Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Controlling the speciation and selectivity of Si3N4 supported palladium nanostructures for catalysed acetylene selective hydrogenation

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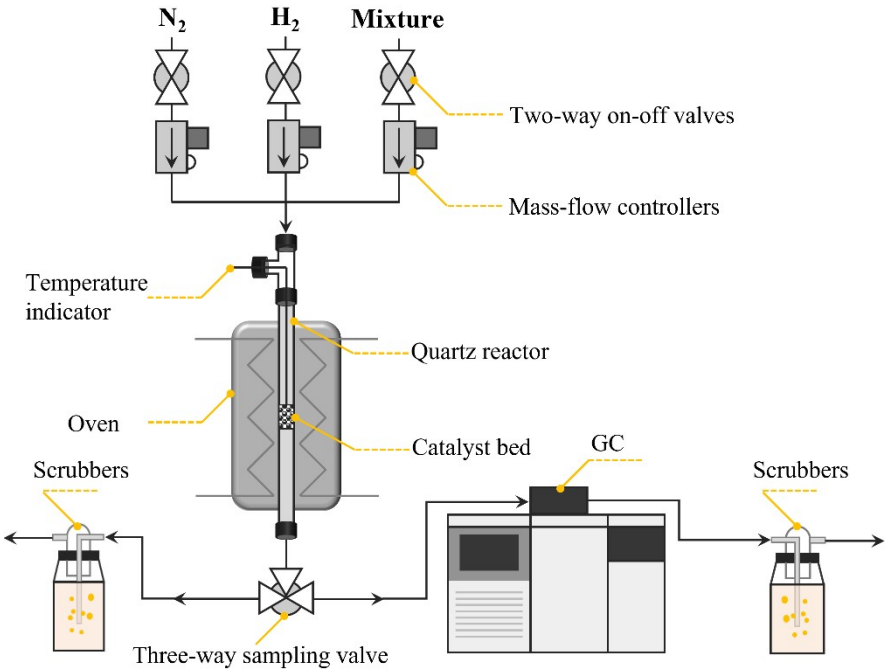

Figure S1. Scheme of the laboratory set-up used for selective hydrogenation of acetylene.

