Electronic Supplementary Material (ESI) for Nanoscale.

Toward Rational Nanoparticle Synthesis: Predicting Surface Intermixing in Bimetallic Alloy Nanocatalysts

Electronic Supplementary Information

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Supplementary Discussion

Energy cutoff

We verified the convergence of calculated activation energy barriers with respect to the DFT energy cutoff by comparing the barriers calculated at a cutoff of 300 eV with those calculated at 400 eV for a system with a Pt adatom on Pd(100) with two unit cell sizes. