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Supporting Information

Adsorption of Aromatics on the (111) Surface of PtM and PtM_3 (M = Fe, Ni) Alloys

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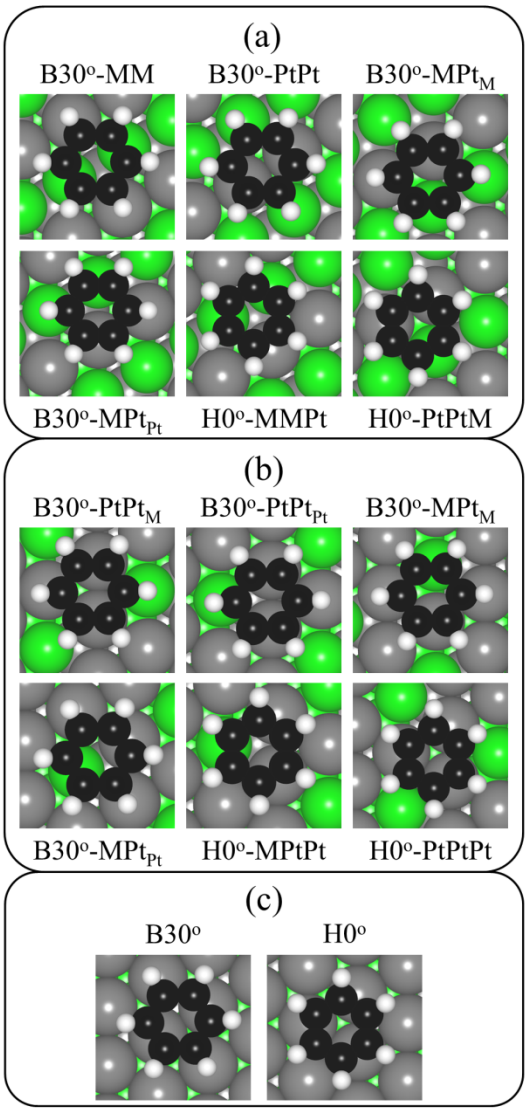

Figure S1. Adsorption sites for benzene on the PtM (111) surface alloys: (a) PtM, (b) $Pt_3M/PtM_3/PtM$, and (c) Pt/M/PtM. The surface sphere coloring is identical to that in Figure 1 and the black and white spheres represent carbon and hydrogen, respectively. The sites are labeled based on which surface (M or Pt) and subsurface (subscript M or Pt) species are interacting with the adsorbate (e.g. the B30°-MPtPt site has benzene bridging a surface M and Pt species with a subsurface Pt species directly below the adsorbate).