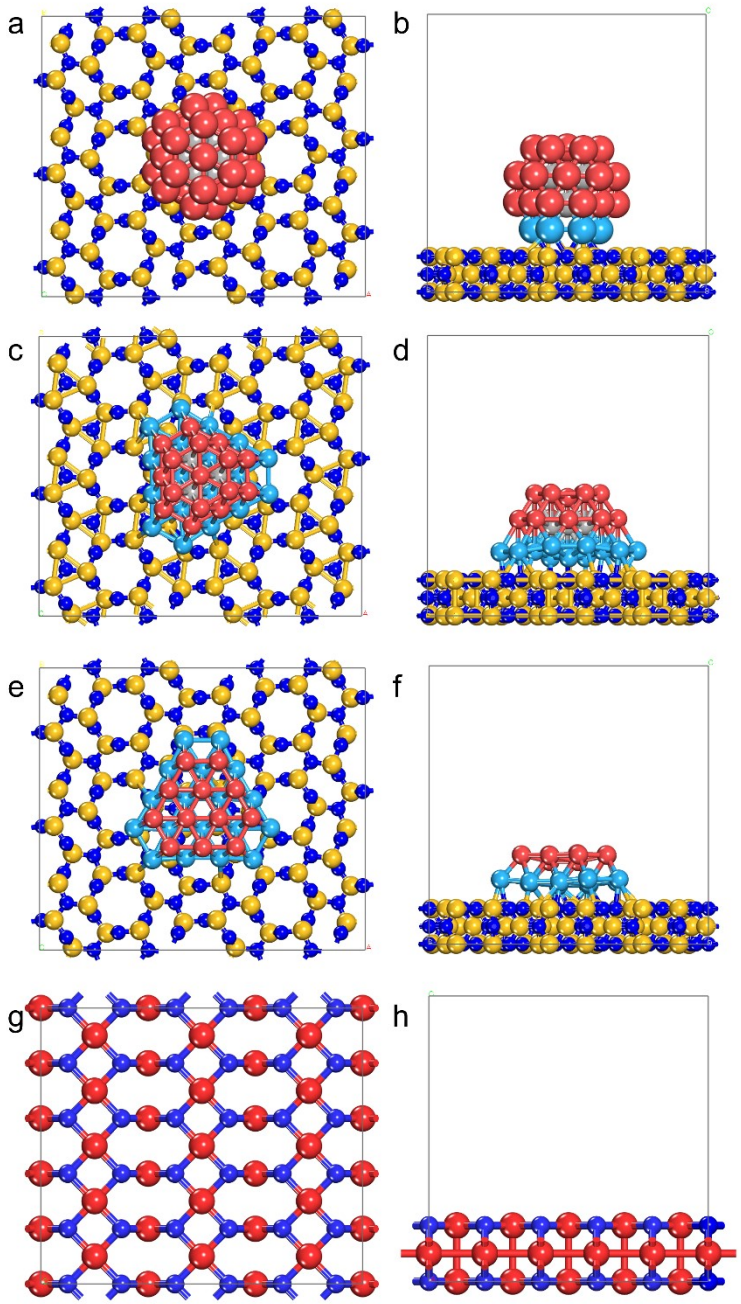

Figure S2. Top and side views of the computational model. (a) and (b) Pd NSs; (c) and (d) Pd NEs; (e) and (f) Pd NIs; (g) and (h) Pd NShs.

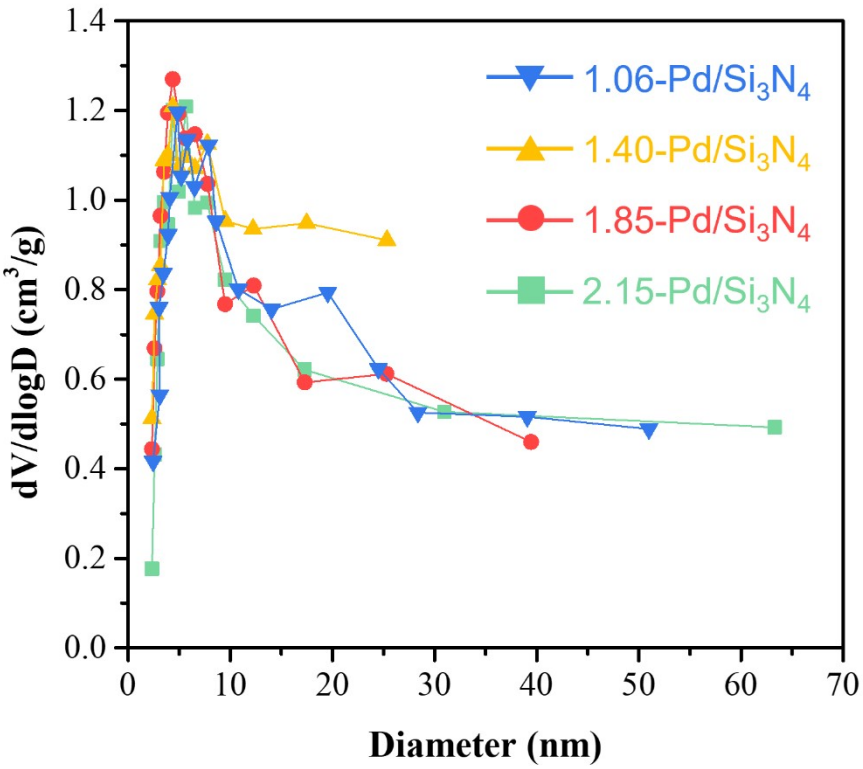

Figure S3. BJH pore size distribution.

