Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The intrinsic effect of strain on low-index surfaces of Platinum: The roles of five 5d orbitals

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Supporting information

1 Supporting figures

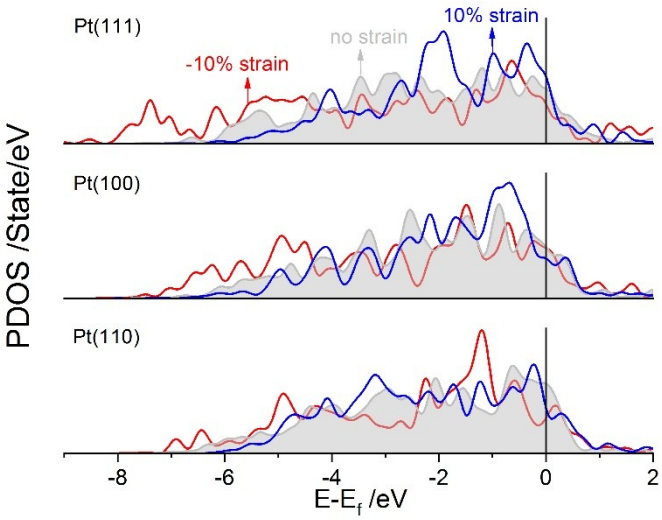

Figure S1. The PDOS of Pt(111), Pt(100) and Pt(110) when -10% strain (red), no strain (light grey) and 10% strain (blue) were applied on surface.

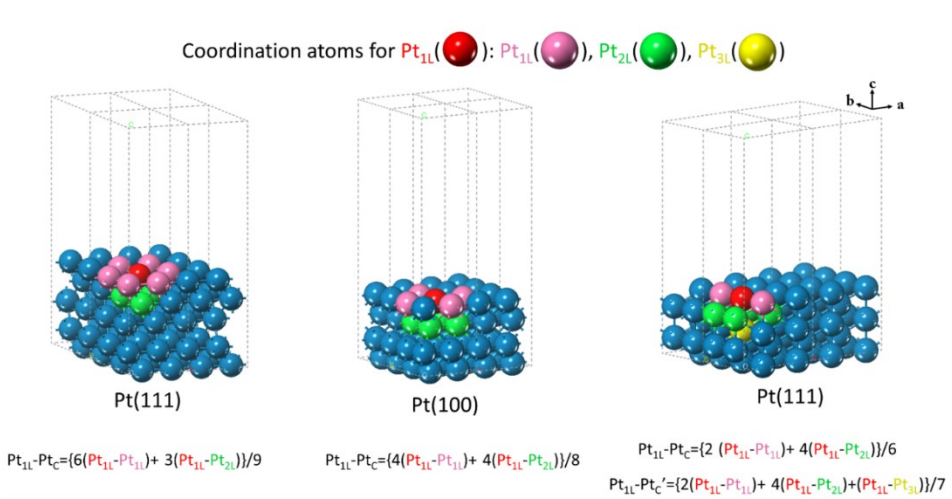

Figure S2. Diagram and definition of Pt_{1L}-Pt_C and Pt_{1L}-Pt_C' for the three low-index Pt surfaces.

