

SI - Trends in Thermodynamic Stability of Ultrathin Supported Oxide Films

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Reference Energies

The reference energy of oxygen was obtained from water and hydrogen by correcting the experimental reaction energy by the zero point energies:

$$E(\text{O}) = E(\text{H}_2\text{O}) - E(\text{H}_2) + 2.75 \text{ eV} \quad (1)$$

The experimental formation enthalpies of oxides below were obtained from the literature.^{1,2}

Table S1: Oxides and formation energies. Metals have also been included with a formation energy of 0.

Ni(bulk)	0.00
Ni ₂ O ₃	-5.07
Co(bulk)	0.00
Co ₃ O ₄	-9.23
CoO	-2.47
MnO ₂	-5.39
Mn ₃ O ₄	-14.38
Mn(bulk)	0.00
Mn ₂ O ₃	-9.94
MnO	-3.99
TiO ₂	-9.78
Ti(bulk)	0.00
Ti ₂ O ₃	-15.76
Ti ₃ O ₅	-25.49
Fe ₃ O ₄	-11.59
Fe(bulk)	0.00
Fe ₂ O ₃	-8.54
FeO	-2.82
V ₂ O ₅	-16.07
V(bulk)	0.00
V ₂ O ₃	-12.63
VO	-4.48
V ₃ O ₅	-20.03
CrO ₂	-6.20
Cr ₃ O ₄	-15.87
Cr(bulk)	0.00
Cr ₂ O ₃	-11.81

Formation energies

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Clean slab references

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spec	2x1	2x1_U	1x1
Ni	-10944.1340	-10934.2334	-5471.9654
Co	None	None	-4356.3786
Ag	-10331.7540	-10331.7540	-5165.8768
Pt	-7907.9113	-7907.9113	-3953.9556
Ru	-5463.1100	-5463.1100	-2731.5548
Rh	-25373.3714	-25373.3714	-12686.6855
Ir	-6748.7040	-6748.7040	-3374.3520
Au	-9294.2580	-9294.2580	-4647.1289
Pd	-8570.8424	-8570.8424	-4285.4211
Os	-7268.7842	-7268.7842	-3634.3920
Cu	-12776.5350	-12776.5350	-6388.2666

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bulk references

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spec	2x1	2x1_U	1x1
Ni	-1368.3668	-1367.1154	-1368.3269
Ir	-844.0632	-844.0632	-844.0632
Co	-1089.7023	-1087.7413	-1089.4620
Pt	-988.8009	-988.8009	-988.8009
Ag	-1291.6357	-1291.6357	-1291.6357
Ru	-683.4636	-683.4636	-683.4636
Rh	-3172.0768	-3172.0768	-3172.0768
Ca	-1016.7632	-1016.7632	-1016.7632
Mn	-2903.3265	-2899.9051	-2903.3265
Ti	-1587.0929	-1583.9139	-1587.0929
Au	-1161.9468	-1161.9468	-1161.9468
Fe	-3458.9743	-3457.0387	-3458.2347
Pd	-1071.6413	-1071.6413	-1071.6413
V	-1955.6522	-1951.9850	-1955.6522
Cr	-2368.1173	-2364.7671	-2368.1173
Os	-909.2295	-909.2295	-909.2295
Cu	-1597.2712	-1597.2712	-1597.2712

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Adsorption energies. spec1 is the support, spec2 is the adsorbate.

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spec1	spec2	2x1	2x1_U	1x1
Ni	Ni	None	0.5005	1.2624
Ni	Co	1.1997	None	1.9585
Ni	Mn	0.2413	None	2.7551
Ni	Ti	1.9399	None	1.9975
Ni	Fe	None	-0.8212	1.3957
Ni	V	None	None	1.8649
Ni	Cr	None	-1.7027	2.7271
Co	Ni	None	None	0.9853
Co	Co	None	None	1.5559
Co	Mn	None	None	1.9456
Co	Ti	None	None	1.7576
Co	Fe	None	None	0.8762
Co	V	None	None	1.1963
Co	Cr	None	None	1.8304
Ag	Ni	2.3260	2.1027	2.2856
Ag	Co	2.8969	1.4245	3.4514
Ag	Mn	1.8364	-1.1815	5.2816
Ag	Ti	5.0767	2.8520	5.5591
Ag	Fe	2.0070	0.4696	3.1934

