Supplemental Information for "Activity Trends for Catalytic CO and NO Co-Oxidation at Low Temperature Diesel Emission Conditions"

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1. Lattice Constants for All Metals

Table S 1. Bulk lattice constants calculated by DFT compared to experimental measurements.[1,2]

	Computational Value		Experimental Value[1,2]	
	a/Å	c/Å	a/Å	c/Å
Au	4.215	-	4.079	-
Ag	4.227	-	4.086	-
Cu	3.683	-	3.615	-
Pd	3.990	-	3.890	-
Pt	4.000	-	3.923	-
Rh	3.866	-	3.803	-
Ni	3.560	-	3.524	-
Ir	3.893	-	3.839	-
Co (hcp)	2.514	4.081	2.507	4.069
Co (fcc)	3.555	-	3.545	-
Ru (hcp)	2.689	4.402	2.706	4.282
Ru (fcc)	3.836	-	3.867[a]	
Fe	2.870	-	2.866	-

[a] This value is the measured smallest lattice constant for *fcc* Ru in Ref. [2].

2. Slab Model and Adsorption Sites

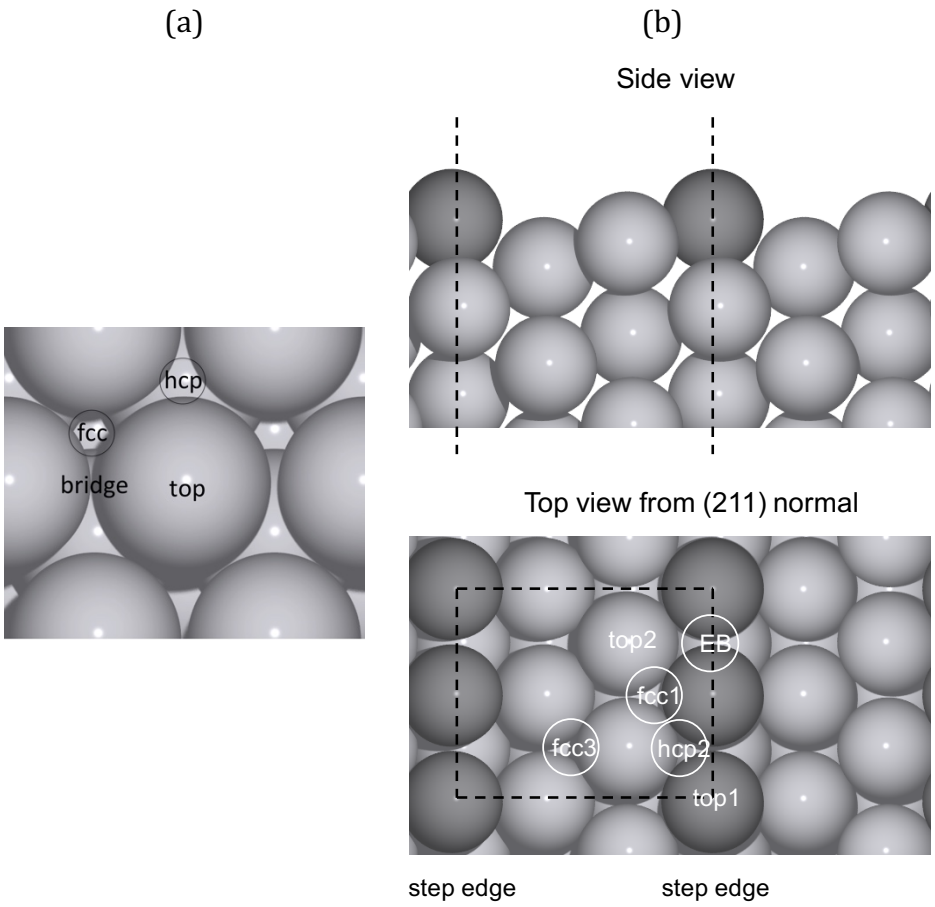


Figure S 1. (a) Terrace surface (top view); (b) Step surface for fcc structure metal (top view and side view)

