Supplementary Information: Site blocking effects on P-modified Pd/Al_2O_3 catalysts for LOHC hydrogenation: an *in situ* DRIFTS study

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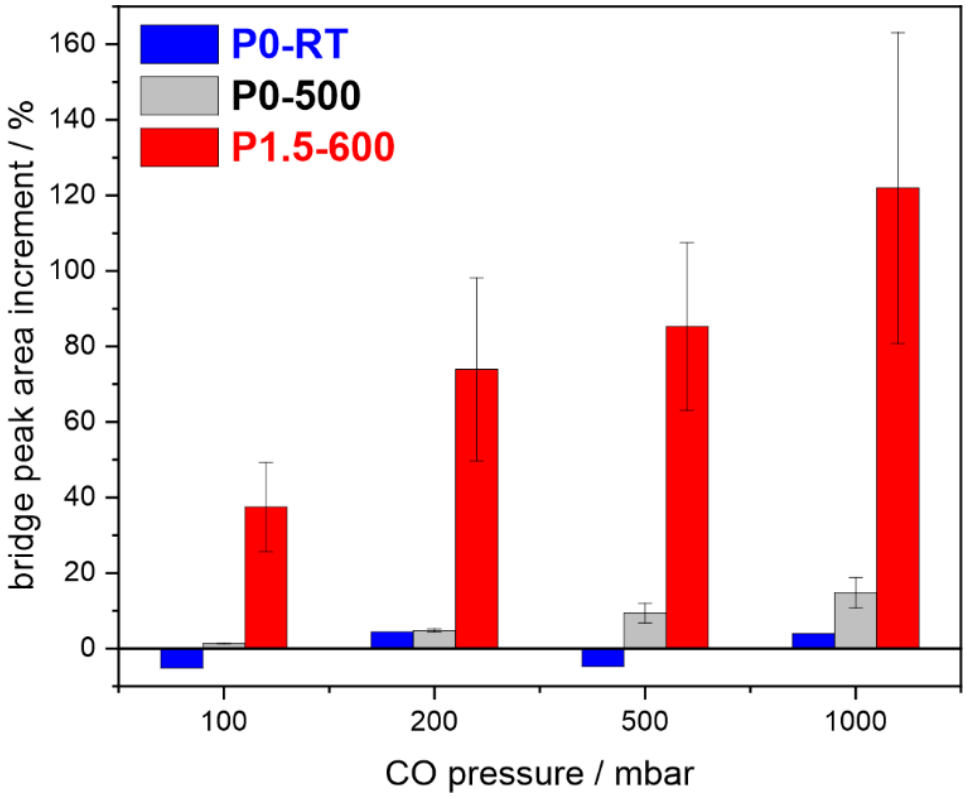

Figure S1: Relative increase of the CO_{br+h} peak area for P0-RT, P0-500, and P1.5-600 under increasing CO pressure from 50 mbar to 1000 mbar.