	Ag		V		3.7897		0.8878		5.4326	
	Ag		Cr		2.4485		-0.6916		5.8382	
	Pt		Ni		1.0349		0.7534		1.0330	
	Pt		Co		1.3451		0.4203		1.6427	
	Pt		Mn		-0.0988		-2.8113		2.3175	
	Pt		Ti		1.2217		0.8960		1.2223	
	Pt		Fe		0.2648		-0.6283		1.0989	
	Pt		V		1.2059		-0.2972		1.2379	
	Pt		Cr		0.9077		-1.5618		2.1932	
	Ru		Ni		0.8028		0.8353		0.7626	
	Ru		Co		1.1894		0.6923		1.2261	
	Ru		Mn		0.2170		-2.4619		1.6519	
	Ru		Ti		1.6662		1.1073		1.6660	
	Ru		Fe		0.2545		-0.6884		0.5079	
	Ru		V		1.1641		-0.2238		1.1644	
	Ru		Cr		1.1187		-1.5192		1.7245	
	Rh		Ni		1.0931		1.0860		1.0524	
	Rh		Co		1.4593		0.6015		1.5913	
	Rh		Mn		0.3200		-2.3937		2.0269	
	Rh		Ti		1.5765		1.2357		1.5771	
	Rh		Fe		0.5036		-0.4076		0.9348	
	Rh		V		1.2097		-0.0634		1.2095	
	Rh		Cr		1.2182		-1.3584		1.9321	
	Ir		Ni		0.8156		0.7831		0.7751	
	Ir		Co		1.2566		0.7428		1.2383	
	Ir		Mn		0.1756		-2.4545		1.7162	
	Ir		Ti		1.5589		1.0883		1.5591	
	Ir		Fe		0.3454		-0.5869		0.6213	
	Ir		V		1.1278		-0.1966		1.1272	

	Ir		Cr		1.0547		-1.4590		1.7315	
	Au		Ni		1.8934		1.7712		1.8639	
	Au		Co		2.4579		1.1015		2.8911	
	Au		Mn		1.1266		-1.7816		4.4454	
	Au		Ti		4.0813		None		4.2255	
	Au		Fe		1.5256		None		2.5828	
	Au		V		3.1040		0.7602		4.2549	
	Au		Cr		1.9448		-0.9947		4.8322	
	Pd		Ni		1.3438		1.0052		1.4233	
	Pd		Co		1.6242		None		2.1021	
	Pd		Mn		0.1316		-2.6458		2.8815	
	Pd		Ti		1.6736		1.1416		1.6725	
	Pd		Fe		0.5342		-0.3583		1.5495	
	Pd		V		1.6800		-0.2964		1.8449	
	Pd		Cr		1.2476		-1.3985		2.8164	
	Os		Ni		0.5370		0.5218		0.4971	
	Os		Co		0.9894		None		0.8710	
	Os		Mn		0.3080		-2.2713		1.4551	
	Os		Ti		1.9659		1.2194		1.9666	
	Os		Fe		0.2452		-0.7096		0.2754	
	Os		V		1.3529		-0.1519		1.3530	
	Os		Cr		1.1715		-1.4822		1.7206	
	Cu		Ni		1.8215		1.6771		1.7804	
	Cu		Co		2.4553		1.1005		2.8294	
	Cu		Mn		1.3980		-1.5153		4.4653	
	Cu		Ti		4.3765		2.3705		4.5951	
	Cu		Fe		1.6239		0.1981		2.5473	
	Cu		V		3.2775		0.8892		4.4591	
	Cu		Cr		2.0953		-0.9331		4.9216	

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Supported oxide formation free energies per metal of the overlayer at $\mu_0 = -3.73$ eV.
spec2 is the support, spec1 is the overlayer.