3. Microkinetic Model Summary

The CatMap tutorial file[3] has reproduced the micro-kinetic models for CO oxidation from Ref 4 and 5. The energetic data they used were adopted from these two references and the values are available online. However, in our work, we use the CO_2, CO, and O_2 gas phase energies and O and CO adsorption energies from our DFT calculations, which are different from the values in Ref 3. In order to ensure data consistency, we kept activation energies (E_a) consistent and recalculated the transition states with reference to our calculated energies. For example, we calculated the E_a of the O_2 dissociation reaction using the $E'_{O_2}(g)$ and E'_{O-O} in Ref 3, following the equation:

$$E_a = E'_{O-O} - E'_{O_2}(g)$$

With this E_a, we were able to calculate the transition energies for our model by the following equation, where $E_{O_2}(g)$ is our DFT calculated value:

$$E_{O-O} = E_a + E_{O_2}(g)$$

Following the same procedure, we can calculate the transition state energies for CO oxidation and the O_2 adsorption energies on terrace surfaces. For the calculation of the O_2 adsorption energies on stepped surfaces, the adsorption energies E'_{O_2} are not available in Ref 3 and has to be extracted from the figures in Ref 5. We can also calculate the O and CO adsorption energies using this method and compare the values with our DFT calculation results. The difference is generally within ± 0.1 eV. With these energy data, we are able to get a similar volcano plot for CO oxidation as in the references.

Table S 2. Energies and vibrational frequencies of all species used in the microkinetic model. The energies are referenced to $CH_4(g)$, $H_2(g)$, $H_2O(g)$ and NO (g). Overbinding correction of 0.2 eV is included for CO.

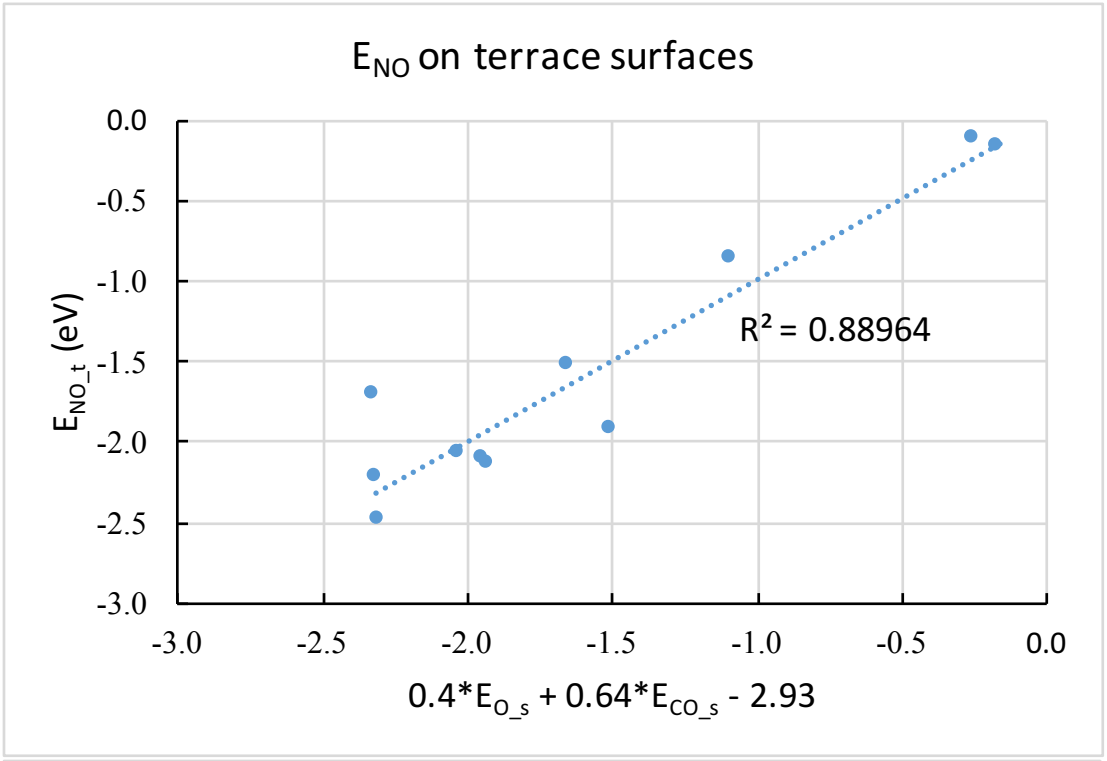
surface	site	species	formation energy (eV)	frequencies	reference
None	gas	O_2	5.34	[1542.2]	calculation
None	gas	CO	2.80	[2101.1]	calculation
None	gas	CO_2	2.12	[627.9, 627.9, 1303.4, 2344.4]	calculation
None	gas	NO	0.00	[1894.8]	calculation
None	gas	NO_2	2.10	[723.0, 1325.9, 1652.0]	calculation
None	gas	N_2	-6.75	[2399.6]	calculation
Ag	111	O_2	5.02	[]	[3]
Cu	111	O_2	4.44	[]	[3]
Pt	111	O_2	4.48	[110.2, 116.3, 217.8, 368.0, 526.3, 871.8]	[3]
Pd	111	O_2	4.21	[]	[3]
Rh	111	O_2	3.55	[]	[3]
Ru	111	O_2	3.07	[]	[3]
Ni	111	O_2	3.68	[]	[3]
Au	111	O	2.53	[]	calculation
Ag	111	O	2.12	[]	calculation
Cu	111	O	0.97	[]	calculation
Pt	111	O	1.45	[360.3, 361.5, 403.7]	calculation
Pd	111	O	1.31	[]	calculation
Rh	111	O	0.61	[]	calculation
Ru	0001	O	-0.06	[]	calculation
Ni	111	O	0.31	[]	calculation
Co	0001	O	0.04	[]	calculation
Ir	111	O	0.89	[]	calculation
Fe	110	O	-0.66	[]	calculation
Ag	111	O-O	5.90	[]	[3]
Cu	111	O-O	4.66	[]	[3]
Pt	111	O-O	5.27	[145.8, 220.7, 285.7, 444.8, 566.3]	[3]
Pd	111	O-O	5.26	[]	[3]
Rh	111	O-O	3.71	[]	[3]
Ru	111	O-O	3.26	[]	[3]
Au	111	CO	3.00	[]	calculation
Ag	111	CO	3.05	[]	calculation
Cu	111	CO	2.49	[]	calculation

