Supplementary information

Descriptor Study by Density Functional Theory Analysis for the Direct Synthesis of Hydrogen Peroxide using Palladium-Gold and Palladium-Mercury Alloy Catalysts

Mawan Nugraha[a], Meng-Che Tsai[a], Wei-Nien Su[b], Hung-Lung Chou[b*], Bing Joe Hwang[a*]

[a]*Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10617, Taiwan*

[b]*Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10617, Taiwan*

[*]Corresponding authors: Hung-Lung Chou (hlchou@mail.ntust.edu.tw) and Bing-Joe Hwang (bjh@mail.ntust.edu.tw)

The figure S1 is electron density difference (EDD) which calculated using formula;

$$Q_{diff} = Q_{A/surf} - Q_{surf} - Q_A$$

where $Q_{A/surf}$, Q_{surf} and Q_A represent the total electron density matrix at the adsorbate-bonded surface, the surface and the single adsorbate molecule, respectively.

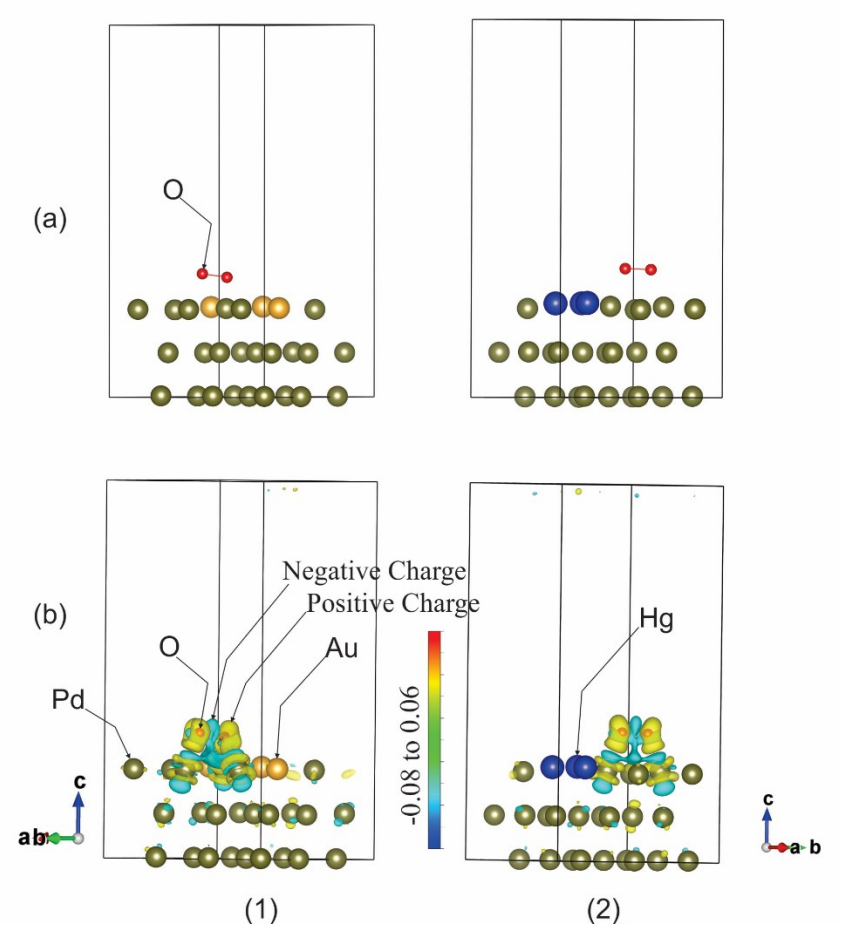

Figure S1. Electron density difference (EDD) calculation on O_2-surface, (a) before and (b) after calculation. EDD change of (1) O_2-Pd_6Au_3/Pd(111) and, (2) O_2-Pd_6Hg_3/Pd(111) with color range of −0.08 to 0.06 and starts from blue to red.

We have recalculated all possible arrangements of the surface based on one Palladium atom surrounded by three Hg atoms, referring to previous work [3], which was established and verified by both experiment and theoretical studies. We also showed the symmetry inequivalent arrangements of the surface atoms only, as seen in Figure S2, The binding energy (E_b) in eV/atom of these models (Figure S2) can be found in Table S1.