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spec1	spec2	2x1	2x1_U	1x1
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2x2-Ni	Ru	1.8552	2.0790	1.8159
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2x2-Ni	Co	None	None	2.8589
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2x2-Ni	Ag	2.3012	2.4502	2.2620
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2x2-Ni	Pt	1.8646	2.0556	1.8252
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2x2-Ni	Ni	2.7166	2.9215	2.5757
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2x2-Ni	Rh	1.9308	2.1212	1.8915
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2x2-Ni	Ir	1.8297	2.0180	1.7904
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2x2-Ni	Au	2.2090	2.3585	2.1694
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2x2-Ni	Pd	1.9707	2.1661	1.9315
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2x2-Ni	Os	1.9146	2.1335	1.8754
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2x2-Ni	Cu	2.5556	2.7118	2.5159
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2x2-Ti	Ru	0.6063	0.6340	0.6072
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2x2-Ti	Co	None	None	3.2620
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2x2-Ti	Ag	1.1118	0.9108	1.1128
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	2x2-Ti		Pt		0.1377		0.0872		0.1388	
	2x2-Ti		Ni		2.9073		None		2.9316	
	2x2-Ti		Rh		0.7278		0.7398		0.7288	
	2x2-Ti		Ir		0.3709		0.3462		0.3720	
	2x2-Ti		Au		0.6041		0.4219		0.6048	
	2x2-Ti		Pd		0.6320		None		0.6330	
	2x2-Ti		Os		0.6949		None		0.6959	
	2x2-Ti		Cu		2.7250		2.6548		2.7648	
	sqrt3xsqrt3-Co		Ru		1.3018		1.1647		1.0708	
	sqrt3xsqrt3-Co		Ag		2.5437		None		2.4681	
	sqrt3xsqrt3-Co		Pt		1.8496		1.3556		1.9183	
	sqrt3xsqrt3-Co		Ni		1.7020		1.6870		1.4096	
	sqrt3xsqrt3-Co		Rh		1.6063		1.3545		1.4188	
	sqrt3xsqrt3-Co		Ir		1.6770		1.3198		1.4897	
	sqrt3xsqrt3-Co		Au		2.5341		1.7824		2.5827	
	sqrt3xsqrt3-Co		Pd		1.8531		1.4031		1.8176	
	sqrt3xsqrt3-Co		Os		1.3143		1.1717		1.0869	
	sqrt3xsqrt3-Co		Cu		1.9645		1.7916		1.7908	
	k-phase-Ti		Ru		-0.4198		None		-0.4198	
	k-phase-Ti		Co		0.4558		None		0.4558	
	k-phase-Ti		Ag		0.6023		None		0.6023	
	k-phase-Ti		Pt		-0.5315		None		-0.5315	
	k-phase-Ti		Ni		0.3063		None		0.3063	
	k-phase-Ti		Rh		-0.1922		None		-0.1922	
	k-phase-Ti		Ir		-0.3055		None		-0.3055	
	k-phase-Ti		Au		0.1979		None		0.1979	
	k-phase-Ti		Pd		-0.3361		None		-0.3361	
	k-phase-Ti		Os		-0.1472		None		-0.1472	
	k-phase-Ti		Cu		0.7913		None		0.7913	

sqrt3xsqrt3-Cr	Ru	-0.0280	-0.9871	0.1971
sqrt3xsqrt3-Cr	Ag	1.1862	-0.3957	2.4709
sqrt3xsqrt3-Cr	Pt	0.2367	-0.8959	0.7546
sqrt3xsqrt3-Cr	Ni	0.3290	-0.6221	0.3054
sqrt3xsqrt3-Cr	Rh	0.0985	-0.9047	0.5260
sqrt3xsqrt3-Cr	Ir	0.0721	-0.9478	0.5688
sqrt3xsqrt3-Cr	Au	0.9267	-0.4271	1.6786
sqrt3xsqrt3-Cr	Pd	0.3614	-0.7865	0.8809
sqrt3xsqrt3-Cr	Os	0.0653	-0.9326	0.2736
sqrt3xsqrt3-Cr	Cu	0.6869	-0.3915	1.0380
sqrt3xsqrt3-V	Ru	-0.6643	-1.1687	-0.6642
sqrt3xsqrt3-V	Ag	1.1226	-0.2194	1.1273
sqrt3xsqrt3-V	Pt	None	-1.1348	-0.2082
sqrt3xsqrt3-V	Ni	-0.2223	-0.5436	-0.3437
sqrt3xsqrt3-V	Rh	-0.5110	-1.0466	-0.5099
sqrt3xsqrt3-V	Ir	None	-1.1296	-0.5198
sqrt3xsqrt3-V	Au	0.8345	-0.3916	0.8578
sqrt3xsqrt3-V	Pd	-0.0863	-1.0237	-0.0575
sqrt3xsqrt3-V	Os	-0.5594	-1.0945	-0.5593
sqrt3xsqrt3-V	Cu	0.3922	-0.2974	0.3995
2x2-Fe	Ru	0.9134	1.1313	0.2980
2x2-Fe	Co	None	None	1.1808
2x2-Fe	Ag	1.4819	1.3392	1.0612
2x2-Fe	Pt	1.0045	0.9618	0.5965
2x2-Fe	Ni	None	None	1.1179
2x2-Fe	Rh	1.1607	1.3680	0.6316
2x2-Fe	Ir	1.0066	1.1754	0.4814
2x2-Fe	Au	1.2696	None	0.9269
2x2-Fe	Pd	1.1681	1.1398	0.7695