surface	site	species	formation energy (eV)	frequencies	reference
Pt	111	CO	1.53	[153.0, 155.3, 305.6, 307.2, 320.2, 1729.4]	calculation
Pd	111	CO	1.35	[]	calculation
Rh	111	CO	1.36	[]	calculation
Ru	0001	CO	1.18	[]	calculation
Ni	111	CO	1.48	[]	calculation
Co	0001	CO	1.66	[]	calculation
Ir	111	CO	1.31	[]	calculation
Fe	110	CO	1.42	[]	calculation
Au	111	O-CO	5.63	[]	[3]
Ag	111	O-CO	5.18	[]	[3]
Cu	111	O-CO	3.99	[]	[3]
Pt	111	O-CO	3.70	[]	[3]
Pd	111	O-CO	3.76	[]	[3]
Rh	111	O-CO	3.18	[]	[3]
Ru	111	O-CO	2.42	[]	[3]
Ni	111	O-CO	3.05	[73.0, 170.6, 254.3, 327.3, 343.4, 388.8, 551.7, 1678.2]	[3]
Au	111	NO	-0.17	[]	calculation
Ag	111	NO	-0.12	[]	calculation
Cu	111	NO	-0.86	[]	calculation
Pt	111	NO	-1.53	[153.5, 157.8, 297.3, 405.5, 411.8, 1505.0]	calculation
Pd	111	NO	-1.93	[]	calculation
Rh	111	NO	-2.15	[]	calculation
Ru	0001	NO	-2.22	[]	calculation
Ni	111	NO	-2.12	[]	calculation
Co	0001	NO	-2.07	[]	calculation
Ir	111	NO	-1.72	[]	calculation
Fe	110	NO	-2.49	[]	calculation
Au	111	O-NO	2.40	[]	calculation
Ag	111	O-NO	2.05	[]	calculation
Cu	111	O-NO	0.88	[]	calculation
Pt	111	O-NO	1.27	[67.5, 132.8, 135.4, 233.9, 290.4, 343.4, 645.4, 1683.6]	calculation
Pd	111	O-NO	0.93	[]	calculation
Rh	111	O-NO	0.16	[]	calculation
Ru	0001	O-NO	-0.10	[]	calculation

