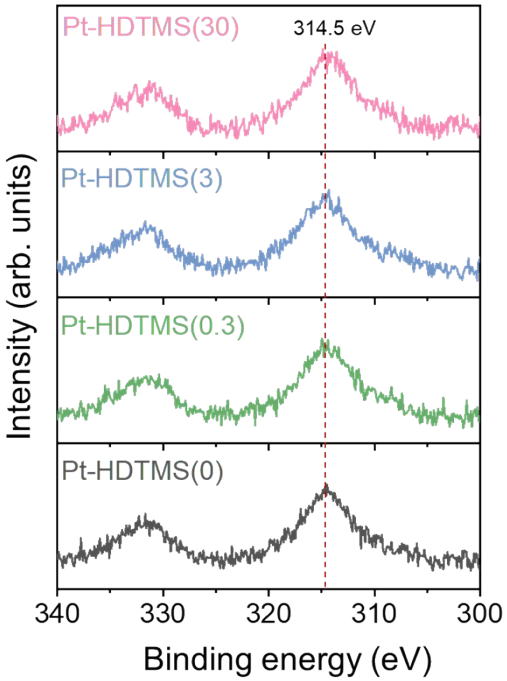

Figure S12. Pt 4d XPS spectra of Pt-HDTMS(*x*) catalysts.

References

1 J. Aarons, M. Sarwar, D. Thompsett and C.-K. Skylaris, *The Journal of Chemical Physics*, 2016, **145**.