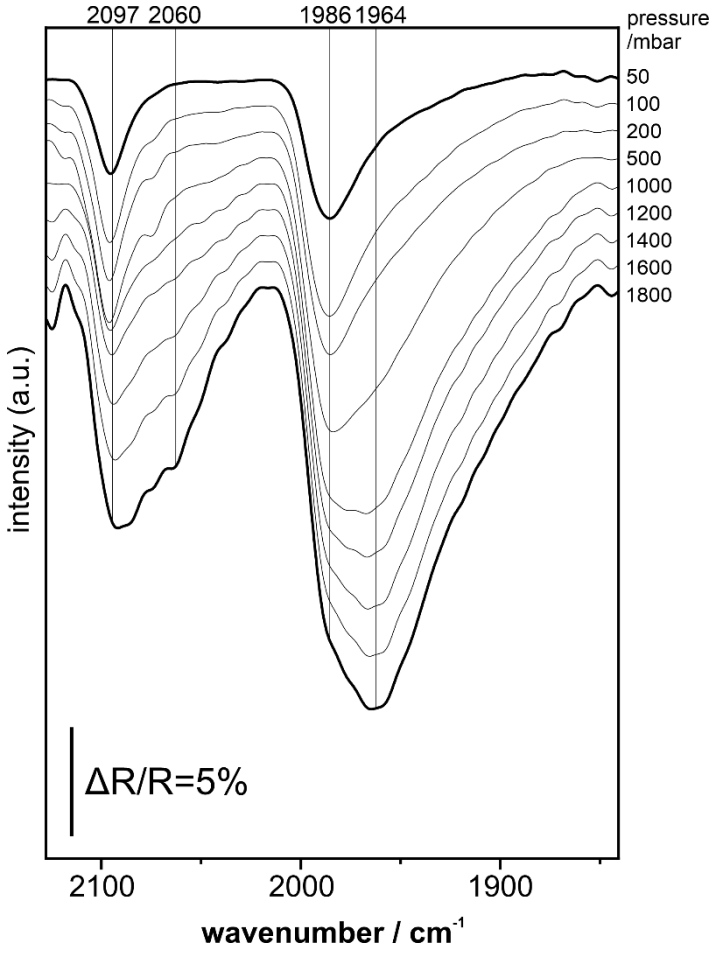

Figure S2: CO-DRIFTS spectra recorded under increasing CO pressure from 50 mbar to 1800 mbar with P1.5-500.

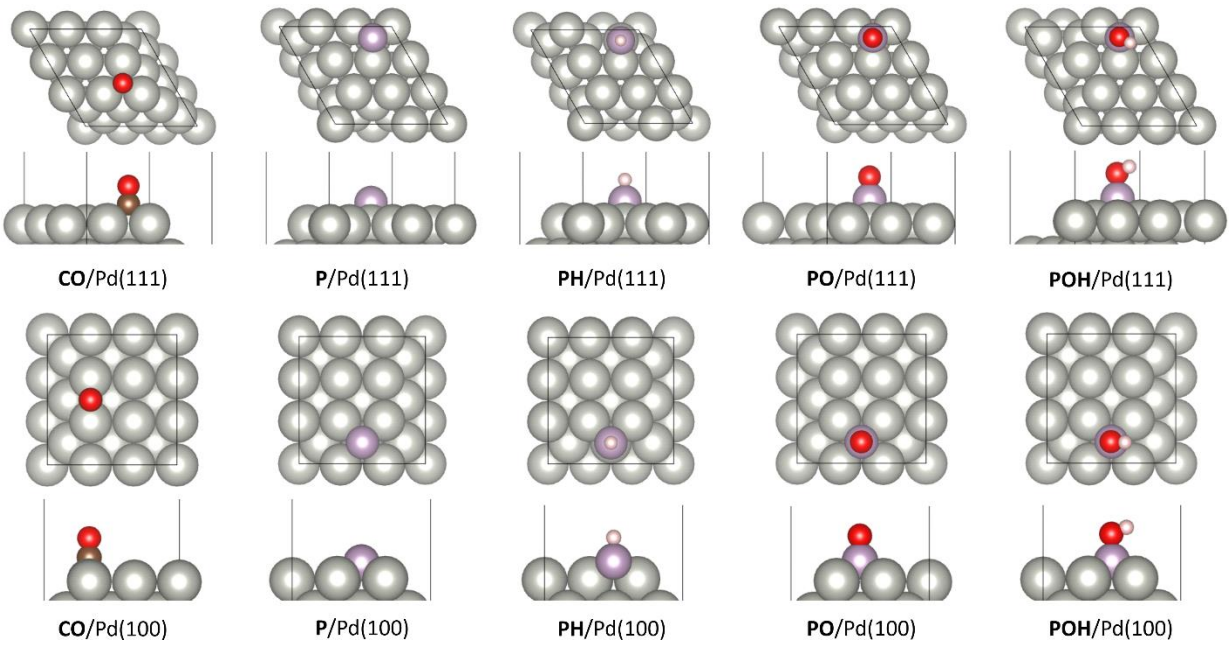

Figure S3: Adsorption geometries of CO and PO_xH_y (viz. PH, P, PO and POH) on Pd(111) and Pd(100) *p*(3x3) surfaces. Spheres represent: Oxygen (red), carbon (brown), phosphorous (pink), hydrogen (white) and palladium (grey)

Table S1: Adsorption energy of CO on different Pd(111) and Pd(100) high symmetry adsorption sites. Energies reported without zero-point energy calculations and relative to CO in the gas phase.