surface	site	species	formation energy (eV)	frequencies	reference
Ni	111	O-NO	0.15	[]	calculation
Co	0001	O-NO	0.39	[]	calculation
Ir	111	O-NO	0.57	[]	calculation
Fe	110	O-NO	-0.55	[]	calculation
Au	211	O_2	5.37	[]	[5]
Ag	211	O_2	5.00	[]	[5]
Pd	211	O_2	3.92	[52.9, 152.7, 223.1, 400.5, 482.8, 1021.3]	[5]
Au	211	O	2.58	[]	calculation
Ag	211	O	2.09	[]	calculation
Cu	211	O	0.89	[]	calculation
Pt	211	O	1.16	[143.3, 451.2, 519.2]	calculation
Pd	211	O	1.36	[]	calculation
Rh	211	O	0.45	[]	calculation
Ru	211	O	-0.46	[]	calculation
Ni	211	O	0.15	[]	calculation
Co	211	O	-0.25	[]	calculation
Ir	211	O	0.11	[]	calculation
Fe	210	O	-0.85	[]	calculation
Au	211	O-O	6.10	[]	[3]
Ag	211	O-O	5.26	[]	[3]
Pt	211	O-O	4.82	[]	[3]
Pd	211	O-O	4.52	[418,228,340,372,389]	[3]
Au	211	CO	2.71	[]	calculation
Ag	211	CO	2.88	[]	calculation
Cu	211	CO	2.33	[]	calculation
Pt	211	CO	1.27	[40.8, 190.4, 333.4, 361.1, 383.8, 1844.0]	calculation
Pd	211	CO	1.39	[]	calculation
Rh	211	CO	1.29	[]	calculation
Ru	211	CO	1.26	[]	calculation
Ni	211	CO	1.45	[]	calculation
Co	211	CO	1.57	[]	calculation
Ir	211	CO	0.89	[]	calculation
Fe	210	CO	1.52	[]	calculation
Au	211	O-CO	5.56	[]	[3]
Ag	211	O-CO	5.09	[]	[3]
Cu	211	O-CO	3.92	[]	[3]

surface	site	species	formation energy (eV)	frequencies	reference
Pt	211	O-CO	3.53	[]	[3]
Pd	211	O-CO	3.93	[]	[3]
Rh	211	O-CO	2.94	[]	[3]
Ru	211	O-CO	2.27	[]	[3]
Ni	211	O-CO	2.94	[23.6, 171.4, 240.4, 292.4, 329.3, 380.9, 557.0, 671.07]	[3]
Co	211	O-CO	2.80	[]	[3]
Au	211	NO	-0.38	[]	calculation
Ag	211	NO	-0.25	[]	calculation
Cu	211	NO	-0.97	[]	calculation
Pt	211	NO	-2.02	[56.4, 185.2, 311.7, 356.8, 507.0, 1632.0]	calculation
Pd	211	NO	-1.95	[]	calculation
Rh	211	NO	-2.37	[]	calculation
Ru	211	NO	-2.63	[]	calculation
Ni	211	NO	-2.26	[]	calculation
Co	211	NO	-2.24	[]	calculation
Ir	211	NO	-2.50	[]	calculation
Fe	210	NO	-2.52	[]	calculation
Au	211	O-NO	2.35	[]	calculation
Ag	211	O-NO	2.04	[]	calculation
Cu	211	O-NO	0.86	[]	calculation
Pt	211	O-NO	0.82	[44.4, 97.2, 228.6, 291.6, 311.8, 392.9, 584.3, 1756.4]	calculation
Pd	211	O-NO	0.98	[]	calculation
Rh	211	O-NO	0.07	[]	calculation
Ru	211	O-NO	-0.69	[]	calculation
Ni	211	O-NO	-0.13	[]	calculation
Co	211	O-NO	-0.29	[]	calculation
Ir	211	O-NO	0.12	[]	calculation
Fe	210	O-NO	-0.58	[]	calculation

(a)



(b)

