Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Benzene and hydrogen adsorption on binary Pt_3M alloys and surface alloys: a DFT study

Supporting Information

Maarten K. Sabbe, Lucia Laín, Marie-Françoise Reyniers* en Guy B. Marin

Laboratorium voor Chemische Technologie, Universiteit Gent, Krijgslaan 281 S5, B-9000 Gent, Belgium

Table S1 Comparison of 4- and 5-layered slabs for Pt_3Cu and Pt_3Pd bulk alloys: Surface antisegregation energies $\Delta E_{antiseg}$ (eV) for empty surfaces and for surfaces with benzene adsorbed at the most stable site ($\Delta E_{antiseg}^{ads}$), calculated in a 4x4 unit cell and expressed per (anti)segregating solute atom M.

Non-segregated alloys	**Restructured alloys**	$\Delta E_{antiseg}$ (eV)		$\Delta E_{antiseg}^{ads}$ (eV)	
		4 layers	5 layers	4 layers	5 layers
Bulk alloys	*M antisegregation*				
Pt_3Cu	$Pt/PtCu/Pt_3Cu$	-0.16	-0.17	-0.07	-0.10
Pt_3Pd	$Pt/PtPd/Pt_3Pd$	-0.03	-0.02	-0.02	-0.02

Table S2: Comparison of 4- and 5-layered slabs for Pt_3Cu and Pt_3Pd bulk alloys: Benzene adsorption energies.

Alloy	Adsorption site	E_{ads}(eV)	
		4 layers	5 layers
Non-segregated			
Pt_3Cu	Pt_3-hcp^0	-0.89	-0.86
Pt_3Pd	Pt_2-bri^{30}-M	-1.20	-1.32
Antisegregated			
$Pt/PtCu/Pt_3Cu$	hcp-M^0-Pt_2M	-0.36	-0.35
	bri-M-Pt_2M/fcc-PtM_2	-0.53	-0.56
$Pt/PtPd/Pt_3Pd$	bri-M-Pt_2M/fcc-PtM_2	-1.16	-1.31

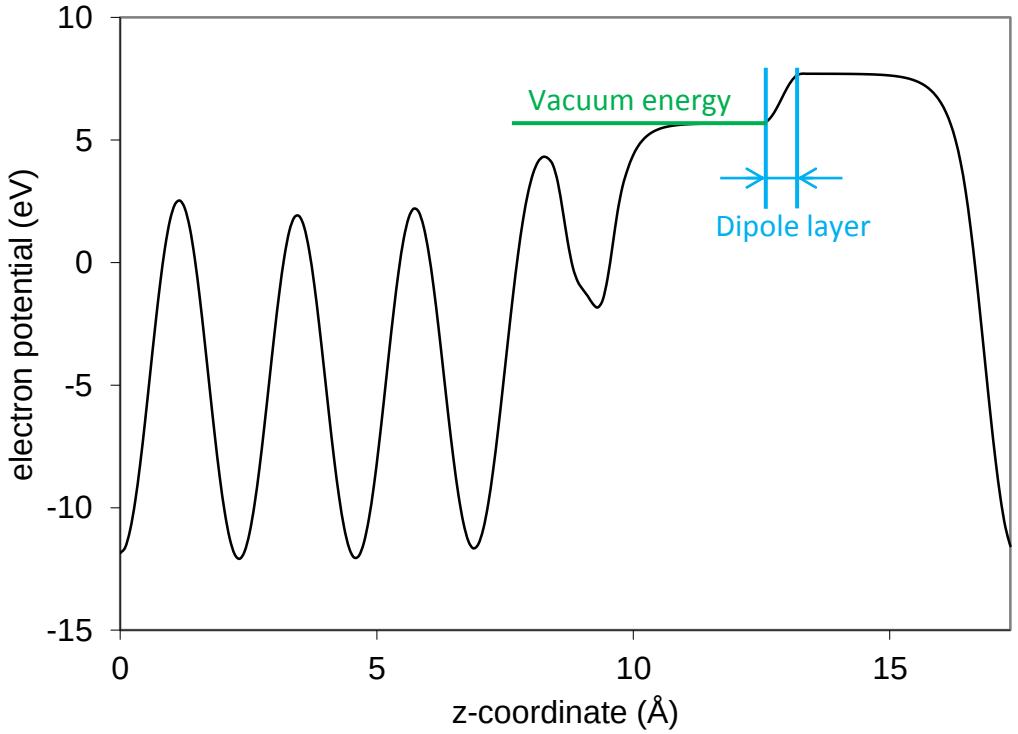

Figure S1: Calculated electron potential along the z-axis of a unit cell, averaged out over the x and y coordinates, with indication of the dipole layer and the vacuum energy (benzene adsorbed on 4-layered Pt(111)).

