Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Are scaling relations truly universal?

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Note 1: Differential adsorption energies for the OH and OOH intermediates

Only for Pt(111) and Ir(111), the lowest differential OH adsorption energy is at the 1/3 ML OH coverage, i.e. in a half dissociated water layer.[30,32,33] On all the other metals and alloys the OH is most stable in water bilayer at the 1/9 ML OH coverage. As for OOH, the highest binding energy is obtained at 1/6 ML coverage irrespective of the catalyst surface. For the strained Pt(111), Pd(111) and Ag(111) we assume the same OH/OOH coverages as those on pristine surfaces.

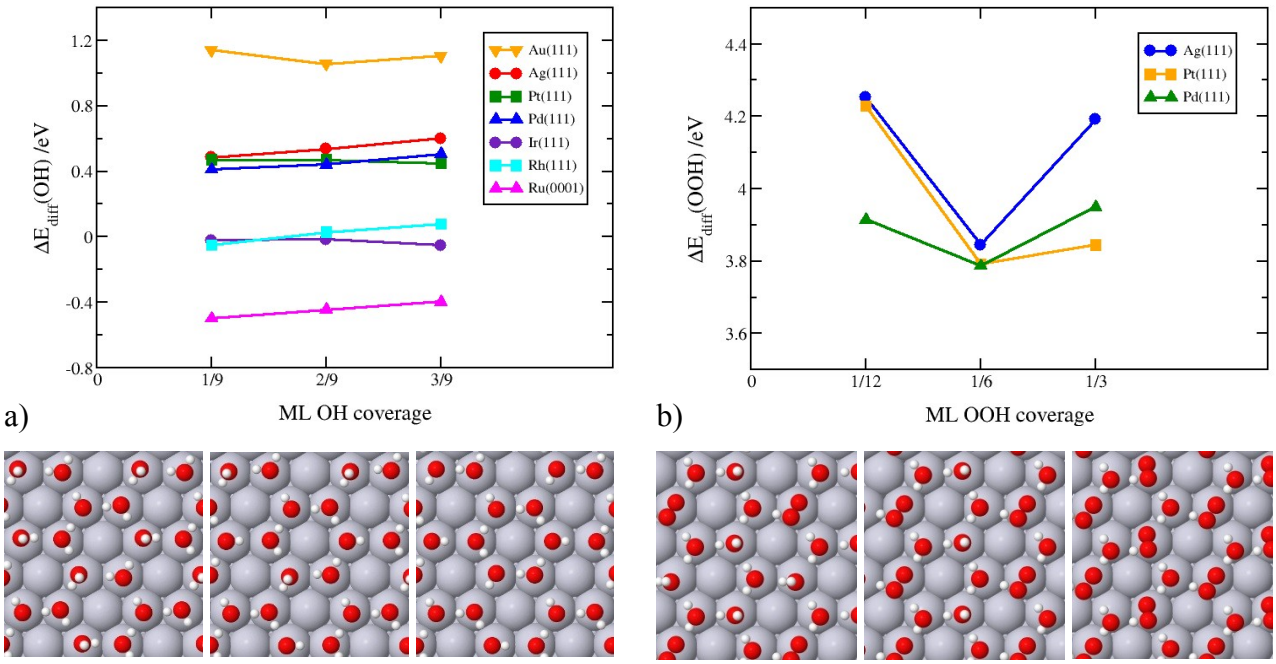

Figure S1 Differential adsorption energies of a) OH and b) OOH on the (111) surfaces of late transition metals. Snapshots show structures at different OH/OOH coverages in the water bilayer.

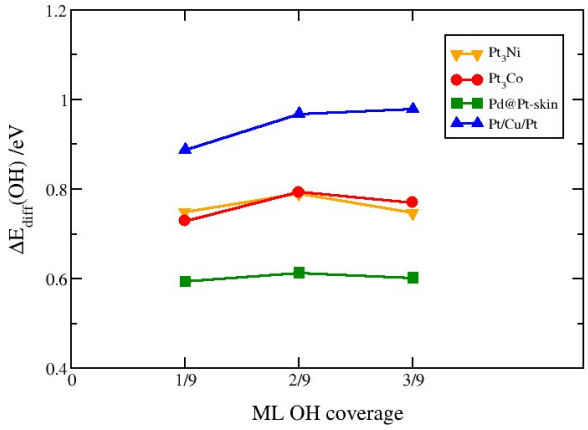

Figure S2 Differential adsorption energies of OH on the (111) surfaces of selected Pt-alloys. For the OOH the 1/6 ML coverage found on metals was assumed.

Note 2: Calculated values of lattice constants and binding energies of different intermediates

Table S1 The RPBE optimized lattice constants.

Element	Lattice Constant	Element/alloy	Lattice Constant
Pt	3.991	Rh	3.865
Pd	3.980	Ru	3.850
Ag	4.172	Pt_3Ni	3.907
Au	4.186	Pt_3Co	3.911
Ir	3.883		

Table S2 Binding energies of O, 'dry' and 'hydrated' OH and OOH intermediates.

Surface	OH	OH-wl	O	OOH	OOH-wl
Pt(111)	0.961	0.427	1.457	3.948	3.792
+1%	0.931	0.401	1.393	3.937	3.786
+2%	0.871	0.201	1.308	3.891	3.718
Pt/Cu/Pt(111)	1.320	0.888	1.717	4.255	4.111
Pd@Pt-skin(111)	1.045	0.581	1.513	4.009	3.862
Pt_3Ni(111)	1.080	0.660	1.719	4.075	3.987
Pt_3Co(111)	1.128	0.725	1.811	4.128	4.010
Pd(111)	0.904	0.412	1.444	4.009	3.787
+1%	0.853	0.308	1.385	4.008	3.741
+2%	0.812	0.319	1.338	3.960	3.725
-1%	0.936	0.462	1.499	4.040	3.816
-2%	0.971	0.481	1.559	4.060	3.826
-3%	1.005	0.492	1.631	4.088	3.893
-4%	1.052	0.570	1.705	4.118	3.927
-5%	1.064	0.700	1.756	4.128	3.987
Pt@Pd-skin(111)	0.740	0.148	1.360	3.945	3.668
Ag(111)	0.831	0.487	2.056	4.123	3.846
-1%	0.849	0.510	2.069	4.111	3.804
-2%	0.903	0.515	2.116	4.135	3.820
+1%	0.799	0.468	2.032	4.107	3.830

+2%	0.751	0.421	1.983	4.070	3.822
+3%	0.696	0.403	1.926	4.032	3.817
+4%	0.651	0.391	1.886	4.000	3.847
+5%	0.607	0.387	1.839	3.965	3.809
Au(111)	1.482	1.057	2.610	4.677	4.35
Ir(111)	0.291	-0.121	0.805	3.664	-
Rh(111)	0.463	-0.049	0.697	3.716	3.575
Ru(0001)	0.027	-0.497	-0.150	-	-