The Pd_6Au_3/Pd(111) configurations seen in Figure S2(a) and (b) have the total energies of slab -125.99 eV and -125.88 eV, respectively. The calculated binding energies are identical as -1.04 eV/atom for two different configurations in Figure S2(a) and (b), respectively, as summarized in Table S1. In addition, the Pd_6Hg_3/Pd(111) configurations in Figure S2(c) and (d) have the total energies of slab -118.83 eV and -118.36 eV, while the binding energies are -0.89 eV/atom and -0.92 eV/atom, respectively.

Because the difference of stability, indicated by E_b, between the atom arrangements is not significant (less than 4%), we chose the model of Figure S2 (b) and (d) for our calculation and to neglect the effect of different surface arrangements between Pd-Au and Pd-Hg alloy surface.

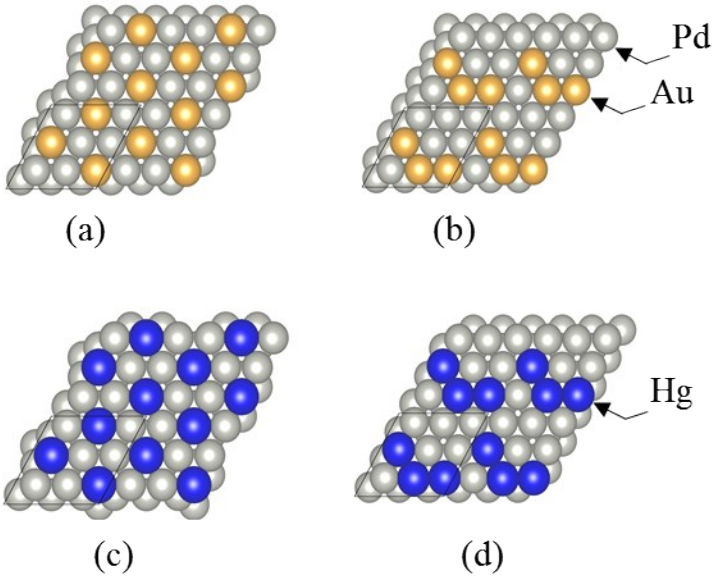

Figure S2. Surface configurations of the three Au (a and b) or Hg (c and d) atoms surrounding Pd central atom in a top view.

Table S1 Binding energy (E_b) of possible atom arrangement, eV/atom, calculated based on Figure S2

Catalyst	The binding energy (E_b) in different surface configurations (eV/atom)	
Pd_6Au_3/Pd(111)	(a)	(b)
	-1.04	-1.04
Pd_6Hg_3/Pd(111)	(c)	(d)
	-0.89	-0.92