The benzene-surface distances on Pt_3M/Pt surface alloys, are with 202.1 to 205.3 pm very similar to the distance of 203.3 pm on Pt(111). For bulk alloys, benzene-surface distances are larger than for the surface alloys and for Pt(111), about 210-214 pm for antisegregated Pt/PtM/Pt_3M compared to 203-205 pm on surface alloys, related to the weaker adsorption energies of benzene on bulk alloys. The largest distances, in the range of 300 pm, are clearly observed on the Au/Pt and Ag/Pt alloys, confirming benzene only physisorbs on these. Non-segregated Pt_3Pd(111) has both a similar adsorption energy and *d*(Pt-B) distance to pure Pt. The distance between the first layer and the second layer *d(1,2)* is very similar for most alloys, about 230 pm, only for the antisegregated alloys the distance is shorter by about 5 %, while the Ag and Au monolayer on Pt(111) have a significantly larger separation between the 2 top layers (237 to 241 pm).

Table S3 Optimized FCC lattice constants *a* compared to experimentally observed lattice constants and those obtained by Ma and Balbuena [47] (Å).

Bulk alloys	**Experimental**	**Ma** [a]	**This work**
Pt	3.920[b]	3.970	4.011
Pt_3Fe	3.900[c]	3.906	3.923
Pt_3Co	3.831[e]	3.889	3.880
Pt_3Ni	3.841[d]	3.880	3.889
Pt_3Cu	3.860[f]	3.903	3.911
Pt_3Pd	3.916[g]	3.961	3.975
Pt_3Ag	-	4.002	4.013
Pt_3Au	-	4.019	4.027

[a] See ref. [47]; [b] See ref. [86]; [c] See ref. [42]; [d] See ref. [87]; [e] See refs. [88, 89]; [f] See ref. [90]; [g] See ref. [91].

Table S4 Distances (pm) between the center of the benzene molecule and the first layer (*d*(Pt-B)), with benzene adsorbed at the preferred site, and between the top and the second layer (*d*(1,2)) in the non-covered alloys, on the most stable Pt_3M/Pt surface and Pt_3M bulk alloys. For *d*(Pt-z), the position of the first layer is determined by the center of the atoms to which benzene is bound..

Surface alloys	**C_6H_6 site**	***d*(Pt-z)** pm	***d*(1,2)** pm	**Bulk alloys**	**C_6H_6 site**	***d*(Pt-B)** pm	***d*(1,2)** pm
Pt/Pt_3Fe/Pt	bri-M[30]	205.3	224.1	**Pt/PtFe/Pt_3Fe**	bri-M-Pt_3/fcc-PtM_2	213.7	224.8
Pt/Pt_3Co/Pt	bri-M[30]	205.1	224.0	**Pt/PtCo/Pt_3Co**	bri-M-	213.2	225.6

					Pt_3/fcc-PtM_2		
Pt/Pt_3Ni/Pt	bri-M[30]	204.5	224.0	**Pt/PtNi/Pt_3Ni**	bri-M-Pt_3/fcc-PtM_2	211.3	225.7
Pt/Pt_3Cu/Pt	bri-M[30]	204.5	224.4	**Pt/PtCu/Pt_3Cu**	bri-M-Pt_3/fcc-PtM_2	210.2	224.9
Pt_3Pd/Pt	Pt_3-hcp[0]	202.1	229.2	**Pt_3Pd**	Pt_2-bri[30]-M	206.4	230.8
Pt_3Ag/Pt	Pt_3-hcp[0]	203.1	231.7	**Ag/Pt**	Bri	294.6	237.8
Pt_3Au/Pt	Pt_3-hcp[0]	204.4	233.1	**Au/Pt**	bri	**309.9**	241.4
Pt (111)	Pt_3-hcp[0]	203.3	229.9	**Pt (111)**	bri	**203.9**	229.9

Table S5: C-C bond distances (Å), orthogonal distance between the carbon and hydrogen plane (Å) and the off-planarity angles of the C-H bonds with the surface plane (degrees). The orthogonal distance between the carbon and hydrogen plane is calculated as the difference between the average z-coordinate of the C atoms and that of the H atoms.

