Supporting Information

Understanding the Facet Effects of Heterogeneous Rh$_2$P Catalysts for Styrene Hydroformylation

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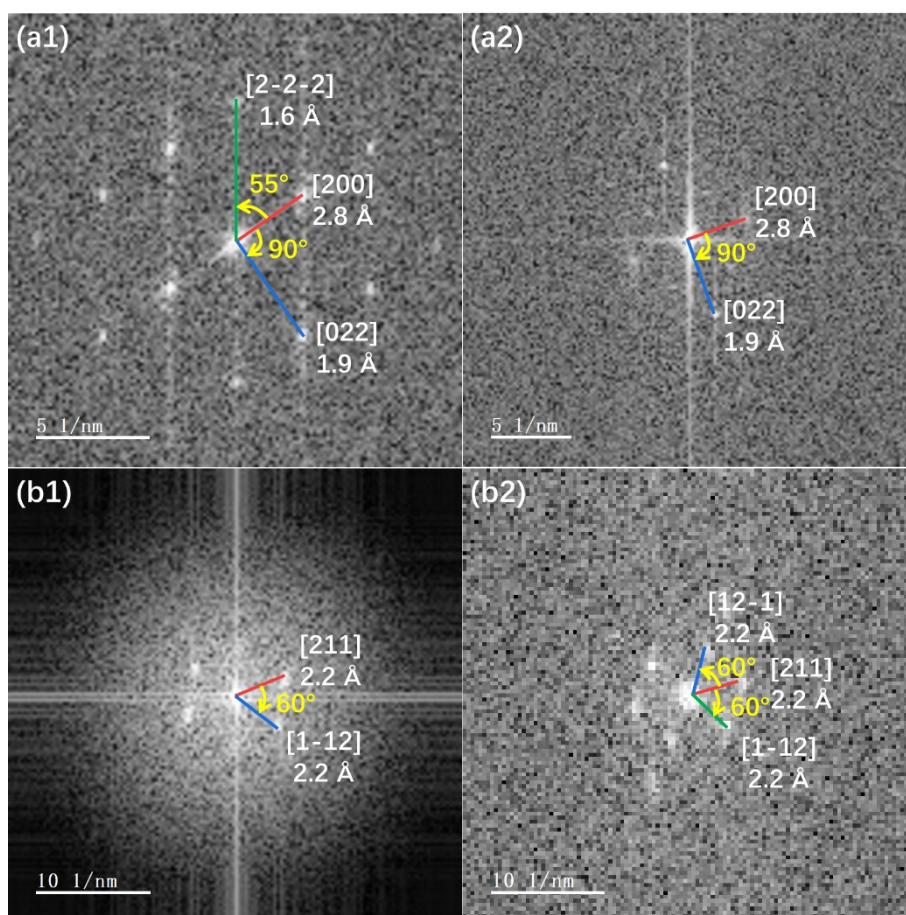*Corresponding author: Tiefeng Wang, wangtf@tsinghua.edu.cn

Figure S1. Fast Fourier transition (FFT) patterns of Rh_2P/SiO_2 catalysts with Rh_2P (110) facet (a) and Rh_2P (111) facet (b).

Table S1. Energetics (eV) of surface reactions on Rh_2P (111), Rh_2P (110) and Rh_2P (100) surfaces.

ID	Rh_2P (111)			Rh_2P (110)			Rh_2P (100)		
	Energy (eV)	Gibbs free energy (eV)[a]	Activation energy (eV)	Energy (eV)	Gibbs free energy (eV)[a]	Activation energy (eV)	Energy (eV)	Gibbs free energy (eV)[a]	Activation energy (eV)
SS0	0.00	0.00		0.00	0.00		0.00	0.00	
SS1	-2.18	-1.17		-2.53	-1.48		-4.96	-3.83	
TS_l1	-1.81	-0.78	0.39	-1.94	-0.89	0.59	-4.25	-3.12	0.71
SS_l2	-2.42	-1.28		-2.16	-1.04		-4.62	-3.38	
SS_l3	-2.76	-1.06		-3.93	-2.27		-6.45	-4.60	
TS_l2	-2.49	-0.80	0.26	-2.80	-1.06	1.21	-4.87	-3.06	1.54
SS_l4	-3.36	-1.62		-3.59	-1.80		-5.83	-3.99	
TS_l3	-2.62	-0.91	0.70	-2.79	-1.07	0.73	-5.36	-3.50	0.49
SS_l5	-3.25	-1.37		-3.36	-1.56		-5.60	-3.63	
TS_b1	-1.77	-0.80	0.37	-1.99	-0.92	0.56	-4.19	-3.06	0.77
SS_b2	-2.48	-1.36		-2.87	-1.72		-4.85	-3.64	
SS_b3	-2.99	-1.25		-4.36	-2.69		-6.78	-4.98	
TS_b2	-2.74	-1.02	0.23	-2.70	-0.98	1.71	-5.53	-3.75	1.23
SS_b4	-3.68	-1.93		-3.56	-1.80		-6.08	-4.25	
TS_b3	-2.88	-1.12	0.81	-2.23	-0.45	1.35	-5.24	-3.41	0.84
SS_b5	-3.26	-1.35		-3.07	-1.25		-5.47	-3.54	

