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

Supplementary Information:

Why Bromine Squares Palladium Off? An *Ab Initio* Study of Brominated Palladium and its Nanomorphology

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I. BULK Pd, MOLECULE Br_2 AND CLEAN Pd SURFACES

TABLE I. Detailed comparison of the lattice constant, cohesive energy, and bulk modulus of bulk Pd (FCC) with experimental and theoretical data.

Bulk Pd	VASP	DMol^3		Ref.			
	PBE[a]	PBE[a]	PBEsol[a]	Exp.	LDA	PBE	PBEsol
Lattice constant (Å)	3.954	3.971	3.903	3.876[b]	3.850[c]	3.950[c]	3.876[b]
(Error % with exp.)	(2.0%)	(2.5%)	(0.7%)	-	-	-	-
Cohesive energy (eV)	-3.702	-3.581	-4.283	-3.907[b]	-5.040[c]	-3.630[c]	-4.426[b]
(Error % with exp.)	(-5.2%)	(-8.3%)	(9.6%)	-	-	-	-
Bulk modulus (GPa)	-	160.92	193.05	181[d]	220 [e]	163 [e]	204[f]
(Error % with exp.)	-	(-2.3%)	(-5.4%)	-	-	-	-

[a] This work
[b] Reference 1
[c] Reference 2
[d] Reference 3
[e] Reference 4
[f] Reference 5

TABLE II. Detailed comparison of the bond length and binding energy of molecule Br_2 with experimental and theoretical data.

Br_2	VASP	DMol^3		Ref.			
	PBE[a]	PBE[a]	PBEsol[a]	Exp.	LDA	PBE	PBEsol
Bond length(Å)	2.307	2.344	2.322	2.283[b]	2.270[c]	-	-
(Error % with exp.)	(1.0%)	(2.7%)	(1.7%)	-	-	-	-
Binding energy (eV)	-1.266	-1.135	-1.318	-1.220[d]	-	-	-
(Error % with exp.)	(-2.3%)	(-7.0%)	(8.0%)	-	-	-	-

[a] This work
[b] Reference 6
[c] Reference 7
[d] Reference 3

TABLE III. Calculated structural parameters for clean surfaces of clean Pd(100), (110), (111), (210), (211), (311), and (331) and the reported reference values.

Pd Surface	Method	Δd_{12} (%)	Δd_{23} (%)
(100)	PBEsol[a]	-1.08	-0.06
	PBE[b]	-1.30	0.00
	Exp.[b]	3.0 ± 1.5	-1.0 ± 1.5
(110)	PBEsol[a]	-8.20	$+2.68$
	PBE[b]	-8.49	$+3.47$
	Exp.[b]	$+5.8 \pm 2.2$	$+1.0 \pm 2.2$
(111)	PBEsol[a]	-0.03	-0.43
	PBE[b]	-0.01	-0.41
	Exp.[b]	$+1.3 \pm 1.3$	-1.3 ± 1.3
(210)	PBEsol[a]	-15.15	-4.04
	PW91[c]	-17	-3
	Exp.[c]	-3	$+7$
(211)	PBEsol[a]	-11.67	-10.52
	PW91[c]	-12.3	-13
(311)	PBEsol[a]	-12.39	$+6.74$
	PW91[d]	-12.4	$+6.9$
(331)	PBEsol[a]	-13.25	-4.22
	PW91[c]	-12	-7.7