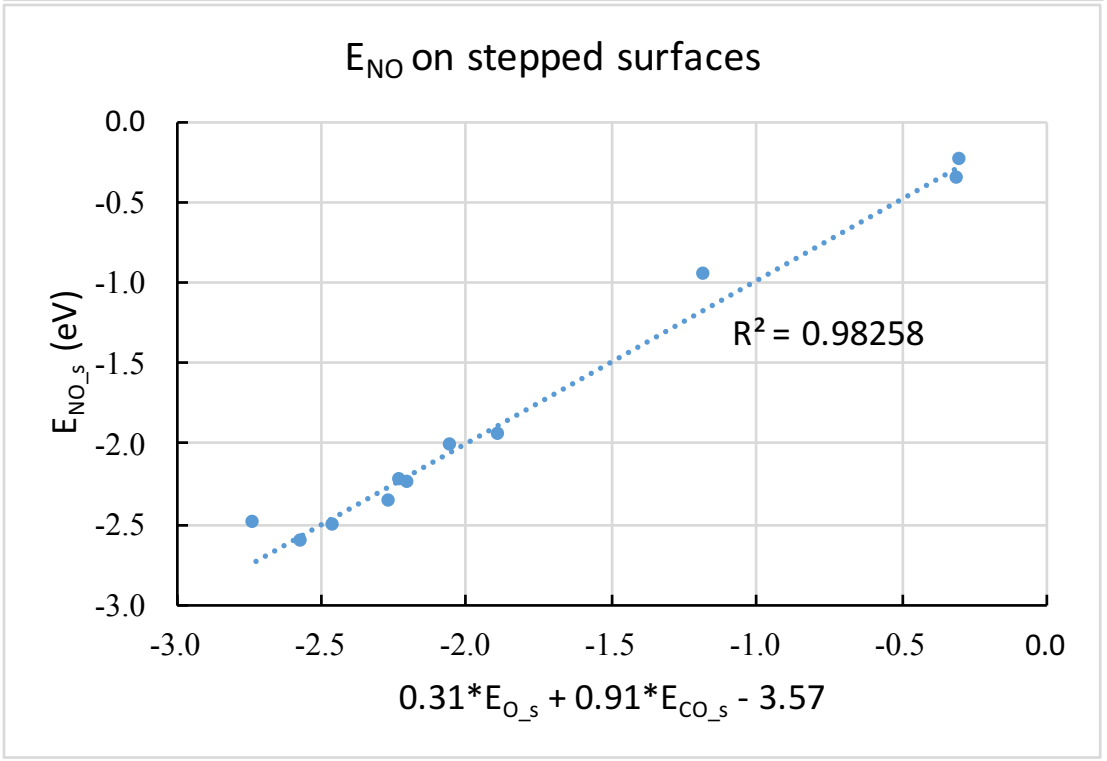


Figure S 2. Scaling lines for NO adsorption on (a) terrace surfaces and (b) stepped surfaces as a function of E_{O_s} and E_{CO_s}. R^2 values are given in the plots.

