Electronic Supplementary Information

Stability, Electronic Properties and CO Adsorption Properties of Bimetallic

PtAg/Pt(111) Surfaces

Luis A. Mancera, Axel Groß, and R. Jürgen Behm

Institute of Theoretical Chemistry, Ulm University, Oberberghof 7, D-89081 Ulm, Germany

TABLE S1. Formation enthalpies (ΔH), surface energies (E_S) and and estimated surface energies of the top surface ($E_{S,top}$, see text) for pure Pt(111) and Ag(111) surfaces and for Ag_{nL}/Pt(111) pseudomorphic overlayers, varying the number of Ag layers. Surface energies and formation enthalpies are given in meV $Å^{-2}$. Ag_{5L}/Pt_{0L} denotes the pure Ag(111) surface, keeping the lateral lattice parameter of Pt(111), whereas Ag_{5L} denotes the pure Ag(111) surface with the Ag lattice parameter. Note the conversion: 1 meV $Å^{-2} \approx 16.02 \times 10^{-3}$ J m^{-2}. For systems with a Pt(111) lattice, 1 meV per surface atom corresponds to 0.1451 meV $Å^{-2}$ for a slab of identical thickness (nearest neighbor distance 2.82 Å). Results were obtained using RPBE/PAW (for data derived from PBE/PAW see Table 1).

Ensemble	ΔH	E_S	$E_{S,top}$
Pt_{5L}	0.00	84.9	84.9
Ag_{1L}/Pt_{4L}	-39.2	65.1	45.3
Ag_{2L}/Pt_{3L}	-36.3	66.8	48.7
Pt_{1L}/Ag_{1L}/Pt_{3L}	-20.3	74.5	64.1
Ag_{3L}/Pt_{2L}	-30.5	69.7	54.5
Pt_{2L}/Ag_{1L}/Pt_{2L}	+11.6	90.4	95.9
Pt_{1L}/Ag_{2L}/Pt_{2L}	-18.9	75.6	66.3
Ag_{5L}/Pt_{0L}	--	3.4	--
Ag_{5L}	--	36.0	--

TABLE S2. Mean enthalpies of formation (upper lines), differential enthalpies of formation (middle lines), and surface energies (bottom lines), for the different $PtAg/Ag_{nL}/Pt(111)$ surface alloys considered. Surface energies and formation enthalpies are given in meV $Å^{-2}$ (1 meV $A^{-2} \approx 16.02 \times 10^{-3}$ J m^{-2}). For systems with a Pt(111) lattice, 1 meV per surface atom corresponds to 0.1451 meV $Å^{-2}$ for a slab of identical thickness (nearest neighbor distance 2.82 Å). Results were obtained using RPBE/PAW. For results obtained using PBE/PAW see Table 2.

		Pt_1	Pt_2	Pt_3	Pt_4
	θ_{Pt}	$^1/_9$	$^2/_9$	$^3/_9$	$^4/_9$
$PtAg/Pt_{4L}$	ΔH	-34.8	-30.5	-26.1	-21.8
	ΔH_{diff}	-34.8	-26.1	-17.4	-8.7
	E_S	67.4	69.5	72.2	74.4
$PtAg/Ag_{1L}/Pt_{3L}$	ΔH	-37.7	-39.2	-40.6	-39.2
	ΔH_{diff}	-37.7	-40.6	-43.5	-34.8
	E_S	66.4	65.6	64.8	65.2
$PtAg/Ag_{2L}/Pt_{2L}$	ΔH	-29.0	-27.6	-27.6	-26.1
	ΔH_{diff}	-29.0	-26.1	-27.6	-21.8
	E_S	70.6	71.1	71.1	71.8
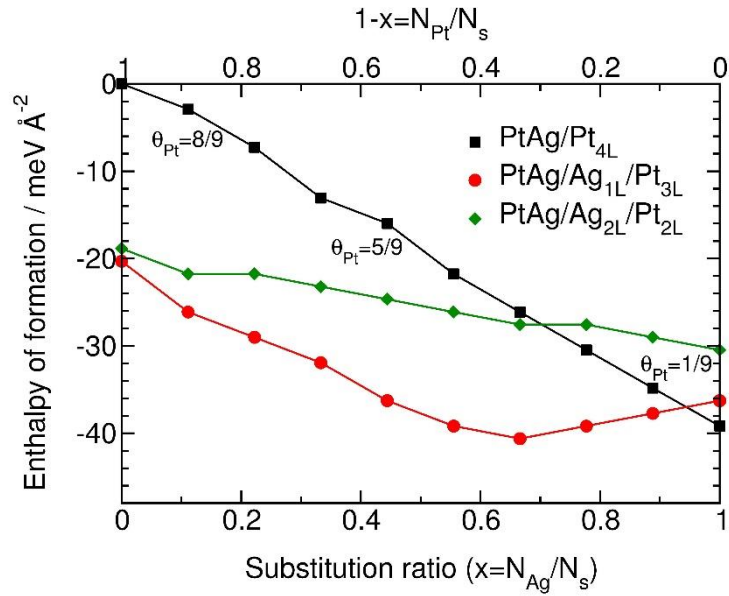
Figure S1. Formation enthalpies ΔH in meV Å^{-2} for the $Pt_{1-x}Ag_x/Ag_{nL}/Pt(111)$ monolayer surface alloys as a function of the substitution ratio x in the surface layer, i.e., the number of Pt atoms replaced by Ag atoms in the topmost layer relative to the total number of surface atoms (9). The 1-x scale at the upper x-axis describes the fraction of Pt atoms in the topmost layer, which also corresponds to the Pt coverage Θ_{Pt} in the topmost layer. Results were obtained using RPBE/PAW (for similar data obtained by PBE/PAW see Figure 1).