2x2-Fe	Os	0.9577	1.2217	0.2971	
2x2-Fe	Cu	1.9137	2.3131	1.2195	
sqrt3xsqrt3-Mn	Ru	-0.0916	-2.0187	0.7473	
sqrt3xsqrt3-Mn	Ag	0.6709	-1.7799	2.2842	
sqrt3xsqrt3-Mn	Pt	0.4983	-2.0751	1.3395	
sqrt3xsqrt3-Mn	Ni	0.2927	None	0.7850	
sqrt3xsqrt3-Mn	Rh	0.0654	-1.9129	0.9646	
sqrt3xsqrt3-Mn	Ir	0.0330	-1.9747	0.9923	
sqrt3xsqrt3-Mn	Au	None	-1.8367	None	
sqrt3xsqrt3-Mn	Pd	0.1067	-2.0049	1.4119	
sqrt3xsqrt3-Mn	Os	-0.0105	-1.9508	0.7985	
sqrt3xsqrt3-Mn	Cu	0.5765	-1.3779	1.4076	
2x2-Mn	Ru	0.0153	-1.3379	0.2590	
2x2-Mn	Co	None	None	0.7105	
2x2-Mn	Ag	0.6162	-1.2279	1.5924	
2x2-Mn	Pt	-0.0150	-1.6089	0.9065	
2x2-Mn	Ni	1.0023	-0.0482	0.9020	
2x2-Mn	Rh	0.1512	-1.2588	0.7724	
2x2-Mn	Ir	-0.0402	None	0.6141	
2x2-Mn	Au	0.3529	-1.4858	1.3703	
2x2-Mn	Pd	0.2037	-1.4127	1.1186	
2x2-Mn	Os	0.0890	-1.2209	0.2245	
2x2-Mn	Cu	1.0872	-0.1740	1.3130	
sqrt3xsqrt3-Ni	Ru	1.1792	1.1772	1.1389	
sqrt3xsqrt3-Ni	Ag	2.3507	None	2.3113	
sqrt3xsqrt3-Ni	Pt	1.9769	2.0356	1.9524	
sqrt3xsqrt3-Ni	Ni	2.1616	None	1.9923	
sqrt3xsqrt3-Ni	Rh	1.5109	1.5490	None	
sqrt3xsqrt3-Ni	Ir	1.6325	1.6494	1.5926	