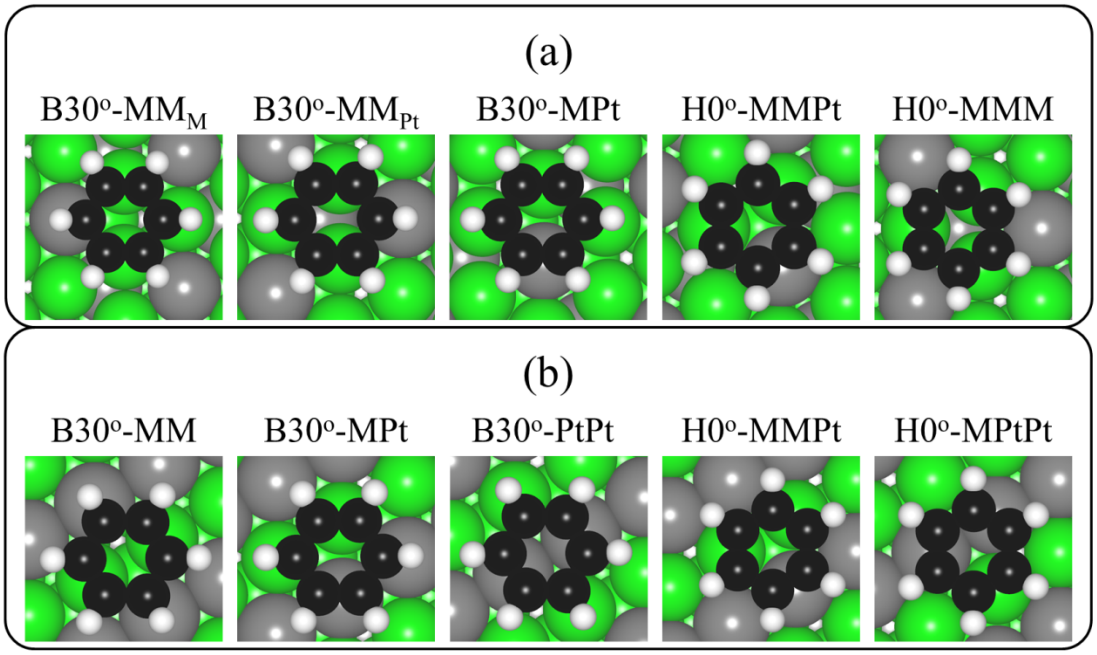

Figure S2. Adsorption sites for benzene on the PtM_3 (111) surface alloys: (a) PtM_3 and (b) $PtM/M/PtM_3$. The surface sphere coloring is identical to that in Figure 1 and the black and white spheres represent carbon and hydrogen, respectively. The sites are labeled in a manner similar to that presented for Figure S1.

Table S1. Adsorption energy (E_{ads}), distortion (E_{dist}) energy, and geometric parameters for benzene adsorbed on the three most stable PtM (111) surface structures (M = Fe, Ni) in the B30° and H0° configurations with the optB88-vdW functional.[a]

PtFe Alloys						
Surface	Site	E_{ads} (eV)	E_{dist} (eV)	$d_{C\text{-}C}$ (Å)	$\theta_{C\text{-}H}$ (°)	$d_{A\text{-}M}$ (Å)
PtFe	B30° – FeFe	-1.22	0.87	1.40, 1.45	14, 24	2.25
	B30° – PtPt	-1.09	0.34	1.41, 1.43	9, 15	2.38
	B30° – $FePt_{Fe}$	-1.20	0.80	1.42, 1.45	12, 18, 24	2.22
	B30° – $FePt_{Pt}$	-1.05	0.75	1.43, 1.44	14, 18, 24	2.26
	H0° – FeFe	-1.22	0.69	1.41, 1.43	11, 13, 16	2.35
	H0° – PtPt	-1.01	0.44	1.42, 1.45	16, 18	2.25
$Pt_3Fe/PtFe_3/PtFe$	B30° – $PtPt_{Fe}$	-0.87	0.01	1.40	0, 1	3.04
	B30° – $PtPt_{Pt}$			Unstable		
	B30° – $FePt_{Fe}$	-0.89	0.02	1.40	0, 1, 2	3.01
	B30° – $FePt_{Pt}$	-0.90	0.02	1.40	0, 1, 2	2.99
	H0° – FePt	-0.86	0.02	1.40	0, 1	3.06
	H0° – Pt	-0.89	0.02	1.40	0, 1, 2	3.01
Pt/Fe/PtFe	B30°	-0.854	0.01	1.40	0	3.14
	H0°	-0.853	0.01	1.40	0	3.16
PtNi Alloys						
Surface	Site	E_{ads} (eV)	E_{dist} (eV)	$d_{C\text{-}C}$ (Å)	$\theta_{C\text{-}H}$ (°)	$d_{A\text{-}M}$ (Å)
PtNi	B30° – NiNi	-1.62	1.24	1.41, 1.46	16, 31	2.15
	B30° – PtPt	-1.26	0.96	1.44, 1.45	15, 24	2.16
	B30° – $NiPt_{Ni}$	-1.55	1.12	1.42, 1.46	17, 27	2.14
	B30° – $NiPt_{Pt}$	-1.49	1.13	1.42, 1.46	16, 28	2.14
	H0° – NiNi	-1.41	0.76	1.43, 1.46	17, 18	2.20
	H0° – PtPt	-1.28	0.67	1.42, 1.45	16, 18	2.21
$Pt_3Ni/PtNi_3/PtNi$	B30° – $PtPt_{Ni}$	-0.94	1.01	1.44, 1.46	14, 25	2.23
	B30° – $PtPt_{Pt}$	-0.81	0.99	1.43, 1.45	14, 20, 30	2.25
	B30° – $NiPt_{Ni}$	-1.01	1.18	1.41, 1.46	14, 30	2.24
	B30° – $NiPt_{Pt}$	-0.98	1.18	1.41, 1.46	14, 30	2.24
	H0° – NiPt	-0.91	0.69	1.42, 1.45	12, 15	2.36
	H0° – Pt	-0.83	0.55	1.43, 1.46	14, 17	2.30
Pt/Ni/PtNi	B30°	-0.86	0.01	1.40	0, 1	3.14
	H0°	-0.85	0.01	1.40	0	3.15