	Site	E_{ads} / kJ mol^{-1}	Vibrational modes / cm^{-1}					
Pd(111)	**fcc**	**-214.20**	**1771**	339	338	323	154	153
	hcp	-212.27	1771	342	342	326	155	154
	atop	-161.13	2035	411	304	304	48	43
	bridge	-199.72	1848	406	346	281	178	***50i***
Pd(100)	**bridge**	**-216.13**	**1861**	410	350	335	173	38
	4f-hollow	-211.30	1671	254	254	249	147	144
	atop	-172.71	2021	416	286	286	13	25

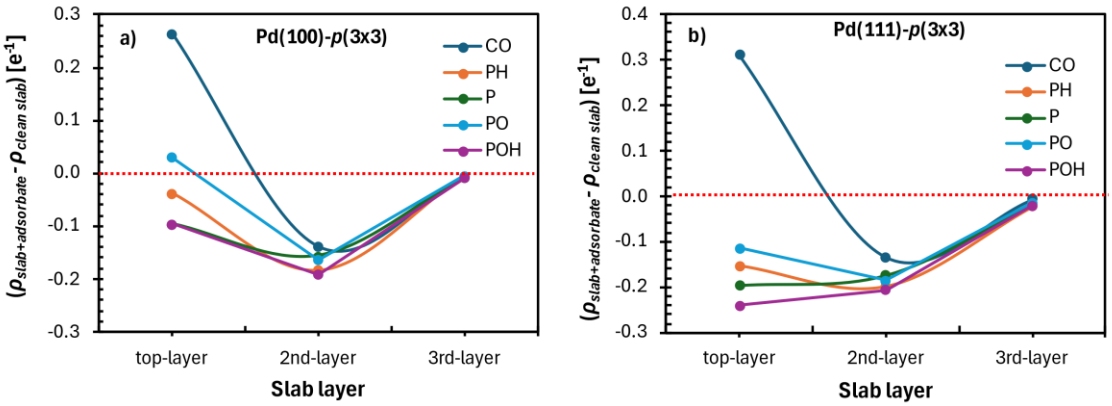

Figure S4: Effect of adsorption on Bader charge of the top three surface layers relative to a clean slab for the (a) Pd(100) and (b) Pd(111) surface terminations. All negative shifts indicate an accumulation of electrons upon adsorption relative to a clean slab. Note that $\rho_{clean\ slab}$ ($\rho_{slab+adsorbate}$) is the total Bader charge associated with a given slab layer for a clean slab (slab with an adsorbate).

Table S2: Adsorption energy and C-O bond length for CO adsorption on Pd(111)-p(3×3) precovered with CO, POH, and P.

Cov.	CO		POH		P	
[ML]	Eads [kJ/mol]	*d*(C-O)	Eads [kJ/mol]	*d*(C-O)	Eads [kJ/mol]	*d*(C-O)
0,00	-214	1,193	-214	1,193	-214	1,193
0,11	-207	1,191	-218	1,195	-210	1,193
0,22	-208	1,189	-226	1,197	-210	1,193

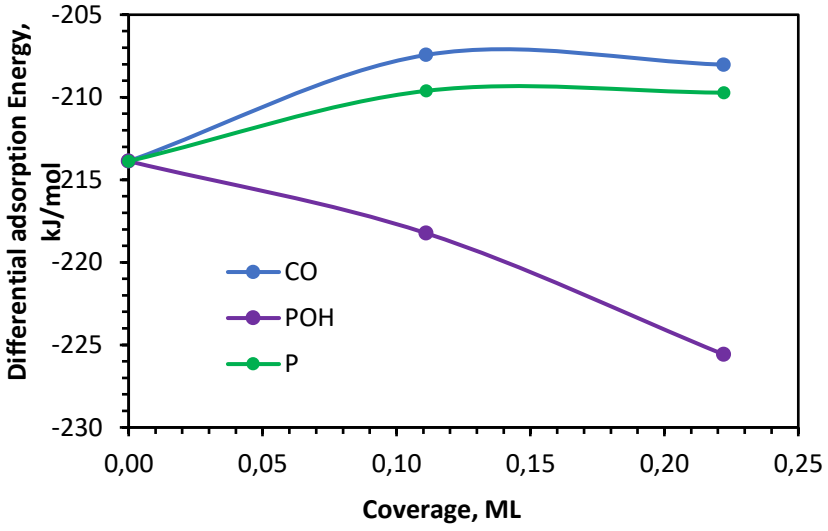

Figure S5: Differential adsorption energy of CO on Pd(111)-p(3×3) surfaces pre-covered with CO, POH, and P.