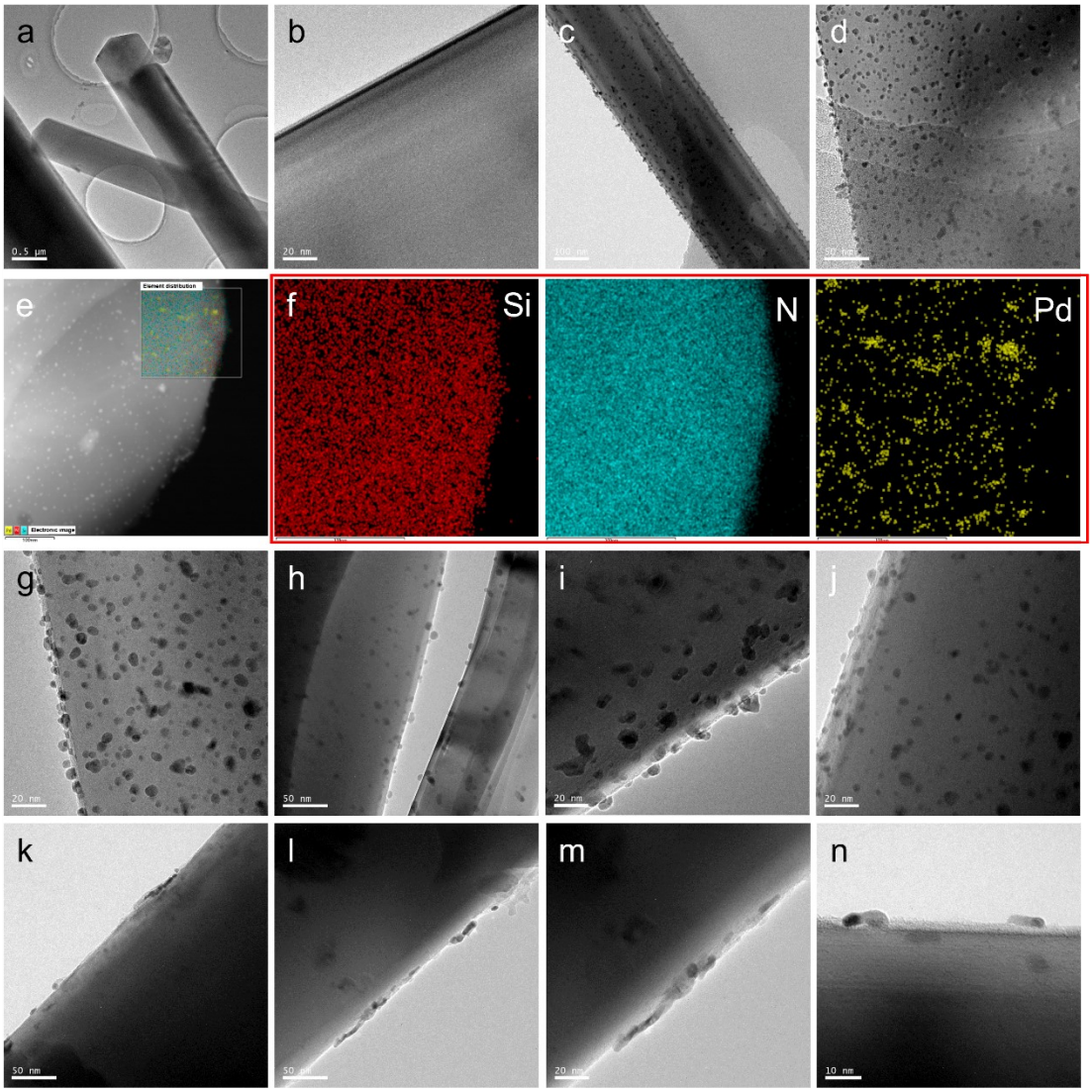

Figure S4. TEM images. (a) and (b) Si_3N_4; (c), (d) and (g) 2.15-Pd/Si_3N_4; (h) 1.85-Pd/Si_3N_4; (i) 1.40-Pd/Si_3N_4; (j) 1.06-Pd/Si_3N_4; (k-n) 2.15-Pd/Si_3N_4 with thermal activation for 8h; (e)~(f) Elements mapping of 2.15-Pd-Si_3N_4.

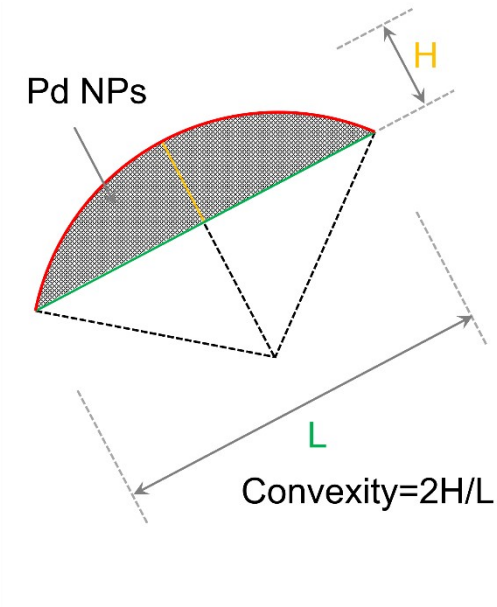

Figure S5. The formula for calculating the convexity.

