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

Formulating the Bonding Contribution Equation in Heterogeneous Catalysis: A Quantitative Description between Surface Structure and Adsorption Energy

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Table S1 The substitution positions (p_1 and p_2), solute metals (s_1 and s_2), predicted adsorption energies ($\Delta E_{predict}$), calculated adsorption energies (ΔE_{DFT}), distances between oxygen atom and three closest surface atoms (x_1, x_2 and x_3), and adsorption sites (site) of 50 generated two-atom substitution alloy surfaces.

p_1	s_1	p_2	s_2	ΔEpredict	ΔE_{DFT}	x_1	x_2	x_3	site
type1	Ir	type1	Ir	-0.57	-0.69	2.01	2.01	2.08	hollow
type2	Ir	type4	Ir	0.37	0.31	2.07	2.07	2.07	hollow
type3	Ir	type2	Ir	0.32	0.28	2.04	2.06	2.06	hollow
type3	Ir	type4	Ir	0.20	0.13	2.05	2.07	2.07	hollow
type1	Ir	type1	Os	-1.11	-1.03	1.96	2.07	2.10	hollow
type1	Ir	type4	Os	0.07	-0.10	1.97	2.08	2.08	hollow
type3	Ir	type1	Os	-0.75	-0.68	1.89	2.17	2.19	hollow
type3	Ir	type4	Os	0.44	0.41	2.04	2.06	2.06	hollow
type2	Ir	type1	Pd	0.20	0.17	2.02	2.02	2.08	hollow
type2	Ir	type4	Pd	0.26	0.32	2.04	2.04	2.04	hollow
type3	Ir	type3	Pd	0.09	0.06	2.04	2.05	2.05	hollow
type4	Ir	type1	Pd	0.08	0.07	2.02	2.03	2.08	hollow
type3	Ir	type3	Re	0.42	0.35	2.04	2.08	2.08	hollow
type3	Os	type1	Ir	-0.05	-0.21	1.99	2.07	2.10	hollow
type1	Os	type3	Os	-0.59	-0.71	1.86	2.23	2.23	hollow
type2	Os	type1	Os	-0.12	-0.43	1.89	2.21	2.21	hollow
type1	Os	type1	Pd	-0.87	-0.94	1.85	2.19	2.22	hollow
type1	Os	type3	Pd	-0.82	-0.75	1.89	2.17	2.18	hollow
type1	Os	type4	Pd	-0.81	-0.73	1.88	2.19	2.19	hollow
type3	Os	type2	Pd	0.27	-0.01	2.02	2.06	2.06	hollow
type3	Os	type3	Pd	0.25	0.13	2.03	2.06	2.07	hollow
type1	Os	type3	Re	-0.49	-0.62	1.91	2.16	2.18	hollow
type3	Os	type3	Re	0.57	0.39	2.06	2.07	2.09	hollow
type1	Pd	type1	Ir	-0.33	-0.46	1.93	2.07	2.11	hollow
type1	Pd	type3	Ir	0.04	0.05	2.01	2.02	2.08	hollow
type2	Pd	type3	Ir	0.12	-0.06	2.03	2.05	2.05	hollow
type2	Pd	type4	Ir	0.16	-0.10	2.05	2.05	2.05	hollow
type1	Pd	type2	Os	0.67	0.47	2.03	2.03	2.11	hollow
type1	Pd	type4	Os	0.31	0.29	2.02	2.02	2.08	hollow
type1	Pd	type3	Pd	-0.03	-0.06	2.01	2.02	2.06	hollow
type1	Pd	type4	Pd	-0.02	0.12	2.01	2.01	2.06	hollow
type4	Pd	type3	Pd	0.03	0.09	2.03	2.03	2.04	hollow
type1	Pd	type2	Re	0.97	0.69	2.05	2.05	2.15	hollow
type1	Pd	type3	Re	0.29	0.21	2.00	2.04	2.11	hollow
type3	Pd	type2	Re	1.02	0.73	2.07	2.07	2.08	hollow
type4	Pd	type3	Re	0.36	0.44	2.02	2.07	2.07	hollow
type3	Re	type1	Ir	0.05	-0.16	2.00	2.06	2.12	hollow
type3	Re	type4	Ir	0.46	0.26	2.04	2.09	2.09	hollow
type4	Re	type3	Ir	0.59	0.70	2.03	2.05	2.05	hollow
type3	Re	type4	Os	0.69	0.44	2.04	2.10	2.10	hollow
type4	Re	type1	Os	-0.33	-0.33	1.94	2.11	2.11	hollow
type2	Re	type1	Pd	0.97	0.69	2.05	2.05	2.15	hollow
type3	Re	type3	Pd	0.35	0.23	2.03	2.08	2.08	hollow
type4	Re	type1	Pd	0.46	0.57	2.02	2.02	2.08	hollow
type3	Ir	type1	Re	-1.10	-1.57	1.71	3.36	3.36	top
type4	Ir	type1	Re	-1.06	-1.33	1.72	3.27	3.27	top
type2	Os	type1	Re	-0.47	-1.51	1.71	3.30	3.43	top
type1	Re	type4	Ir	-1.06	-1.39	1.72	3.37	3.37	top
type1	Re	type1	Pd	-1.22	-1.55	1.74	2.66	2.87	top
type3	Re	type1	Re	-0.84	-1.67	1.71	3.43	3.43	top