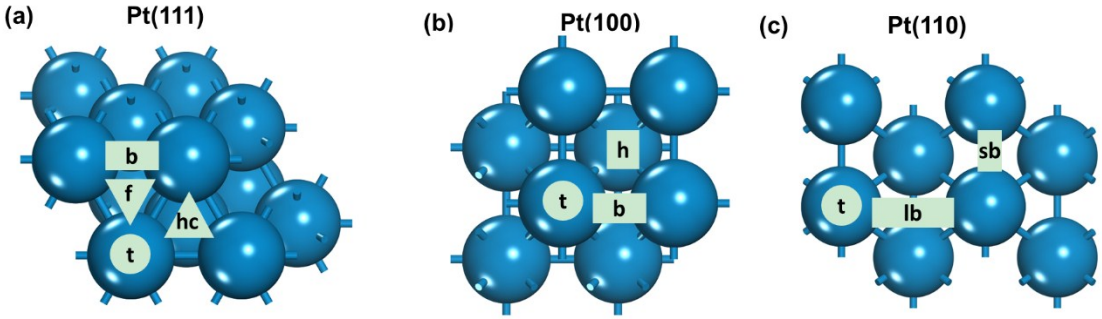

Figure S3. The adsorption sites of three low-index Pt surfaces. (a) one-fold top (t) , two-fold bridge (b) site, three-fold fcc (f) and hcp (hc) sites of Pt(111); (b) t site, b site and four-fold hollow site (h) of Pt(100); (c) t site, two-fold short bridge (sb) and long bridge (lb) sites of Pt(110).

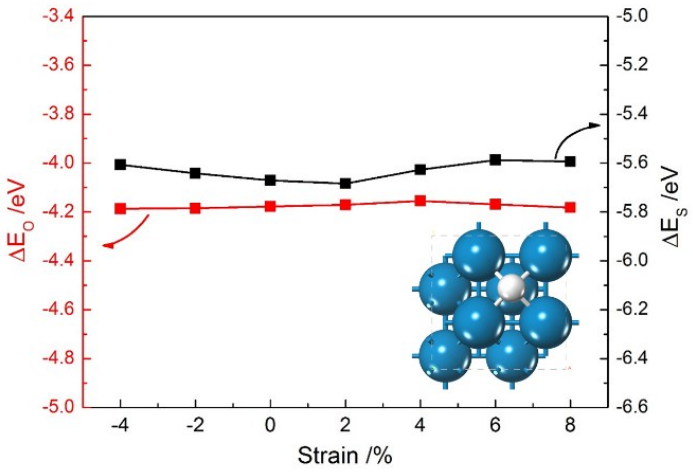

Figure S4. ΔE_a -strain curves for O and S adsorption on the four-fold hollow site of the Pt(100) surface (the inset is the structure diagram).

2 The definition of 5d-orbital center

The d-band center is calculated using the following equation:

$$\varepsilon_d = \frac{\int_{-\infty}^{E_F} E\rho_d(E)dE}{\int_{-\infty}^{E_F} \rho_d(E)dE}$$

where E is the energy with respect to the Fermi level (E_F), and $\rho_d(E)$ is the density of states projected onto all five d-orbitals of the Pt_{1L} atom at energy E.

The 5d-orbital center, which is similar to the d-band center, is defined as the weighted average energy level of states for each individual 5d orbital and is calculated by the following equation:

$$\text{5d - orbital } center = \frac{\int_{-\infty}^{E_F} E\rho(E)dE}{\int_{-\infty}^{E_F} \rho(E)dE}$$

where ρ(E) is the density of states projected onto individual d-orbitals of the Pt_{1L} atom at energy E.

To analyse the interaction between the adsorbate and the individual Pt valence orbitals, the projected crystal orbital Hamilton population (COHP) method developed by the Dronskowski group[1-

[3] was used. The integrals of the projected crystal orbital Hamilton population data (-∫pCOHP) for the interaction between the adsorbate and the individual Pt valence orbitals on the unstrained three low-index Pt surfaces are listed in Tables S4-S6.

3 Supporting tables

Table S1 The adsorption energy of adsorbates at the various sites on unstrained low-index Pt surfaces.

Surface	Adsrobate (Adsorption Site)	Adsorption Site						
		t	b	sb	lb	f	hc	h
Pt(111)	**H**	-2.750	-2.686	-	-	-2.708	-2.679	-
	O	-3.090	-3.876	-	-	-4.478	-4.015	-
	S	-3.019	-4.421	-	-	-5.100	-4.865	-
Pt(100)	**H**	-2.765	-2.916	-	-	-	-	-2.595
	O	-3.798	-4.545	-	-	-	-	-4.178
	S	-3.312	-4.707	-	-	-	-	-5.671
Pt(110)	**H**	-2.861	-	-2.911	-2.480	-	-	-
	O	-3.941	-	-4.815	-4.400	-	-	-
	S	-3.641	-	-5.018	-4.844	-	-	-

Table S2 The adsorption energy of adsorbates at the favorable adsorption sites on strained low-index Pt surfaces.