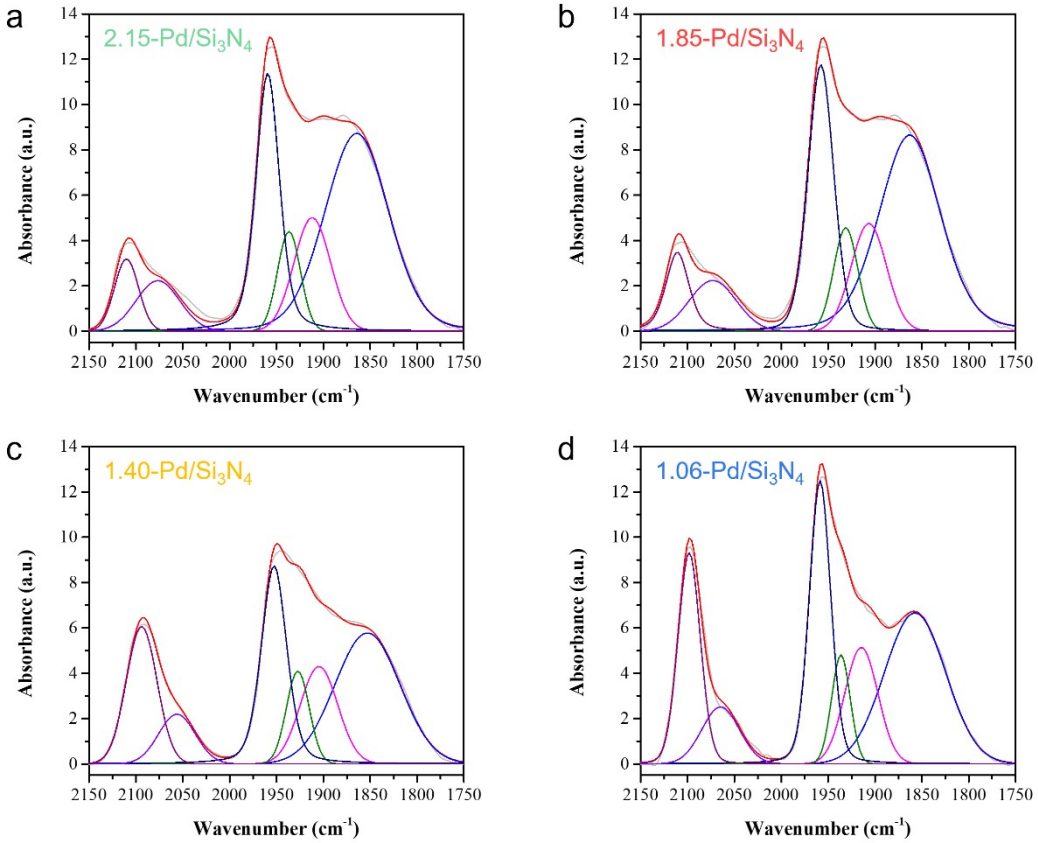

Figure S6. Fittings of the in situ DRIFTS of CO chemisorption using a Gaussian-Lorentzian function for estimation of the peak areas at 2100, 1960, and 1850 cm^{-1}.

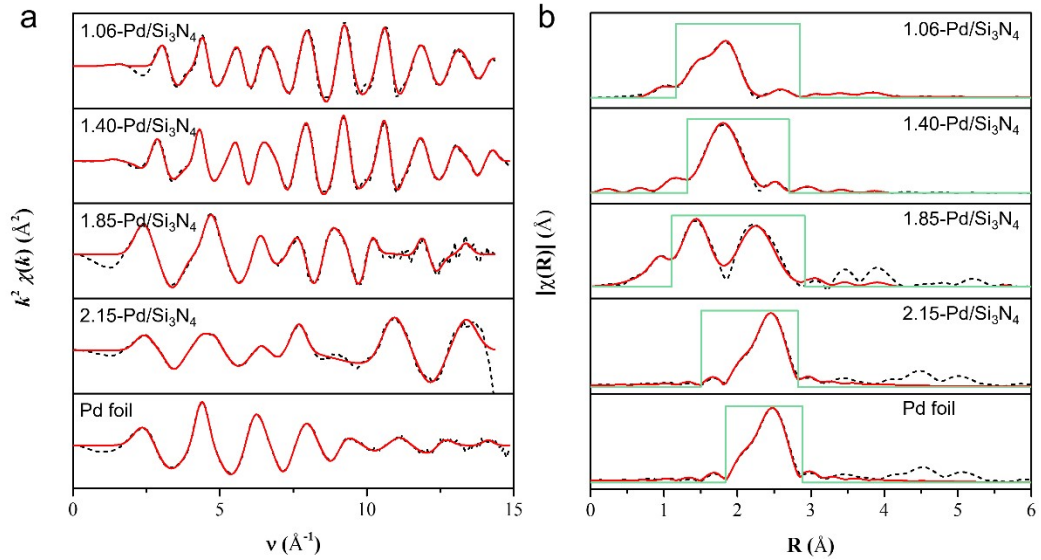

Figure S7. Experimental and fitted EXAFS spectra of Pd foil, 2.15-Pd/Si_3N_4, 1.85-Pd/Si_3N_4, 1.40-Pd/Si_3N_4, and 1.06-Pd/Si_3N_4 samples at the Pd-*K* edge. (a) k-space; (b) R-space.