Alloy	**site**	C-C bond distances (Å)						C-H plane (Å)	Angle of C-H bonds with surface plane (degrees):					
surface alloys – non-segregated *(Pt_3-fcc site)*														
Pt_3Fe/Pt		1.436	1.436	1.436	1.467	1.467	1.467	0.379	19.7	20.0	20.0	20.4	21.1	21.1
Pt_3Co/Pt		1.436	1.436	1.436	1.466	1.466	1.466	0.372	19.1	19.4	19.5	20.0	20.8	20.8
Pt_3Ni/Pt		1.436	1.436	1.437	1.465	1.465	1.466	0.366	18.7	18.9	19.2	19.6	20.6	20.6
Pt_3Cu/Pt		1.435	1.435	1.436	1.465	1.465	1.466	0.373	19.1	19.4	19.6	20.1	21.0	21.0
Pt_3Pd/Pt		1.436	1.436	1.437	1.463	1.464	1.465	0.372	19.1	19.2	19.4	19.8	21.0	21.1
Pt_3Ag/Pt		1.433	1.433	1.433	1.464	1.465	1.465	0.383	19.6	19.9	19.9	20.5	21.6	21.7
Pt_3Au/Pt		1.429	1.430	1.430	1.464	1.465	1.465	0.366	18.7	19.0	19.2	19.4	20.6	20.8
surface alloys - antisegregated *(bri-M^{30} site)*														
Pt/Pt_3Fe/Pt		1.430	1.430	1.466	1.468	1.470	1.470	0.415	16.2	16.9	17.7	19.2		32.0
Pt/Pt_3Co/Pt		1.430	1.431	1.467	1.468	1.470	1.470	0.417	16.3	17.0	17.7	19.3		32.2
Pt/Pt_3Ni/Pt		1.431	1.431	1.467	1.469	1.471	1.471	0.417	16.3	17.1	17.3	19.0	32.5	33.5
Pt/Pt_3Cu/Pt		1.431	1.431	1.467	1.468	1.470	1.470	0.416	16.2	16.8	17.7	19.2		32.8
Pt/Pt_3Pd/Pt		1.433	1.434	1.469	1.470	1.472	1.472	0.427	16.9	17.4	17.7	19.2		34.5
Pt/Pt_3Ag/Pt		1.432	1.432	1.467	1.468	1.471	1.471	0.426	16.9	17.6	17.7	19.5		34.3
Pt/Pt_3Au/Pt		1.433	1.434	1.469	1.470	1.472	1.472	0.432	17.4	17.8	18.1	19.6	33.5	34.7