Table S2 The substitution positions (p_1, p_2 and p_3), solute metals (s_1, s_2 and s_3), predicted adsorption energies ($\Delta E_{predict}$), calculated adsorption energies (ΔE_{DFT}), distances between oxygen atom and three closest surface atoms (x_1, x_2 and x_3), and adsorption sites (site) of 50 generated three-atom substitution alloy surfaces.

p_1	s_1	p_2	s_2	p_3	s_3	ΔEpredict	ΔE_{DFT}	x_1	x_2	x_3	site
type3	Os	type3	Pd	type1	Re	-0.93	-1.13	1.80	2.42	2.48	hollow
type1	Re	type3	Re	type3	Pd	-0.83	-1.12	1.81	2.39	2.42	hollow
type1	Ir	type2	Ir	type4	Ir	0.08	-0.09	1.98	2.09	2.09	hollow
type3	Ir	type4	Ir	type1	Ir	-0.08	-0.24	1.96	2.09	2.09	hollow
type3	Ir	type4	Os	type3	Ir	0.52	0.47	2.05	2.05	2.07	hollow
type1	Ir	type1	Pd	type1	Ir	-0.61	-0.83	1.99	1.99	2.10	hollow
type1	Ir	type2	Pd	type3	Ir	-0.17	-0.45	1.98	2.07	2.09	hollow
type3	Ir	type1	Pd	type1	Os	-0.79	-0.88	1.85	2.19	2.25	hollow
type1	Ir	type4	Pd	type1	Pd	-0.31	-0.37	1.93	2.08	2.12	hollow
type3	Ir	type1	Pd	type3	Pd	0.05	0.02	2.01	2.03	2.08	hollow
type1	Ir	type1	Re	type2	Ir	-1.22	-1.17	1.88	2.21	2.25	hollow
type1	Ir	type4	Re	type3	Os	0.46	0.14	1.96	2.08	2.08	hollow
type2	Ir	type3	Re	type3	Os	0.82	0.51	2.06	2.07	2.10	hollow
type4	Ir	type3	Re	type3	Os	0.70	0.30	2.08	2.09	2.12	hollow
type1	Ir	type3	Re	type1	Pd	0.01	-0.27	1.96	2.05	2.17	hollow
type1	Ir	type3	Re	type4	Pd	0.07	-0.05	1.99	2.06	2.12	hollow
type3	Os	type3	Ir	type4	Os	0.67	0.50	2.05	2.09	2.10	hollow
type4	Os	type3	Ir	type1	Pd	0.39	0.39	2.03	2.03	2.07	hollow
type1	Os	type1	Ir	type4	Re	-0.61	-0.69	1.99	2.02	2.05	hollow
type1	Os	type3	Os	type3	Re	-0.26	-0.59	1.93	2.17	2.18	hollow
type1	Os	type3	Pd	type2	Ir	-0.58	-0.62	1.90	2.17	2.17	hollow
type3	Os	type3	Pd	type4	Re	0.75	0.72	2.03	2.07	2.08	hollow
type4	Pd	type1	Ir	type1	Ir	-0.55	-0.63	2.01	2.01	2.09	hollow
type1	Pd	type1	Ir	type3	Pd	-0.31	-0.49	1.94	2.07	2.10	hollow
type1	Pd	type3	Ir	type4	Re	0.54	0.66	2.02	2.02	2.07	hollow
type3	Pd	type3	Os	type2	Ir	0.49	0.32	2.04	2.06	2.08	hollow
type3	Pd	type3	Os	type3	Ir	0.33	0.22	2.04	2.06	2.08	hollow
type4	Pd	type3	Os	type1	Pd	0.21	0.27	2.00	2.03	2.10	hollow
type3	Pd	type1	Pd	type1	Pd	-0.07	-0.04	1.98	2.04	2.05	hollow
type3	Pd	type4	Re	type1	Ir	0.23	0.08	1.97	2.06	2.06	hollow
type1	Re	type1	Ir	type3	Ir	-1.38	-1.27	1.89	2.18	2.24	hollow
type3	Re	type1	Ir	type1	Ir	-0.23	-0.50	1.99	2.05	2.12	hollow
type3	Re	type3	Ir	type1	Ir	0.13	-0.12	2.00	2.07	2.11	hollow
type3	Re	type1	Ir	type1	Re	-1.13	-1.17	1.90	2.15	2.22	hollow