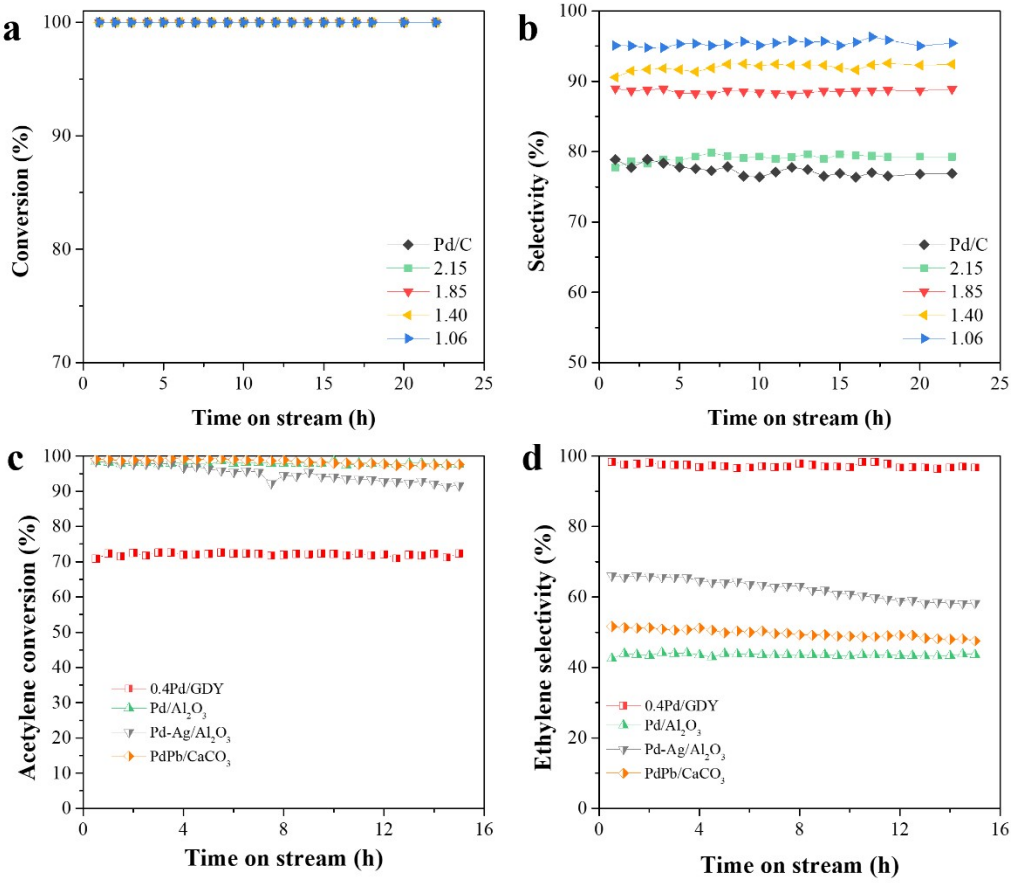

Figure S8. Long-term stability of mentioned Pd-based catalysts for acetylene selective hydrogenation. Reaction conditions: T = 433 K, GHSV = 8000 h^{-1}.

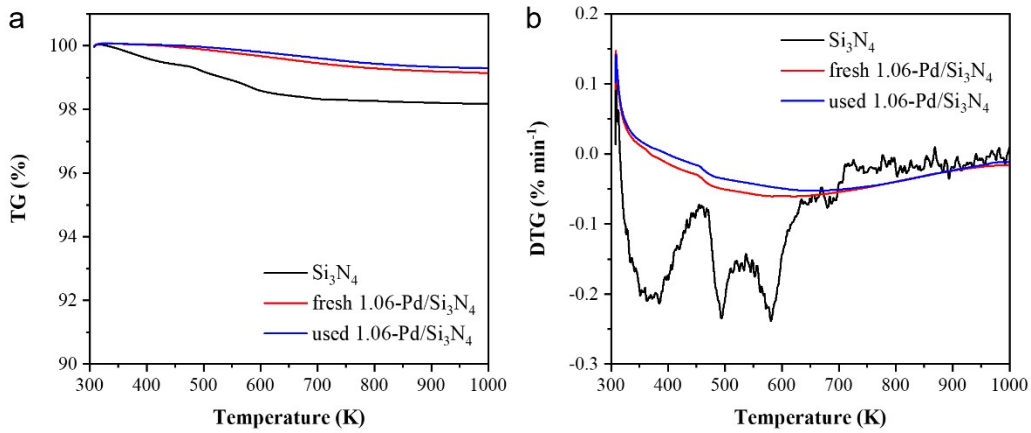

Figure S9. (a) TG and (b) DTG profiles of fresh and used 1.06–Pd/Si_3N_4 catalysts along with the reference Si_3N_4.