bulk alloys – non-segregated *(Pt_3-hcp^0 site)*													
Pt_3Fe		1.431	1.432	1.433	1.462	1.463	1.463	0.363	18.1	18.6	18.7	19.5	20.7	21.0
Pt_3Co		1.431	1.433	1.433	1.461	1.462	1.462	0.343	16.3	16.6	18.1	19.2	19.5	20.3
Pt_3Ni		1.433	1.433	1.434	1.460	1.461	1.462	0.333	17.2	17.2	17.3	17.6	18.5	18.8
Pt_3Cu		1.430	1.430	1.431	1.458	1.458	1.459	0.326	16.3	16.4	17.3	17.8	18.2	18.5
Pt_3Pd		1.435	1.436	1.437	1.461	1.462	1.465	0.372	17.2	18.2	18.6	20.5	22.4	22.9
Pt_3Ag		1.431	1.432	1.432	1.459	1.460	1.461	0.371	18.2	18.8	19.5	20.2	21.3	21.5
Pt_3Au		1.430	1.430	1.431	1.462	1.463	1.464	0.361	17.2	18.2	18.2	19.6	21.3	21.7
bulk alloys – antisegregated *(bri-M-Pt_2M/fcc-PtM_2 site)*													
$Pt/PtFe/Pt_3Fe$		1.419	1.430	1.452	1.458	1.458	1.460	0.366	14.3	14.5	15.6	17.3	27.7	28.9
$Pt/PtCo/Pt_3Co$		1.421	1.432	1.456	1.459	1.461	1.463	0.367	14.0	14.5	14.9	16.3	29.4	29.7
$Pt/PtNi/Pt_3Ni$		1.424	1.433	1.458	1.463	1.464	1.466	0.382	13.9	15.2	16.7	16.9	28.1	33.3
$Pt/PtCu/Pt_3Cu$		1.424	1.435	1.458	1.461	1.463	1.464	0.381	14.0	15.9	16.2	16.6	29.5	31.2
$Pt/PdPd/Pt_3Pd$		1.432	1.434	1.468	1.469	1.473	1.473	0.431	17.0	17.4	18.7	19.9	32.4	35.2
$Pt/PtAg/Pt_3Ag$		1.429	1.436	1.462	1.468	1.469	1.470	0.435	16.3	18.2	19.5	21.7	32.1	34.1
$Pt/PtAu/Pt_3Au$		1.432	1.436	1.467	1.471	1.472	1.473	0.439	16.3	17.0	20.3	21.4	33.4	35.1
bulk alloys - fully segregated *(site indicated)*													
Pd/Pt	bridge	1.429	1.429	1.447	1.447	1.448	1.448	0.342	14.8	15.2	16.1	16.2	23.5	23.9
Ag/Pt	fcc	1.398	1.398	1.398	1.402	1.402	1.403	0.000	0.0	0.0	0.0	0.1	0.5	0.6
Au/Pt	fcc	1.397	1.398	1.398	1.401	1.401	1.402	-0.006	0.0	0.0	0.0	0.0	0.0	0.1