Surface	Adsorbate	Strain			
		-4% strain	**no strain**	**4% strain**	**8% strain**
Pt(111)	**H (t site)**	**-2.747**	**-2.752**	-2.735	-2.791
	H (f site)	-2.672	-2.708	**-2.787**	**-2.845**
	O (f site)	**-4.120**	**-4.478**	**-4.736**	**-5.032**
	S (f site)	**-4.581**	**-5.100**	**-5.400**	**-5.642**
Pt(100)	**H (b site)**	**-2.894**	**-2.916**	**-2.921**	**-2.906**
	O (b site)	**-4.398**	**-4.545**	**-4.657**	**-4.733**
	S (b site)	-4.528	-4.707	-4.847	-4.921
	S (h site)	**-5.607**	**-5.671**	**-5.627**	**-5.594**
Pt(110)	**H (sb site)**	**-2.924**	**-2.911**	**-2.626**	**-2.583**
	O (sb site)	**-4.824**	**-4.815**	**-4.533**	**-4.302**
	S (sb site)	-4.893	**-4.979**	**-4.698**	-4.600
	S (lb site)	**-5.021**	-4.844	-4.278	**-5.054**

Table S3. Changes in Pt_{1L}-Pt_{1L} bond length ($\Delta(Pt_{1L}$-$Pt_{1L})$) induced by atom adsorption for the Pt(111)-f site, Pt(100)-b site and Pt(110)-sb site when no surface strain is applied.

Adsorption sites	$\Delta(Pt_{1L}$-$Pt_{1L})$		
	H	**O**	**S**
Pt(111)-f site	0.046	0.081	0.087
Pt(100)-b site	0.040	0.120	0.138
Pt(110)-sb site	-0.008	0.014	0.028

Table S4. Integrals of the projected crystal orbital Hamilton population data (-∫pCOHP) for the interaction between the adsorbate and the individual Pt valence orbitals (the main interactions are highlighted in red) on an unstrained Pt(100) surface.

Atom	-∫pCOHP for Pt(111) surface					
	6s	$5d_{xy}$	$5d_{yz}$	$5d_{z^2}$	$5d_{xz}$	$5d_{x^2-y^2}$
H	0.898	0	0.813	0.008	0	0.334
O	0.133	0.135	0.535	0.259	0.178	0.184

S	0.215	0.091	0.359	0.356	0.244	0.105
O (h site)	0.248	0.194	0.157	0.037	0.157	0.080
S (h site)	0.328	0.172	0.223	0.106	0.223	0.148

Table S5. -∫pCOHP for the interaction between the adsorbate and the individual Pt valence orbitals (the main interactions are highlighted in red) on an unstrained Pt(111) surface.

Atom	**-∫pCOHP for Pt(111) surface**					
	6s	$5d_{xy}$	$5d_{yz}$	$5d_{z^2}$	$5d_{xz}$	$5d_{x^2-y^2}$
H	0.746	0.275	0.124	0.002	0.368	0.096
O	0.181	0.122	0.712	0.688	0.051	0.217
S	0.261	0.129	0.380	0.302	0.102	0.108

Table S6. -∫pCOHP for the interaction between the adsorbate and the individual Pt valence orbitals (the main interactions are highlighted in red) on an unstrained Pt(110) surface.

	-∫pCOHP for Pt(110) surface

	6s	$5d_{xy}$	$5d_{yz}$	$5d_{z^2}$	$5d_{xz}$	$5d_{x^2-y^2}$
H	0.911	0	0.812	0.022	0	0.280
O	0.177	0.149	0.521	0.303	0.249	0.128
S	0.251	0.141	0.279	0.393	0.322	0.058

Reference:

[1] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617–8624.

[2] V. L. Deringer, A. L. Tchougréeff, R.Dronskowski, *J. Phys. Chem. A* **2011**, *115*, 5461–5466.

[3] S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Comput.Chem.* **2013**, *34*, 2557–2567.