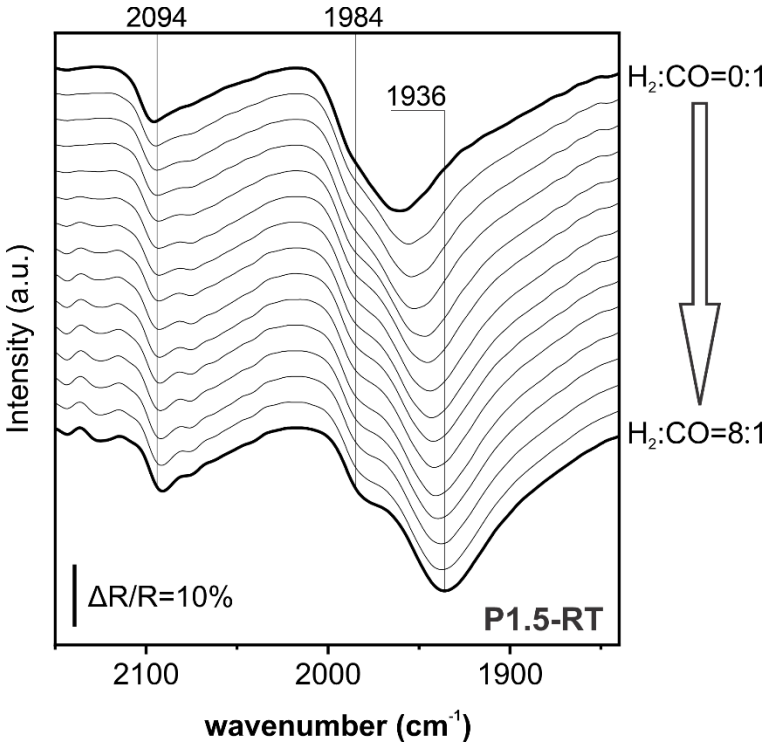

Figure S6: Hydrogen dosing DRIFTS results recorded under 1 bar pressure with P1.5-RT.

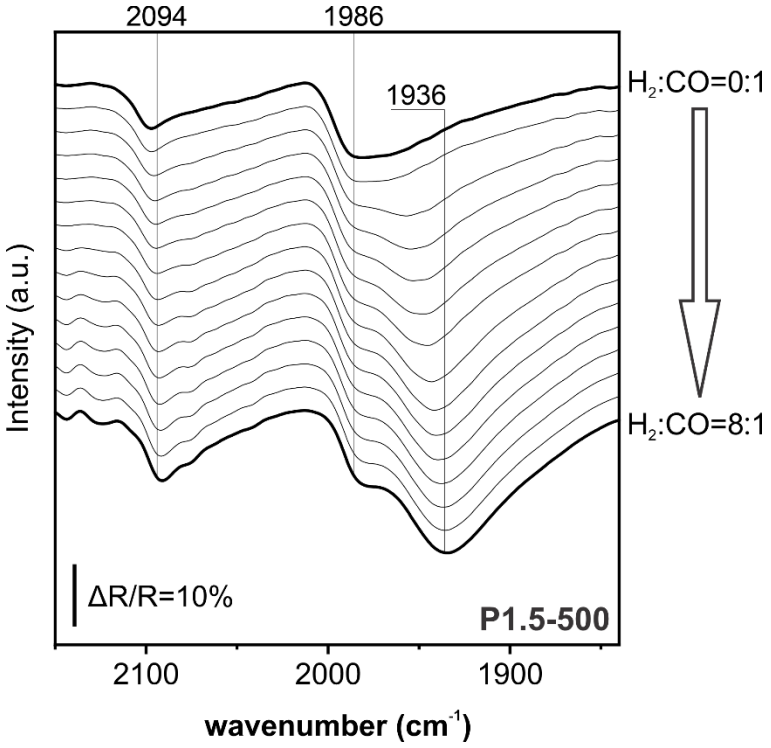

Figure S7: Hydrogen dosing DRIFTS results recorded under 1 bar pressure with P1.5-500.