Table S3. Center of the d-band and relative shift of the d-band in eV for different PtAg surface alloys. Results were obtained using RPBE/PAW. For results using PBE/PAW see Table 3.

	d-band center	$\Delta_{\text{d-band center}}$
Pt(111)	-2.00	
Pt_1Ag_8/Pt_{4L}	-1.48	0.52
Pt_2Ag_7/Pt_{4L}	-1.63	0.37
Pt_3Ag_6/Pt_{4L}	-1.69	0.31
Pt_1Ag_8/Pt_{4L}	-1.48	
$Pt_1Ag_8/Ag_{1L}/Pt_{3L}$	-1.52	0.04
$Pt_1Ag_8/Ag_{2L}/Pt_{2L}$	-1.57	0.09
Ag(111)	-3.87	

TABLE S4. Mean adsorption CO energies for different Pt_n ensembles, adsorption sites and CO_{ad} coverages on Pt_nAg_{9-n}/Pt_{4L} surface alloys, calculated using RPBE/PAW. The configurations are shown in Figure 3 (Pt_2, Pt_3), Figure 4 ($Pt_{3,L}$), Figure 5 ($Pt_{6,L}$), Figure 6 (Pt_1) and Figure 7 ($Pt_{2,d}$, $Pt_{3,d}$). Energies are given in eV per CO_{ad} molecule, angles refer to the tilt of the CO molecules with respect to the surface normal (see text. For energies calculated using PBE/PAW see Figures 3-7.

	Site	$\theta_{CO} = 1/9$	$\theta_{CO} = 2/9$	$\theta_{CO} = 3/9$	$\theta_{CO} = 4/9$
Pt_1	T	-1.74 (0.0°)	-	-	-
	B-B	-	-0.72 (26.6°)	-	-
	H-fcc / H-hcp	-	-0.70 (20°)	-	-
Pt_2	T	-1.67 (0.1°)	-1.61 (4.3°)	-	-
	B	-1.58 (0.0°)	-	-	-
Pt_3	T	-1.66 (-0.3°)	-1.59 (4.4°)	-1.55 (4.3°)	-
	B	-1.58 (-0.1°)	-	-	-
	H-fcc	-1.56 (0.0°)	-	-	-
	H-hcp	-1.54 (0.0°)	-	-	-
$Pt_{2,d}$	T	-1.75 (0.0°)	-1.74 (-0.2°)	-	-
$Pt_{3,d}$	T	-1.70 (0.0°)	-	-1.76 (0.0°)	-
$Pt_{3,L}$	T	-1.40 (0.0°)	-1.57 (5.8°)	-1.32(0.0°)	-
	B	-1.59 (0.0°)	-1.51 (1.8°)	-1.27 (0.0°)	-
$Pt_{6,L}$	T	-1.59 (0.0°)	-	-	-
	$T_{disperse}$	-	-1.53 (0.0°)	-1.43 (3.5°-7.6°)	
	$T_{compact}$	-	-1.52 (5.1°)	-1.44 (4.0°- 7.5°)	-1.40 (4.0°- 7.0°)
	B_{out}	-1.58 (0.0°)	-	-	-
	B_{in}	-1.48 (0.0°)	-	-	-
	H-fcc	moves to B	-	-	-
	H-hcp	-1.48 (0.0°)	-	-	-