[a] This work

[b] Reference 8

[c] Reference 9

[d] Reference 10

II. $E_\mathrm{b}(\Theta)$ FOR LOW MILLER-INDEX SURFACES: Br/Pd AND K/Pd

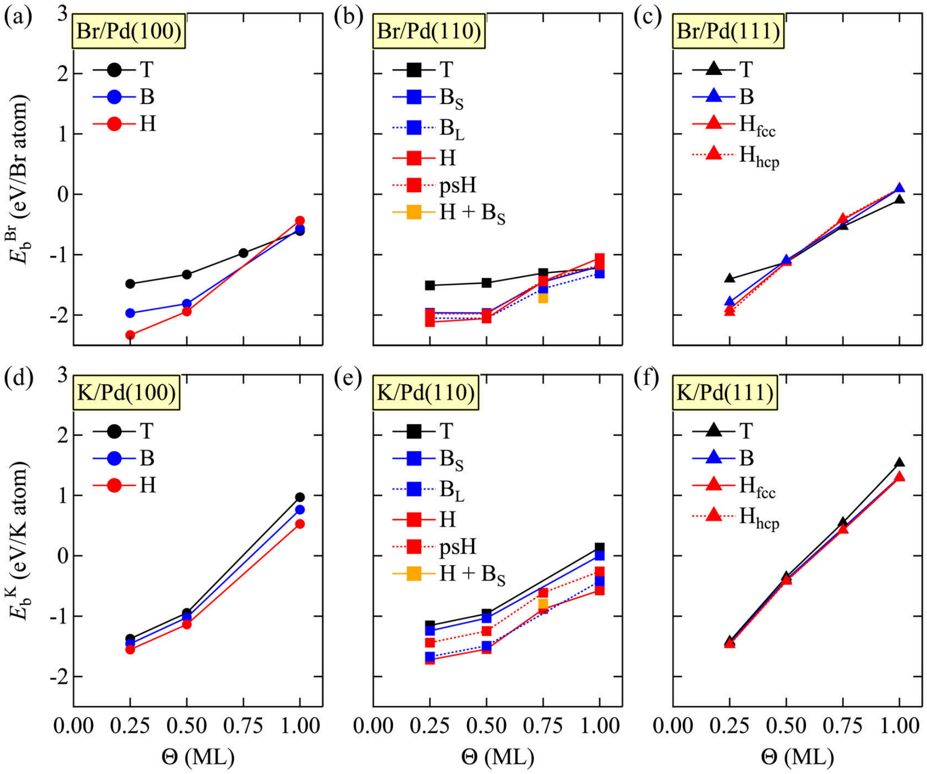

FIG. 1. (Color online) Averaged binding energies of Br (and K) in various symmetry-unique binding sites on Pd surfaces as a function of Br (and K) surface coverage, Θ: (a) Br/Pd(100), (b) Br/Pd(110), (c) Br/Pd(111), (d) K/Pd(100), (e) K/Pd(110), and (f) K/Pd(111).

III. ADSORBATE-SUBSTRATE SYSTEM I: Br/Pd

TABLE IV. Analyzed structural properties for different Br coverage on (100), (110), (111) and (210) Pd surfaces. $d_{\mathrm{Pd-Br}}$ is the average bond length of nearest atoms between Pd and Br. d_{Br1} is the minimum vertical height of Br on utmost Pd surface. Δd_{12} is the interlayer space between the first and second Pd layer. The value is calculated with the center of mass of nth layer. Δd_{23} is the interlayer space between the second and third Pd layer. $E_{\mathrm{b}}^{\mathrm{Br}}$ is the average binding energy of Br.

Br/Pd	Structure	$d_{\mathrm{Pd-Br}}$ (Å)	d_{Br1} (Å)	Δd_{12} (%)	Δd_{23} (%)	$E_{\mathrm{b}}^{\mathrm{Br}}$ (eV/Br atom)
(100)	H (0.25 ML)	2.59	1.66	+0.47	+0.01	−2.33
	H (0.50 ML)	2.63	1.77	+0.22	−0.30	−1.94
(110)	H (0.25 ML)	2.71	1.24	−2.64	+1.15	−2.12
	H (0.50 ML)	2.72	1.30	+1.67	−0.18	−2.06
	H+$\mathrm{B_S}$ (0.75 ML)	2.58	1.11	+0.94	−1.13	−1.72
(111)	$\mathrm{H_{hcp}}$ (0.25 ML)	2.55	1.97	−0.21	−0.28	−1.96
	$\mathrm{H_{hcp}}$ (0.50 ML)	2.69	2.13	+0.03	−0.06	−1.13
(210)	psH (0.17 ML)	2.55	1.44	−8.04	−5.44	−2.15
	psH (0.33 ML)	2.55	1.45	+0.98	−9.10	−2.11
	T+H+$\mathrm{B_S}$ (0.50 ML)	2.52	0.63	+1.70	+2.52	−1.51