[a]C-C bond length, $d_{C\text{-}C}$; C-H dihedral bond angle, $\theta_{C\text{-}H}$; adsorbate to surface distance, $d_{A\text{-}M}$.

Table S2. Adsorption energy (E_{ads}), distortion (E_{dist}) energy, and geometric parameters for benzene adsorbed on the two most stable PtM_3 (111) surface structures (M = Fe, Ni) in the B30° and H0° configurations with the optB88-vdW functional.[a]

$PtFe_3$ Alloys						
Surface	Site	E_{ads} (eV)	E_{dist} (eV)	d_{C-C} (Å)	θ_{C-H} (°)	d_{A-M} (Å)
$PtFe_3$	B30° – $FeFe_{Fe}$	Unstable				
	B30° – $FeFe_{Pt}$	-1.32	0.86	1.43, 1.46	13, 19, 27	2.24
	B30° – FePt	-1.33	1.08	1.44, 1.45	12, 21, 27	2.15
	H0° – FeFePt	-1.01	0.35	1.41, 1.44	11, 12	2.41
	H0° – FeFeFe	-1.37	0.80	1.44, 1.45	17, 19	2.21
$PtFe/Fe/PtFe_3$	B30° – FeFe	-0.86	0.01	1.40	0, 1	3.11
	B30° – FePt	-0.86	0.01	1.40	0, 2	3.01
	B30° – PtPt	-0.83	0.03	1.40	0, 1	3.03
	H0° – FeFePt	-0.84	0.02	1.40	0, 1	3.06
	H0° – FePtPt	-0.85	0.01	1.40	0, 1	3.05
$PtNi_3$ Alloys						
Surface	Site	E_{ads} (eV)	E_{dist} (eV)	d_{C-C} (Å)	θ_{C-H} (°)	d_{A-M} (Å)
$PtNi_3$	B30° – $NiNi_{Ni}$	-1.59	0.99	1.42, 1.45	16, 26	2.14
	B30° – $NiNi_{Pt}$	-1.59	1.05	1.42, 1.45	16, 27	2.14
	B30° –NiPt	-1.43	0.93	1.43, 1.45	16, 24	2.13
	H0° – NiNiPt	-1.37	0.71	1.42, 1.45	17	2.19
	H0° – NiNiNi	-1.43	0.70	1.42, 1.45	16, 17	2.18
$PtNi/Ni/PtNi_3$	B30° – NiNi	-0.90	1.04	1.41, 1.46	13, 28	2.27
	B30° – NiPt	-0.78	0.90	1.42, 1.45	14, 25	2.25
	B30° – PtPt	-0.57	0.68	1.43, 1.44	13, 20	2.27
	H0° – NiNiPt	-0.66	0.51	1.42, 1.45	13, 15	2.34
	H0° – NiPtPt	-0.72	0.53	1.42, 1.45	13, 15	2.35

[a]C-C bond length, d_{C-C}; C-H dihedral bond angle, θ_{C-H}; adsorbate to surface distance, d_{A-M}.