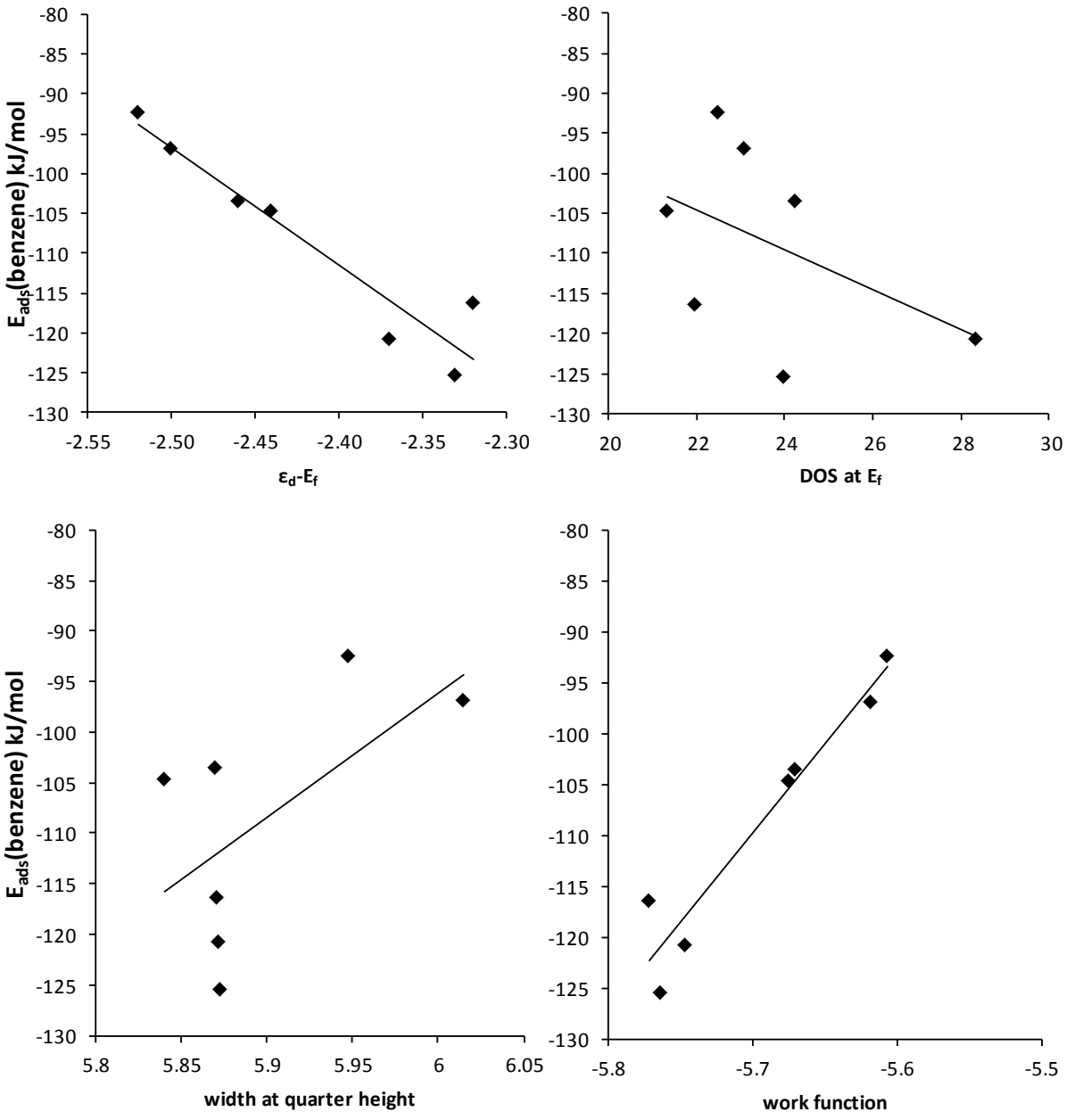

Figure S2: Benzene adsorption energies on the bri-M[30] site of antisegregated surface alloys ($Pt/Pt_3M/Pt_3M$), vs. (clockwise from top left) the d-band center, density at the Fermi level, work function and width at quarter height, with indication of the solute atom M. The R^2 values for the linear regressions are resp. 0.95, 0.76, 0.86 and 0.88. Dotted line in work function is logarithmic fit E_{ads} = 44 +111*log(ϕ+5.83).

Table S6: d-band centers (eV) and DOS at Fermi level (for 4x4 unit cells) for all alloys studied in this work, compared to literature values. Apart from ref. [1], the referred d-band centers are approximate since they have been read from graphs in the respective papers.

	Full top layer		Only Pt atoms in top layer		Reference d-band centers
	Ec-Ef	**DOS at Ef**	**Ec-Ef**	**DOS at Ef**	
Pt(111)	-2.40	27.17	-2.40	27.17	-2.44 (calculated [1])
Surface alloys					
non-segregated					
Pt_3Fe/Pt	-2.49	18.73	-2.42	15.29	
Pt_3Co/Pt	-2.32	27.43	-2.40	16.91	
Pt_3Ni/Pt	-2.06	41.85	-2.37	23.90	
Pt_3Cu/Pt	-2.13	21.69	-2.30	19.40	
Pt_3Pd/Pt	-2.26	28.50	-2.36	21.80	
Pt_3Ag/Pt	-2.62	20.12	-2.35	19.14	
Pt_3Au/Pt	-2.60	22.50	-2.38	20.49	
antisegregated					
Pt/Pt_3Fe/Pt	-2.52	22.48	-2.52	22.48	
Pt/Pt_3Co/Pt	-2.50	23.10	-2.50	23.10	
Pt/Pt_3Ni/Pt	-2.45	27.28	-2.45	27.28	
Pt/Pt_3Cu/Pt	-2.44	21.33	-2.44	21.33	
Pt/Pt_3Pd/Pt	-2.37	28.35	-2.37	28.35	
Pt/Pt_3Ag/Pt	-2.32	21.96	-2.32	21.96	
Pt/Pt_3Au/Pt	-2.33	24.00	-2.33	24.00	
Bulk alloys					
non-segregated					
Pt3Fe	-2.69	13.34	-2.67	9.23	
Pt3Co	-2.50	25.27	-2.67	12.39	
Pt3Ni	-2.26	27.45	-2.56	16.14	
Pt3Cu	-2.30	11.74	-2.47	10.87	
Pt3Pd	-2.25	28.34	-2.35	21.24	
Pt3Ag	-2.57	12.37	-2.25	11.92	
Pt3Au	-2.49	15.95	-2.25	14.90	
restructured					
Pt/PtFe/Pt3Fe	-2.75	12.00	-2.75	12.00	-3.05 (measured on annealed surface) [2]