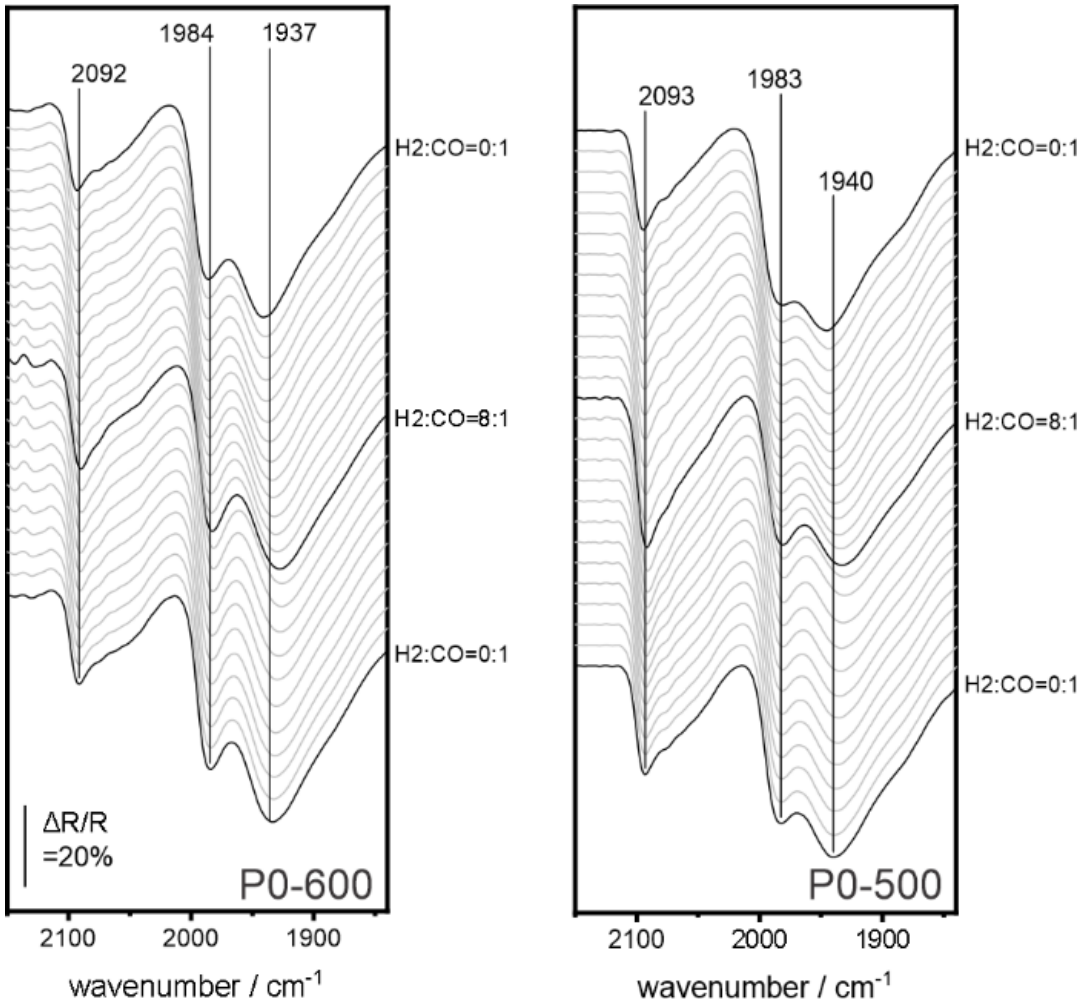

Figure S8: Hydrogen dosing DRIFTS results recorded under 1 bar pressure with P0-500 and P0-600.

Table S3: ICP-OES before and after DRIFTS measurements.

mass loading of Pd / wt%	**mass loading of P / wt%**
ICP-OES on P1.5-500 prior to H_2/CO treatment in DRIFTS	
4,12	1,72
ICP-OES on P1.5-500 after H_2/CO treatment in DRIFTS	
4,09	1,69