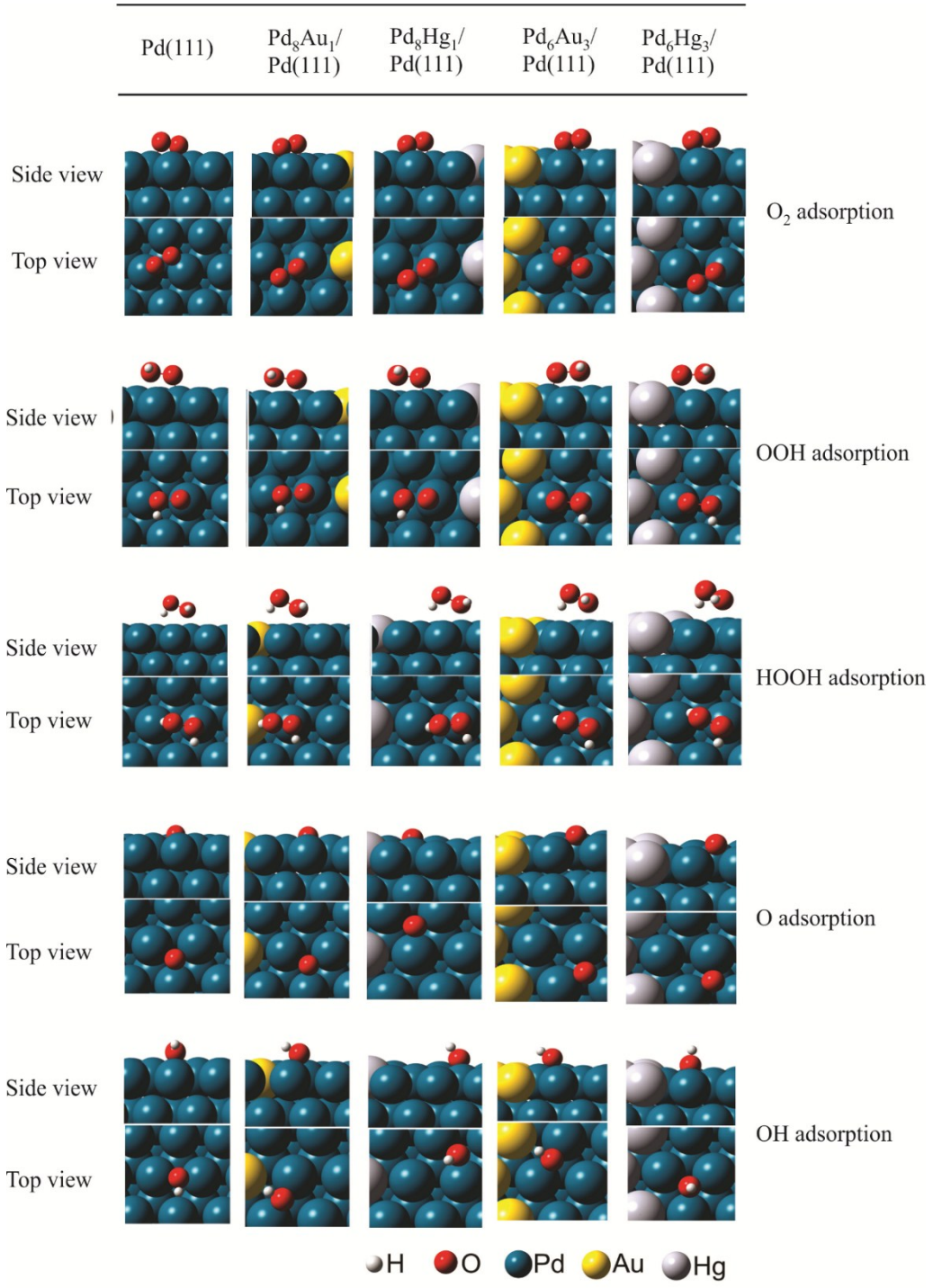
Pd(111)
Pd8Au1/ Pd(111)
Pd8Hg1/ Pd(111)
Pd6Au3/ Pd(111)
Pd6Hg3/ Pd(111)
Side view
Top view
O2 adsorption
OOH adsorption
HOOH adsorption
O adsorption
OH adsorption
H
O
Pd
Au
Hg

Figure S3. The most stable adsorption configuration of species of O_2, OOH, HOOH, OH and O on the surfaces of Pd(111), Pd_8Au_1/Pd(111), Pd_8Hg_1/Pd(111), Pd_6Au_3/Pd(111) and Pd_6Hg_3/Pd(111).

Table S2. Activation barriers (E_a) and reaction energy (ΔE) of elementary steps in the synthesis of H_2O_2 on Pd_6Au_3/Pd(111), Pd_8Au_1/Pd(111), Pd(111), Pd_8Hg_1/Pd(111), Pd_6Hg_3/Pd(111).

Surface	Elementary Reactions				
		O_2* → 2O*	O2* + H* → OOH*	OOH* + H* → HOOH*	OOH* + H* → H*+ O* + OH*
Pd_6Au_3	E_a, eV	1.23	0.62	0.23	0.19
	ΔE, eV	-0.72	-0.01	-0.32	-1.21
Pd_8Au_1	E_a, eV	0.74	0.66	0.21	0.17
	ΔE, eV	-0.12	0.11	-0.241	-1.64
Pd(111)	E_a, eV	0.69	0.66	0.35	0.03
	ΔE, eV	-0.17	0.18	-0.044	-1.27
Pd_8Hg_1	E_a, eV	0.65	0.62	0.59	0.50
	ΔE, eV	-0.02	-0.08	-0.012	-1.43
Pd_6Hg_3	E_a, eV	0.63	0.52	0.22	0.23
	ΔE, eV	-0.49	0.24	-0.58	-1.10