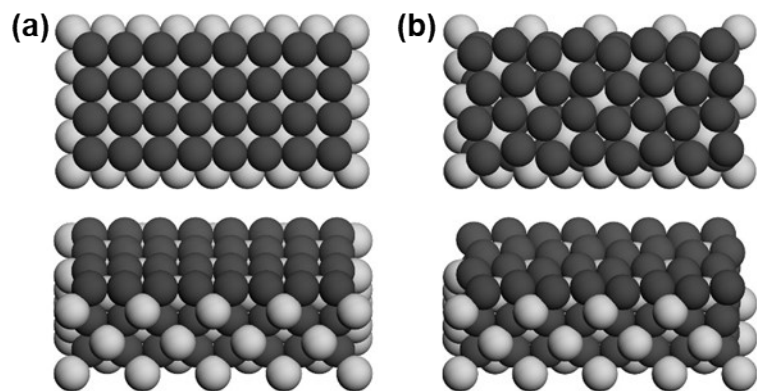[a] Thermal corrections were conducted under 80 °C and 3 MPa of syngas.

Figure S2. Blank Rh$_2$P (100) surface before (a) and after (b) reconstruction. Rh and P atoms are marked by dark gray and light gray, respectively.

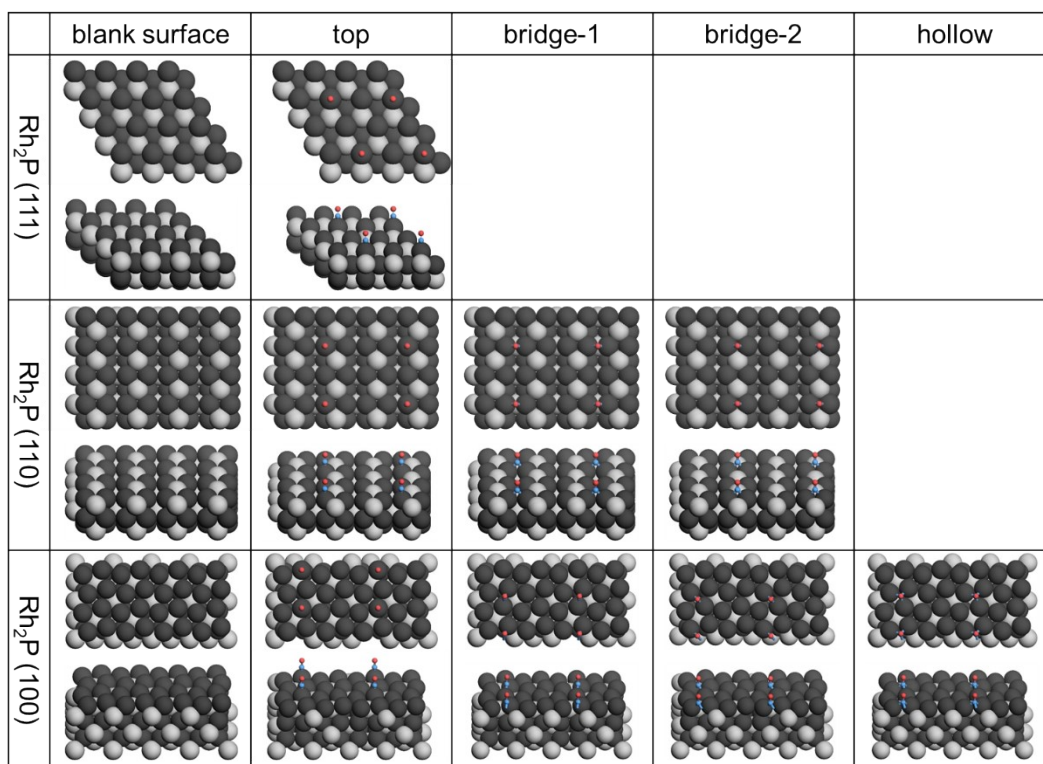|	blank surface	top	bridge-1	bridge-2	hollow
Rh$_2$P (111)					
Rh$_2$P (110)					
Rh$_2$P (100)					