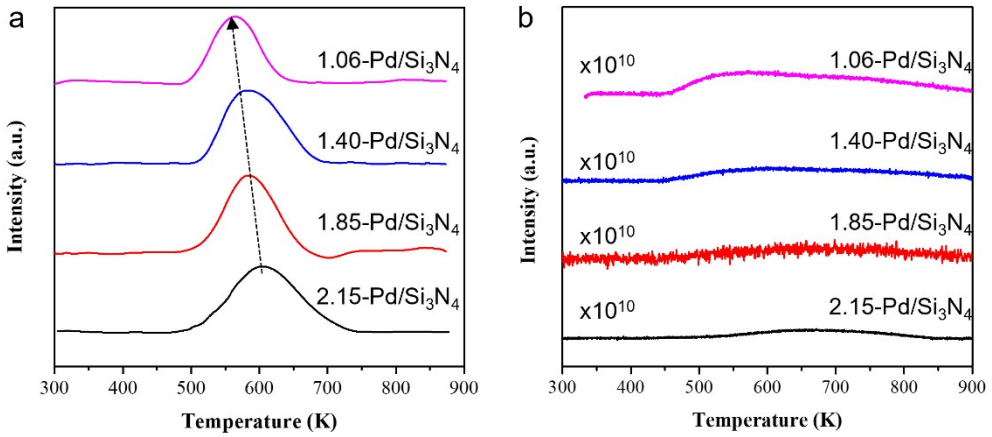

Figure S10. (a) CO_2-TPD profiles and (b) NH_3-TPD profiles of investigated Pd/Si_3N_4 catalysts.

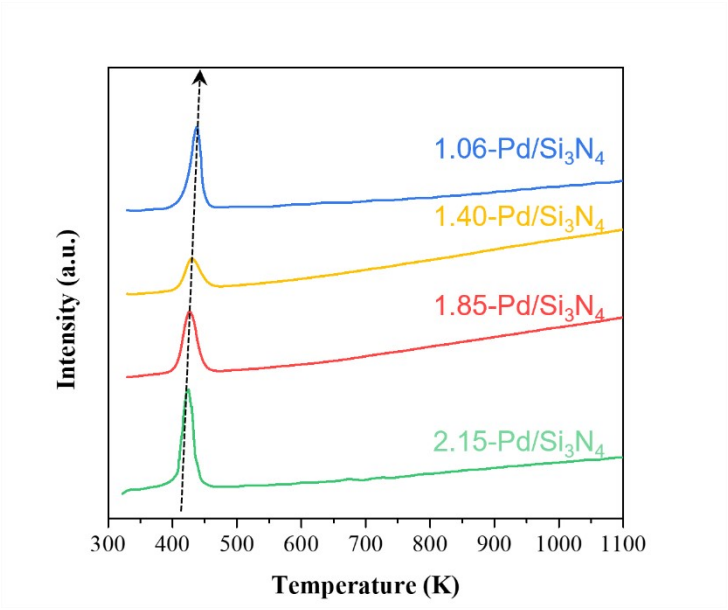

Figure S11. H_2–TPR profiles of investigated Pd/Si_3N_4 catalysts.

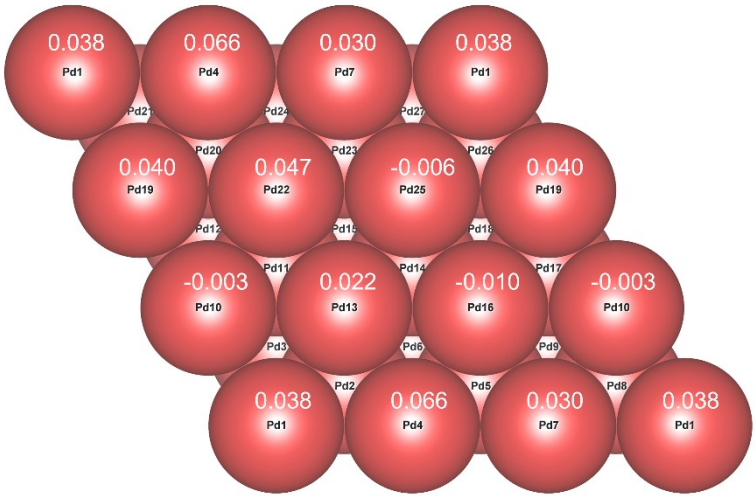

Figure S12. Bader charge on Pd over Pd (111) surface.