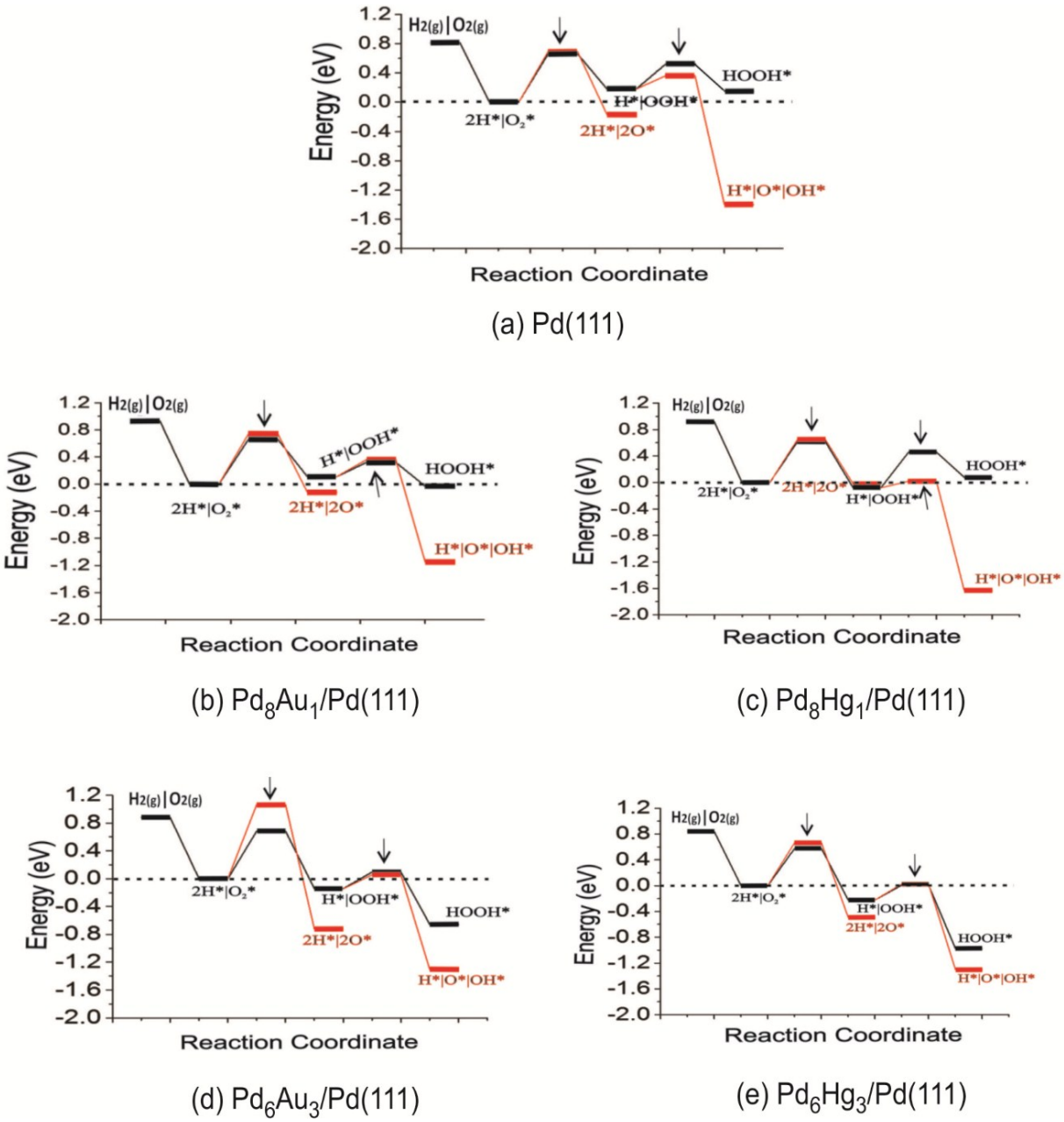

Figure S4. The trend of potential energy surface, drawn using information in Table S1, for selectivity determining steps along the two competitive pathways: desirable path (black) and undesirable one (red) on (a) Pd(111), (b) Pd_8Au_1/Pd(111), (c) Pd_8Hg_1/Pd(111), (d) Pd_6Au_3/Pd(111) and (e) Pd_6Hg_3/Pd(111). The arrow indicates the activation energy barrier (E_a).