Figure S3. CO adsorption geometries on different Rh$_2$P facets. The Rh, P, C, O atoms were marked by dark gray, light gray, blue and red, respectively.
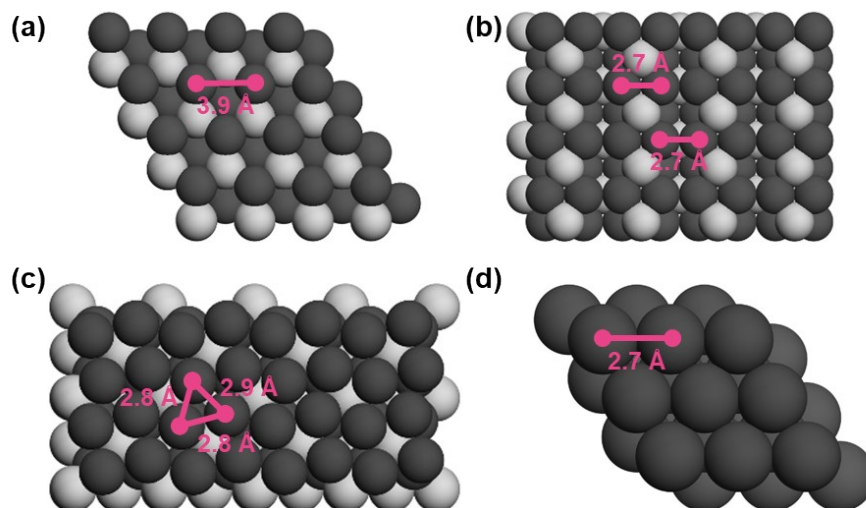
Figure S4. The distance between adjacent Rh atoms on Rh$_2$P (111) (a), Rh$_2$P (110) (b), Rh$_2$P (100) (c) and Rh (111) (d) facets. The Rh, P, C, O atoms were marked by dark gray, light gray, blue and red, respectively.
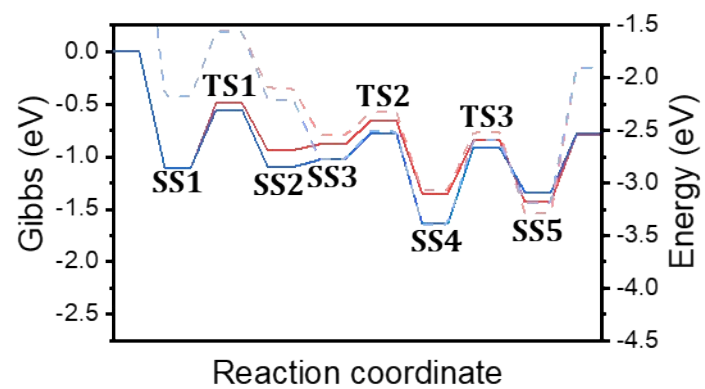
Figure S5. Gibbs free energy of styrene hydroformylation on $Rh_7Pd_1P_4$ (111). The total energy profiles are shown in dashed lines, while the Gibbs free energy at 80 °C and 3 MPa is shown in solid lines.

Table S2. Energetics (eV) of surface reactions on $Rh_7Pd_1P_4$ (111) surfaces.

| ID | Rh₇Pd₁P₄ (111) | | | |
	Energy (eV)	Gibbs free energy (eV)[a]	Activation energy (eV)	TDI / TDTS
SS0	0.00	0.00		
SS1	-2.18	-1.11		
TS_l1	-1.56	-0.49	0.62	$TDTS_l$ $\delta E_l = 1.15\ eV$
SS_l2	-2.10	-0.94		
SS_l3	-2.55	-0.88		
TS_l2	-2.33	-0.66	0.22	
SS_l4	-3.07	-1.35		
TS_l3	-2.51	-0.84	0.51	
SS_l5	-3.29	-1.43		
TS_b1	-1.56	-0.55	0.56	
SS_b2	-2.21	-1.10		
SS_b3	-2.78	-1.03		
TS_b2	-2.50	-0.78	0.25	
SS_b4	-3.39	-1.64		TDI
TS_b3	-2.59	-0.91	0.73	$TDTS_b$ $\delta E_b = 0.73\ eV$
SS_b5	-3.19	-1.34		

[a] Thermal corrections were conducted under 80 °C and 3 MPa of syngas.

$$\delta E = \begin{cases} E_{TDTS} - E_{TDI}, & if\ TDTS\ appears\ after\ TDI \\ E_{TDTS} - E_{TDI} + \Delta G_r, & if\ TDTS\ appears\ before\ TDI \end{cases}$$

Where, ΔG_r is the energy of the reaction.

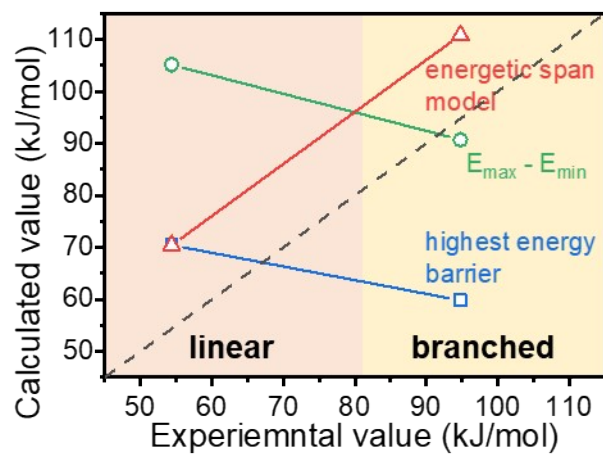The TDTS was determined by maximizing the value of δE.

Figure S6. Experimental value and calculated value of apparent activation energies on $Rh_7Pd_1P_4$ (111).