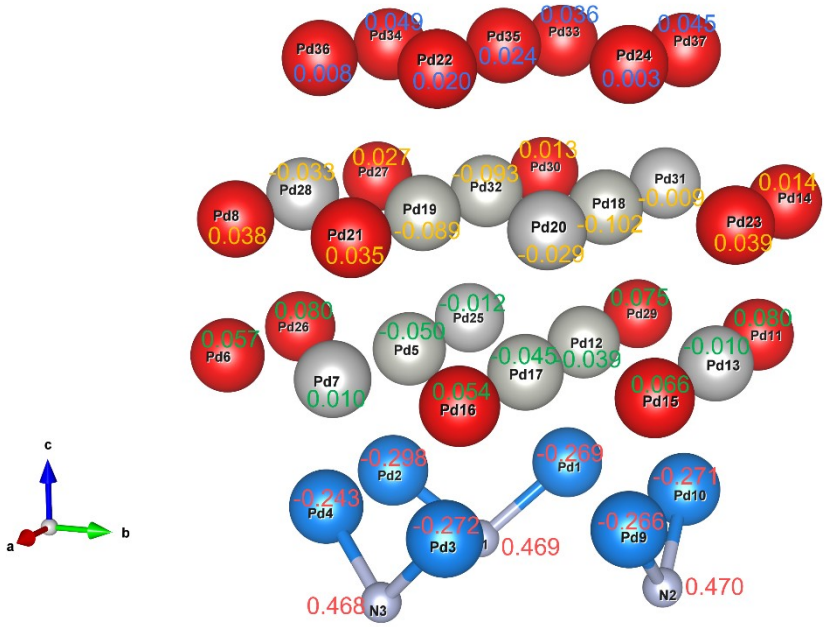

Figure S13. Bader charge on Pd over Pd NSs.

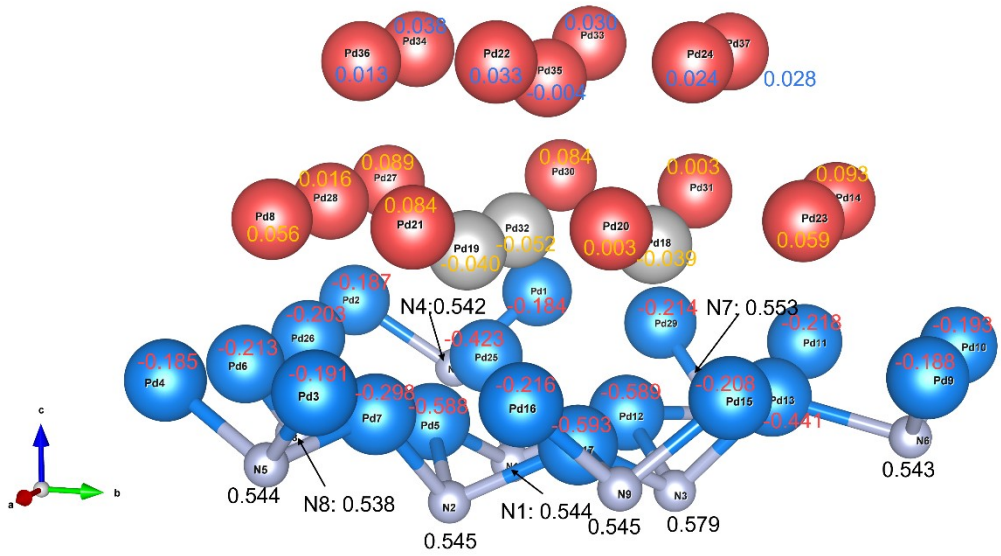

Figure S14. Bader charge on Pd over Pd NEs.

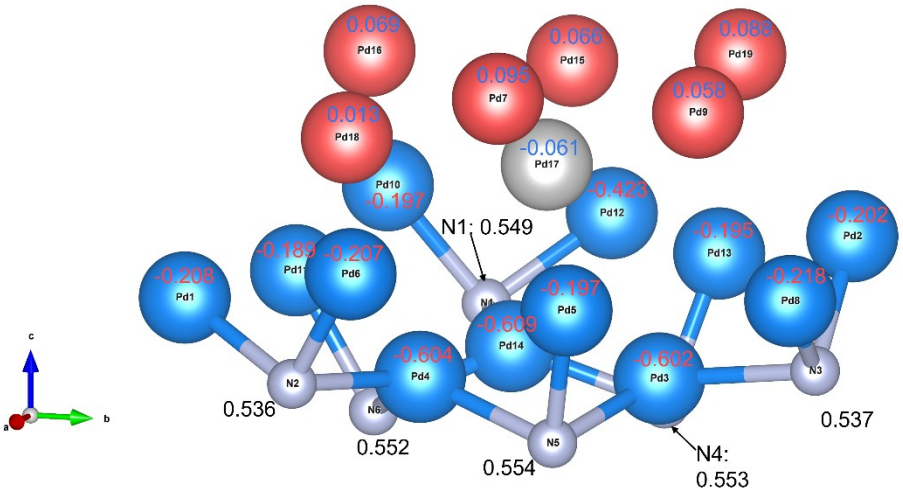

Figure S15. Bader charge on Pd over Pd NIs.