4. A_3B Type Alloy Models and Adsorption Sites

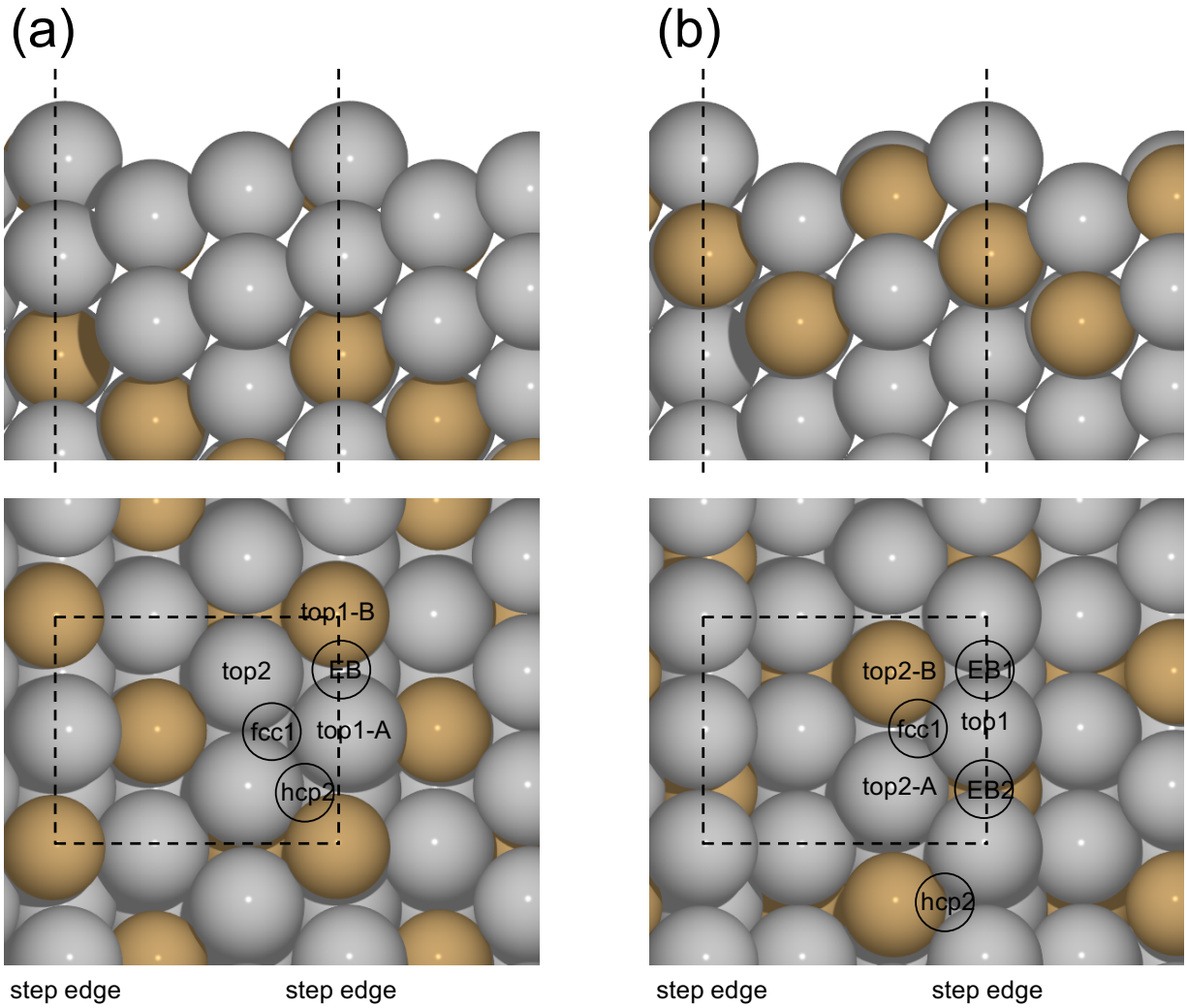


Figure S 3. Side view and top view of (a) AA step and (b) AB step of A_3B type alloys.

5. Adsorption of O and CO on Alloy Surfaces

Table S 3. Adsorption energies of O and CO and the corresponding adsorption sites on alloy surfaces. The energies are referenced to $CH_4(g)$, $H_2(g)$ and $H_2O(g)$. Overbinding correction of 0.2 eV is included for CO.

(211) Surface	AB-type step				AA-type step			
	E_O (eV)	O adsorption site	E_{CO} (eV)	CO adsorption site	E_O (eV)	O adsorption site	E_{CO} (eV)	CO adsorption site
Pt_3Pd	1.34	EB	1.26	top1-Pt	1.10	EB1/EB2	1.18	EB1
Pt_3Ag	1.66	EB	1.37	top1-Pt	1.07	EB2	1.15	EB2
Pd_3Pt	1.20	EB	1.23	top1-Pt	1.34	fcc1	1.44	EB2
Pd_3Ag	1.65	fcc1	1.42	fcc1	1.61	EB2	1.40	EB2
Ag_3Cu	1.35	hcp2	2.36	top1-Cu	1.55	fcc1	2.61	top2-Cu
Ag_3Pt	1.53	hcp2	1.30	top1-Pt	1.75	hcp2	1.48	top2-Pt
Ag_3Pd	1.87	hcp2	1.90	top1-Pd	1.95	hcp2	1.96	top2-Pd
Ag_3Rh	0.90	EB	0.98	top1-Rh	1.16	hcp2	1.01	top2-Rh
Ag_3Ru	-0.21	top1-Ru	0.67	top1-Ru	0.17	top2-Ru	0.59	top2-Ru
Ag_3Ni	0.82	hcp2	1.31	top1-Ni	1.11	hcp2	1.40	top2-Ni
Ag_3Co	0.38	hcp2	1.40	top1-Co	0.63	hcp2	1.38	top2-Co
Ag_3Ir	0.22	EB	0.40	top1-Ir	0.69	hcp2	0.44	top2-Ir
Au_3Cu	1.85	EB	2.35	top1-Cu	2.12	fcc1	2.74	top2-Cu
Au_3Pt	1.69	EB	1.26	top1-Pt	2.20	fcc1	1.55	top2-Pt
Au_3Pd	2.20	EB	1.92	top1-Pd	2.41	hcp2	2.08	top2-Pd
Au_3Rh	1.15	EB	1.17	top1-Rh	1.77	hcp2	1.26	top2-Rh
Au_3Ni	1.29	EB	1.53	top1-Ni	1.78	fcc1	1.75	top2-Ni
Au_3Co	0.68	EB	1.45	top1-Co	1.26	fcc1	1.64	top2-Co
Cu_3Pt	1.05	hcp2	1.44	top1-Pt/EB	1.02	hcp2	1.63	top2-Pt
Cu_3Pd	1.04	fcc1	1.98	top1-Pd	0.97	hcp2	1.99	hcp2
Cu_3Co	0.02	EB	1.44	top1-Co	0.18	hcp2	1.24	top2-Co
(111) Surface	**E_O/eV**				**E_{CO}/eV**			
PdPt	1.28				1.25			
PtAg	1.48				1.36			
PdAg	1.8				1.65			

References

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