Pt/PtCo/Pt3Co	-2.73	11.85	-2.73	11.85	-2.82 (calculated) [2] -2.84 (calculated for Pt/Fe/Pt) [1] -2.8 (calculated for Pt/Fe) [3] -2.85 (measured on annealed surface) [2]
Pt/PtNi/Pt3Ni	-2.66	16.80	-2.66	16.80	-2.73 (calculated) [2] -2.74 (calculated for Pt/Fe/Pt [1]) -2.7 (calculated for Pt/Fe) [3] -2.65 (measured on annealed surface) [2]
Pt/PtCu/Pt3Cu	-2.52	16.20	-2.52	16.20	-2.60(calculated) [2] -2.60 (calculated for Pt/Fe/Pt [1]) -2.58 (calculated for Pt/Fe) [3]
Pt/PdPd/Pt3Pd	-2.37	29.85	-2.37	29.85	
Pt/PtAg/Pt3Ag	-2.24	15.55	-2.25	15.55	
Pt/PtAu/Pt3Au	-2.25	19.89	-2.24	19.89	
Segregated					
Au/Pt	-3.35	2.83	-3.35	2.83	
Ag/Pt	-3.83	1.00	-3.83	1.00	

1. Kitchin, J.R., Norskov, J.K., Barteau, M.A., and Chen, J.G., *Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals.* Journal of Chemical Physics, 2004. **120**(21): p. 10240-10246.
2. Mun, B.S., Watanabe, M., Rossi, M., Stamenkovic, V., Markovic, N.M., and Ross, P.N., *A study of electronic structures of Pt3M (M=Ti,V,Cr,Fe,Co,Ni) polycrystalline alloys with valence-band photoemission spectroscopy.* Journal of Chemical Physics, 2005. **123**(20).
3. Duan, Z. and Wang, G., *A first principles study of oxygen reduction reaction on a Pt(111) surface modified by a subsurface transition metal M (M = Ni, Co, or Fe).* Physical Chemistry Chemical Physics, 2011. **13**(45): p. 20178-20187.

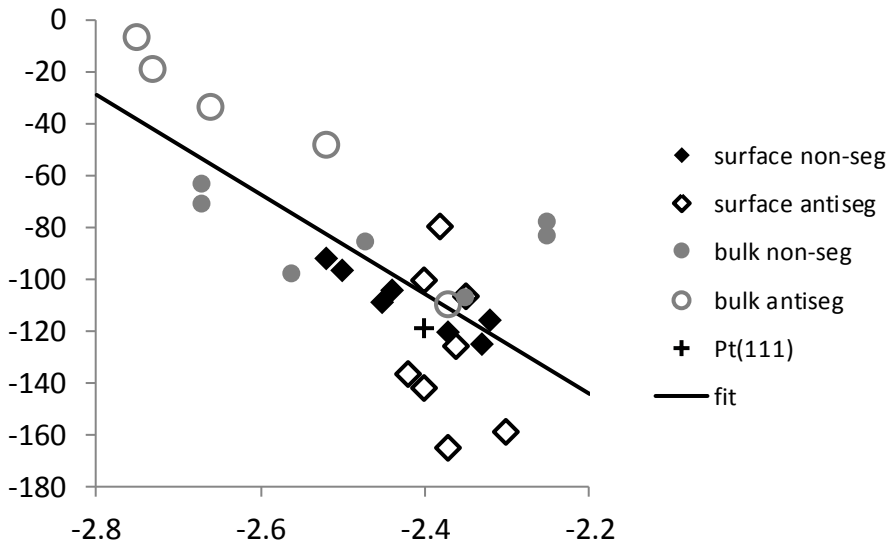

Figure S3: Benzene adsorption energies at the most stable sites of various alloys as function of the d-band center of all Pt atoms in the top layer. Surface alloys: non-segregated, Pt_3-hcp^0 sites (closed black diamonds) and antisegregated, bri-M^{30} sites (open black diamonds). Bulk alloys: non-segregated Pt_3-hcp^0 (closed circles) and antisegregated bri-M-Pt_3/fcc-PtM_2 sites (open circles). Pt(111) reference (cross). Linear fit to all these points is $E_{ads} = -191.5(\varepsilon_d - E_f) - 565.4$; $R^2 = 0.52$.