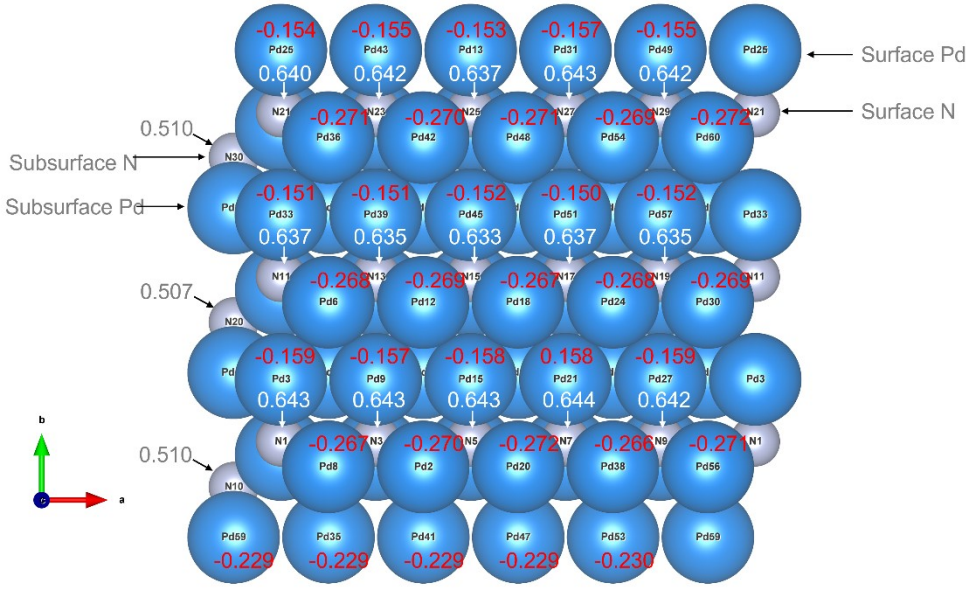

Figure S16. Bader charge on Pd over Pd NShs.

Table S1. The ratios of the IR band area of various CO species on Pd catalysts employed in the present study.

Catalyst	Peak position	FWHM*	Area	% Area	Species	Ratio/ %
2.15-Pd/Si_3N_4	1864.34	80.48	797.97	46.87	hollow sites	59.55
	1910.09	42.87	110.71	6.50		
	1937.16	28.11	105.11	6.17		
	1959.36	29.48	417.50	24.52	bridge sites	24.52
	2075.61	54.61	129.51	7.61	corner sites	15.93
	2108.74	29.79	141.69	8.32		
1.85-Pd/Si_3N_4	1862.95	77.29	745.63	43.85	hollow sites	57.07
	1908.85	40.47	100.39	5.90		
	1931.61	28.74	124.48	7.32		
	1957.77	32.27	410.46	24.14	bridged sites	24.14
	2071.85	58.95	140.14	8.24	corner sites	18.79
	2106.64	34.34	179.40	10.55		
1.40-Pd/Si_3N_4	1857.60	76.97	544.29	35.41	hollow sites	52.92
	1914.43	41.16	146.02	9.50		
	1936.42	23.49	123.17	8.01		
	1958.57	26.69	381.58	24.82	bridged sites	24.82
	2071.89	20.94	42.31	2.75	corner sites	22.26
	2096.81	29.08	299.88	19.51		
1.06-Pd/Si_3N_4	1852.39	77.29	502.98	36.56	hollow sites	48.05
	1899.01	42.67	106.36	7.73		
	1924.13	23.41	51.67	3.76		
	1951.20	34.66	355.85	25.87	bridged sites	25.87
	2057.03	32.67	35.87	2.61	corner sites	26.08
	2090.44	41.43	322.89	23.47		

FWHM: Full Width at Half Maximum.

Table S2. EXAFS parameters fitted for the samples.

Samples	Shell	CN[a]	R (Å) [b]	σ^2 (Å^2)	R-factor[c]
Pd foil	Pd-Pd	12.0	2.74	0.00534	0.0019
2.15	Pd-Pd	3.9	2.73	0.00549	0.0023
1.85	Pd-Pd Pd-N	0.79 4.34	2.60 2.20	0.00656 0.01958	0.0278
1.40	Pd-Pd Pd-N	5.97	2.33	0.0018	0.0170
1.06	Pd-N	6.54	2.33	0.0010	0.0180

a Coordination number (N)
b Atomic distance (R)
c Debye-Waller factor (R-factor)