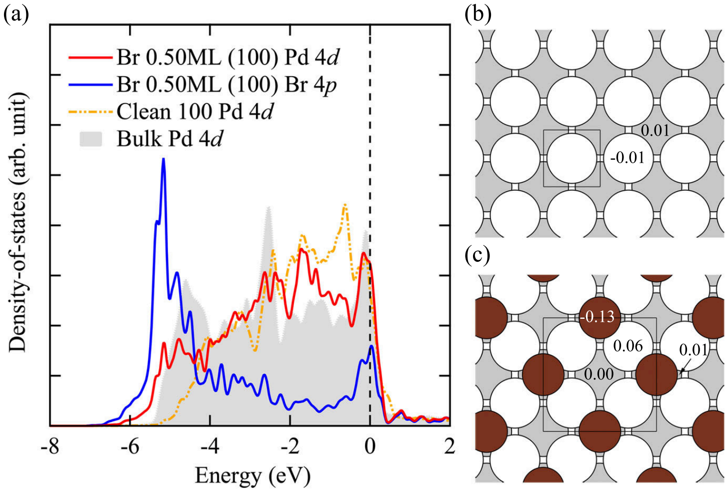

FIG. 2. (Color online) (a) Projected density-of-states (pDOS) for $p(2 \times 2)$-2Br$_\mathrm{H}$, i.e. with Br in the hollow site at the surface coverage of 0.5 ML. The Pd $4d$ pDOS of clean Pd(100) and that of bulk Pd have been included for comparison. Hirshfeld charges (in units of $|e|$) for Pd and Br are shown for (b) clean Pd(100) and (c) $p(2 \times 2)$-2Br$_\mathrm{H}$, where the top-views of the corresponding surfaces are illustrated where the dark brown circles represent the Br atoms while the white and light gray circles are the top-most and second layer Pd atoms, respectively. The more electronegative Br atom is found to gain electrons ($-0.13\,|e|$) from its surrounding Pd atoms ($0.06\,|e|$).

To analyze the nature of bonding, we calculate the projected density-of-states (pDOS) for selected systems and also report the Hirshfeld population charges[11] which have been shown to yield an optimal partitioning of atomic densities which is less sensitive to the quality of the basis set used. In this scheme, integration of the atomic deformation densities (i.e. the total densities of bonded atoms minus that of free atoms) is used to assign the net atomic charges and multipole moments which concisely exemplify the overall charge redistribution.

Since we conclude that $p(2 \times 2)$-2Br$_\mathrm{H}$, i.e. with Br in the hollow site at the surface coverage of 0.5 ML, plays a critical role in the morphology evolution of Pd nanoparticle, we investigate the electronic structure of this structure. To analyze the bonding properties of Br on this surface, we calculate and plot the surface pDOS as well as the surface atomic charges due to the Hirshfeld charges partitioning scheme[11] in Fig. 2. In Fig. 2a, we see that the $4d$ band width of the Pd(100) surface atom is narrowed as compared to that of bulk Pd – commonly understood as a consequence of undercoordination of surface bonds.[12,13] Upon Br adsorption, a renormalization of the Br atomic $4p$ states to lower energies can be seen and a re-brodening of the $4d$ states of the Pd(100) surface atom to lower energies is observed. This hybridization of the Br $4p$ and Pd $4d$ states puts a heavier weight on the bonding states near the bottom of the Pd $4d$ band while partially filling of the antibonding states near the top of the Pd $4d$ band. This corroborates well with the strong binding of Br on this surface. To understand the charge transfer between Br and Pd on this surface, the Hirshfeld charges for the clean Pd(100) surface and $p(2 \times 2)$-2Br$_\mathrm{H}$ are depicted in Figs. 2b and 2c, respectively. Looking at the corresponding charges, we clearly see that Br, being more electronegative, bears a negative charge ($-0.13\,|e|$) while the nearest surface Pd atoms loose charges ($0.06\,|e|$ each). This charge analysis supports the observations in the pDOS described above.

IV. ADSORBATE-SUBSTRATE SYSTEM II: K/Pd

TABLE V. Analyzed structural properties for different K coverage on (100), (110), (111) and (210) Pd surfaces. $d_{\mathrm{Pd-K}}$ is the average bond length of nearest atoms between Pd and K. d_{K1} is the minimum vertical height of K on utmost Pd surface. Δd_{12} is the interlayer space between the first and second Pd layer. The value is calculated with the center of mass of nth layer. Δd_{23} is the interlayer space between the second and third Pd layer. $E_{\mathrm{b}}^{\mathrm{K}}$ is the average binding energy of K.

K/Pd	Structure	$d_{\mathrm{Pd-K}}$ (Å)	d_{K1} (Å)	Δd_{12} (%)	Δd_{23} (%)	$E_{\mathrm{b}}^{\mathrm{K}}$ (eV/K atom)
(100)	H (0.25 ML)	3.13	2.44	−0.85	+0.21	−1.55
	H (0.50 ML)	3.15	2.47	−0.33	+0.28	−1.14
(110)	H (0.25 ML)	3.18	2.06	−8.20	+3.61	−1.72
	H (0.50 ML)	3.17	2.08	−8.09	+4.30	−1.55
(111)	$\mathrm{H_{hcp}}$ (0.25 ML)	3.05	2.52	+0.52	−0.14	−1.47
(210)	3H (0.17 ML)	3.25	1.75	−20.04	−0.16	−1.63
	3H (0.33 ML)	3.20	1.75	−16.96	−0.77	−1.54