Table S3. Adsorption energy (E_{ads}), distortion (E_{dist}) energy, and geometric parameters for phenol adsorbed on the three most stable PtM (111) surfaces and two most stable PtM_3 (111) surfaces (M = Fe, Ni). Both horizontal and vertical adsorption sites are shown and the calculations were performed with the optB88-vdW functional.[a]

Horizontal Adsorption Sites						
Surface	E_{ads} (eV)	E_{dist} (eV)	d_{C-C} (Å)	d_{C-O} (Å)	$\theta_{Dihedral}$ (°)	d_{A-M} (Å)
PtFe	-1.29	1.10	1.40, 1.46	1.36	15, 26	2.28
PtNi	-1.66	1.39	1.41, 1.47	1.36	17, 32	2.18
$Pt_3Fe/PtFe_3/PtFe$	-1.02	0.02	1.40	1.37	1, 2	3.05
$Pt_3Ni/PtNi_3/PtNi$	-1.03	1.22	1.41, 1.46	1.37	15, 30	2.27
Pt/Fe/PtFe	-1.00	0.01	1.40	1.37	0, 1	3.11
Pt/Ni/PtNi	-1.00	0.01	1.40	1.36	0, 2	3.13
$PtFe_3$			Unstable			
$PtNi_3$	-1.62	1.11	1.42, 1.45	1.37	17, 28	2.15
$PtFe/Fe/PtFe_3$	-1.05	0.05	1.40	1.36	2, 4	3.00
$PtNi/Ni/PtNi_3$	-0.92	1.09	1.40, 1.46	1.36	14, 28	2.30
Vertical Adsorption Sites - M						
Surface	E_{ads} (eV)	E_{dist} (eV)	d_{C-C} (Å)	d_{C-O} (Å)	$\theta_{Dihedral}$ (°)	d_{A-M} (Å)
PtFe	-0.73	0.04	1.40	1.40	1	2.26
PtNi	-0.66	0.02	1.40	1.39	1	2.26
$Pt_3Fe/PtFe_3/PtFe$	-0.69	0.01	1.40	1.39	0, 1	2.36
$Pt_3Ni/PtNi_3/PtNi$	-0.61	0.01	1.40	1.39	0, 1	2.36
Pt/Fe/PtFe				-		
Pt/Ni/PtNi				-		
$PtFe_3$	-0.78	0.02	1.40	1.40	1	2.36
$PtNi_3$	-0.61	0.02	1.40	1.39	0, 1	2.27
$PtFe/Fe/PtFe_3$	-0.68	0.02	1.40	1.39	0, 1	2.44
$PtNi/Ni/PtNi_3$	-0.54	0.01	1.40	1.39	0, 1	2.35
Vertical Adsorption Sites - Pt						
Surface	E_{ads} (eV)	E_{dist} (eV)	d_{C-C} (Å)	d_{C-O} (Å)	$\theta_{Dihedral}$ (°)	d_{A-M} (Å)
PtFe	-0.46	0.02	1.40	1.39	0, 2	2.59
PtNi	-0.47	0.01	1.40	1.39	0, 1	2.54
$Pt_3Fe/PtFe_3/PtFe$	-0.45	0.00	1.40	1.39	0, 1	2.69
$Pt_3Ni/PtNi_3/PtNi$	-0.48	0.01	1.40	1.38	0, 1	2.63
Pt/Fe/PtFe	-0.46	0.00	1.40	1.38	0, 1	2.63
Pt/Ni/PtNi	-0.46	0.00	1.40	1.38	0, 2	2.70
$PtFe_3$	-0.40	0.00	1.40	1.38	0, 2	2.71
$PtNi_3$	-0.45	0.00	1.40	1.38	0, 2	2.63
$PtFe/Fe/PtFe_3$	-0.43	0.00	1.40	1.38	0, 1	2.76
$PtNi/Ni/PtNi_3$	-0.44	0.00	1.40	1.38	0, 2	2.71

[a]C-C bond length, d_{C-C}; C-O bond length, d_{C-C}; C-H and C-O dihedral bond angles, $\theta_{Dihedral}$; adsorbate to surface distance, d_{A-M}.