sqrt3xsqrt3-Ni	Au	2.5252	2.6089	2.4850
sqrt3xsqrt3-Ni	Pd	1.8566	1.9011	1.8182
sqrt3xsqrt3-Ni	Os	1.2378	1.2167	1.1977
sqrt3xsqrt3-Ni	Cu	1.7481	1.8057	1.7002
k-phase-V	Ru	-0.5473	None	-0.5473
k-phase-V	Ag	0.8222	None	0.8222
k-phase-V	Pt	-0.5279	None	-0.5279
k-phase-V	Rh	-0.4331	None	-0.4331
k-phase-V	Ir	-0.5444	None	-0.5444
k-phase-V	Au	0.5299	None	0.5299
k-phase-V	Pd	-0.3409	None	-0.3409
k-phase-V	Os	-0.4716	None	-0.4716
k-phase-V	Cu	0.8209	None	0.8209
2x2-V	Ru	-0.4188	-0.5687	-0.4180
2x2-V	Co	None	None	1.0948
2x2-V	Ag	0.7529	0.0073	0.8083
2x2-V	Pt	-0.2795	-0.7551	-0.2797
2x2-V	Ni	1.1075	1.1810	1.0065
2x2-V	Rh	-0.1612	-0.3267	-0.1605
2x2-V	Ir	-0.4105	-0.6177	-0.4096
2x2-V	Au	0.3744	-0.3894	0.4582
2x2-V	Pd	0.0618	-0.4268	0.0665
2x2-V	Os	-0.3329	-0.4912	-0.3328
2x2-V	Cu	1.1109	1.0460	1.1110
sqrt3xsqrt3-Fe	Ru	0.5162	0.2475	0.4190
sqrt3xsqrt3-Fe	Ag	1.3899	0.5419	1.7398
sqrt3xsqrt3-Fe	Pt	0.7151	0.3113	0.9996
sqrt3xsqrt3-Fe	Ni	1.0285	None	0.6364
sqrt3xsqrt3-Fe	Rh	0.7685	0.4120	0.6296

sqrt3xsqrt3-Fe	Ir	0.7246	0.3498	0.6753
sqrt3xsqrt3-Fe	Au	1.3499	0.5254	1.6267
sqrt3xsqrt3-Fe	Pd	0.7630	0.3517	0.9935
sqrt3xsqrt3-Fe	Os	0.5920	0.3253	0.4598
sqrt3xsqrt3-Fe	Cu	1.3398	1.0556	0.9733
2x2-Co	Ru	1.3289	1.5133	1.0898
2x2-Co	Co	None	None	1.8906
2x2-Co	Ag	1.9980	1.9334	1.7587
2x2-Co	Pt	1.4994	1.5460	1.2607
2x2-Co	Ni	2.0523	2.2173	1.7113
2x2-Co	Rh	1.4206	1.5548	1.1818
2x2-Co	Ir	1.3277	None	1.0889
2x2-Co	Au	1.9049	1.7509	1.6658
2x2-Co	Pd	1.6105	1.6897	1.3716
2x2-Co	Os	1.3482	1.5280	1.1092
2x2-Co	Cu	1.9346	2.0739	1.6956
sqrt3xsqrt3-Ti	Ru	-0.5725	-0.7507	-0.5748
sqrt3xsqrt3-Ti	Ag	1.2316	0.5422	1.2327
sqrt3xsqrt3-Ti	Pt	-0.3820	-0.5761	-0.3801
sqrt3xsqrt3-Ti	Ni	0.1298	0.2619	0.1586
sqrt3xsqrt3-Ti	Rh	-0.5366	-0.6423	-0.5360
sqrt3xsqrt3-Ti	Ir	-0.5832	-0.7240	-0.5820
sqrt3xsqrt3-Ti	Au	0.8656	None	0.8674
sqrt3xsqrt3-Ti	Pd	-0.1688	-0.4563	-0.1674
sqrt3xsqrt3-Ti	Os	-0.4469	-0.6391	-0.4459
sqrt3xsqrt3-Ti	Cu	0.7948	0.5385	0.7953
2x2-Cr	Ru	-0.1078	-0.6144	-0.1054
2x2-Cr	Co	None	None	0.6526
2x2-Cr	Ag	0.8387	None	1.5723

	2x2-Cr		Pt		0.0630		-0.8126		0.5468	
	2x2-Cr		Ni		1.0244		0.7684		0.9240	
	2x2-Cr		Rh		0.2110		-0.4955		0.4572	
	2x2-Cr		Ir		-0.0086		-0.7161		0.2512	
	2x2-Cr		Au		0.5291		-0.4938		1.3068	
	2x2-Cr		Pd		0.3580		-0.5581		0.8242	
	2x2-Cr		Os		-0.0604		-0.5434		-0.0597	
	2x2-Cr		Cu		1.1905		0.6048		1.2581	

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References

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- (2) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics, 88th Edition*; CRC Press, 2007.