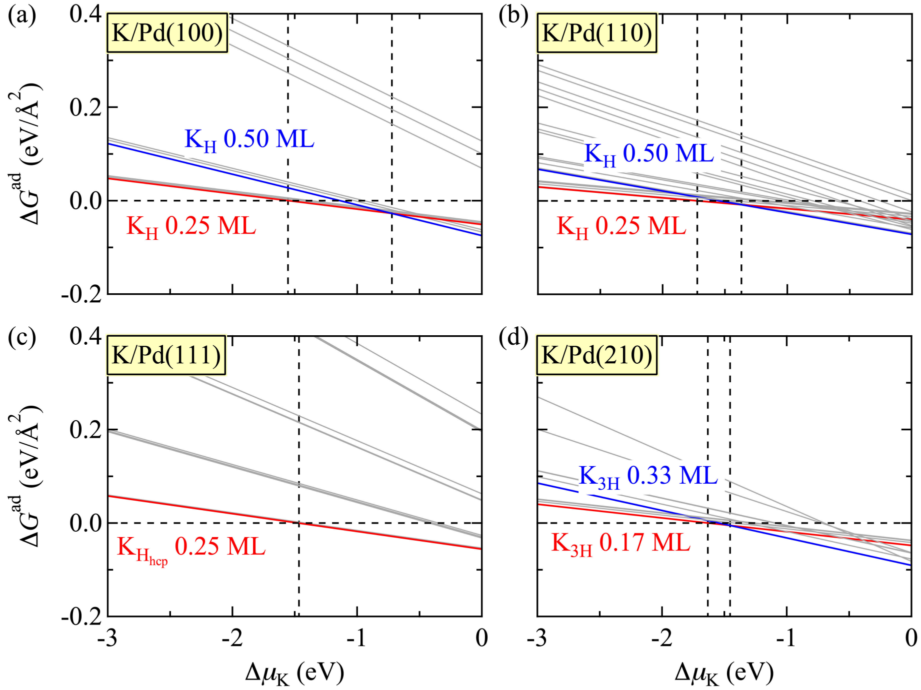

FIG. 3. (Color online) Calculated Gibbs free energy of adsorption of K, ΔG^{ad} on (a) Pd(100), (b) Pd(110), (c) Pd(111), and (d) Pd(210) as a function of the K chemical potential change, $\Delta\mu_{\mathrm{K}}$. The horizontal dashed line (at $\Delta G^{\mathrm{ad}} = 0$) refers to the stable clean (K-free) Pd surface. For each surface, the red and blue lines indicate the first and second stable surface phase with increasing $\Delta\mu_{\mathrm{K}}$, respectively. Other less stable surface structures are represented in gray lines. To guide the eye, the vertical green dashed lines indicate a surface phase change in stability.

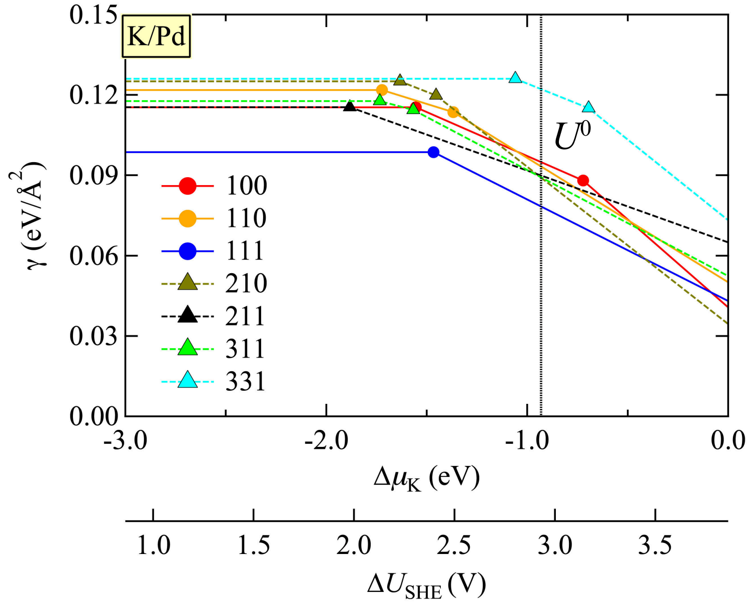

FIG. 4. (Color online) Calculated surface free energy of K/Pd surfaces as a function of the K chemical potential change, $\Delta\mu_K$, and the corresponding electrode potential change, ΔU with respect to the standard hydrogen electrode, U_{SHE}. The variation of surface free energy for the low Miller-index surfaces are traced using solid lines while those for the high Miller-index surfaces are shown in dotted lines. To guide the eye, the black vertical dashed line indicates the oxidation potential of K ($U^0 = 2.924\,V$).

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