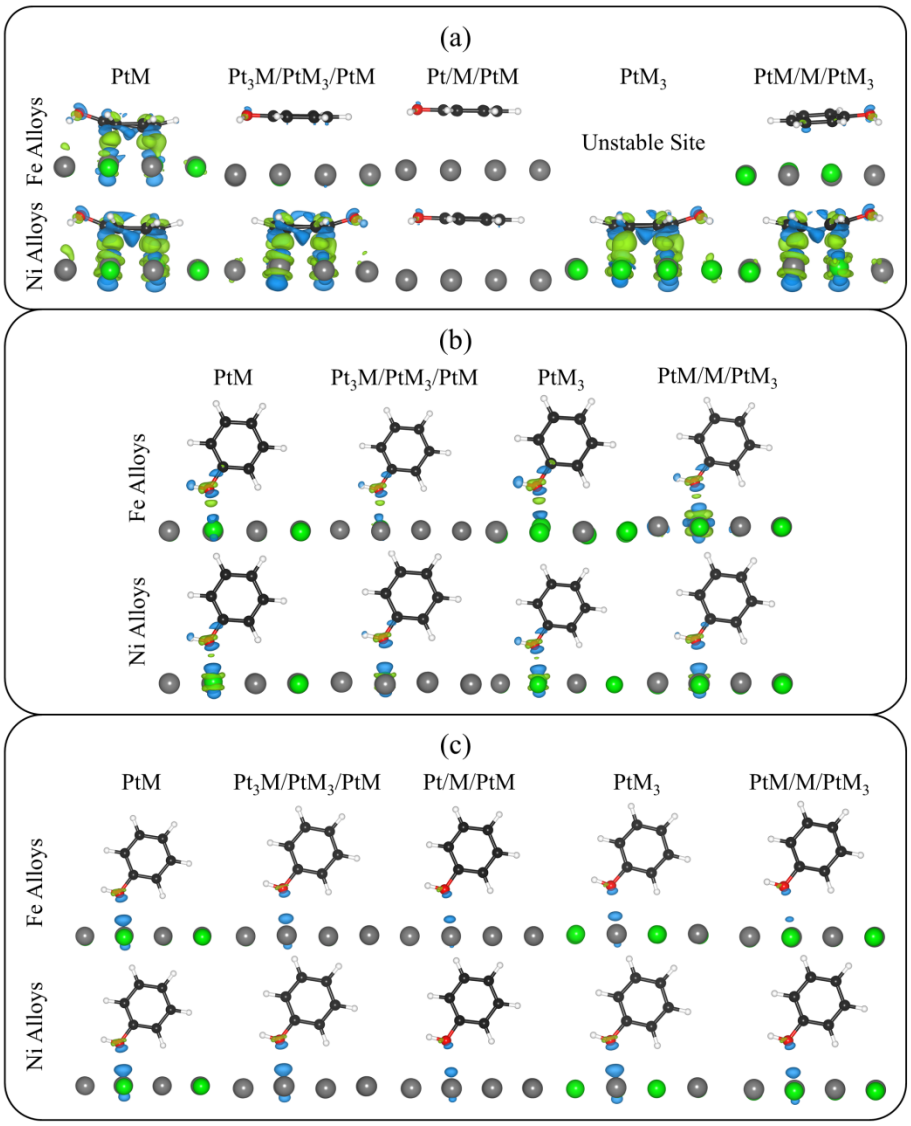

Figure S3. Differential charge density distributions for phenol in all of the studied sites on the PtM and PtM_3 (111) surfaces. The horizontal adsorption sites (a), vertical adsorption sites atop a surface M species (b), and vertical adsorption sites atop a surface Pt species (c) are shown. The surface sphere coloring is identical to that in Figure 1 and the black, white, and red spheres represent carbon, hydrogen, and oxygen, respectively. The isosurface level was set to 0.005 electrons/$Bohr^3$ and the green and blue areas represent a gain and loss of electrons. The calculations were performed using the optB88-vdW functional.