type1	Re	type4	Os	type1	Ir	-1.11	-1.10	1.93	2.13	2.19	hollow
type3	Re	type1	Os	type1	Pd	-0.54	-0.85	1.83	2.26	2.27	hollow
type3	Re	type4	Os	type1	Pd	0.65	0.36	2.02	2.04	2.13	hollow
type3	Re	type1	Os	type3	Re	-0.16	-0.57	1.89	2.22	2.22	hollow
type3	Re	type1	Pd	type4	Ir	0.42	0.24	2.07	2.07	2.08	hollow
type3	Re	type2	Pd	type3	Ir	0.45	0.17	2.03	2.08	2.08	hollow
type3	Re	type3	Pd	type1	Ir	0.06	-0.18	1.99	2.06	2.12	hollow
type3	Re	type3	Pd	type1	Os	-0.48	-0.65	1.91	2.16	2.18	hollow
type4	Re	type1	Re	type1	Os	-1.50	-1.19	2.00	2.04	2.08	hollow
type3	Ir	type1	Pd	type1	Re	-1.14	-1.70	1.72	3.20	3.35	top
type3	Ir	type1	Re	type4	Ir	-0.98	-1.43	1.72	3.37	3.38	top
type3	Ir	type2	Re	type1	Os	0.26	-1.52	2.05	2.16	3.26	bridge
type1	Os	type3	Pd	type2	Re	0.19	-1.44	2.05	2.16	3.24	bridge
type3	Pd	type1	Re	type3	Ir	-1.09	-1.42	1.72	3.24	3.28	top
type3	Re	type2	Ir	type1	Re	-0.60	-1.61	1.70	3.43	3.43	top
type1	Re	type3	Os	type2	Ir	-0.70	-1.31	1.71	3.29	3.42	top

Negative Adsorption Influence of the Second Neighbour

In the manuscript, we showed that a substitution of first neighbour atom to the adsorbate (type I) has a positive adsorption influence (i.e. a substitution with an intrinsically more active solute metal will enhance the adsorption), while a substitution of second neighbour atom (type II, type III or type IV) has a negative influence of adsorption energy. This phenomenon can be understood as follows: The first neighbour atom directly bonds with the adsorbates. Therefore, a substitution with an intrinsically more active metal can enhance the bonding between adsorbate and the adsorption site atom. On the other hands, the second neighbour atom affects the adsorption energy via the first neighbour atom. A second neighbour substitution with an intrinsically more active solute metal will increase the bonding between the substituted second neighbour atom and the first neighbour atom. Due to this competing bonding, the interaction between the adsorbate and the first neighbour atom will decrease.

Example of Calculating the Generalized Parameter

For a substitution of type I (BCCF of 7/27, Equation 2 in manuscript) with an Os atom with the intrinsic bonding ability of -1.17 eV, the O adsorption energy of oxygen atom is changed by -0.75 eV, based on which the generalized parameter of Os can be calculated to be -0.75/-1.17/(7/27) = 2.47. The value 2.75 in the manuscript was obtained by averaging all the generalized parameters of the solute metals from the substitutions of type I.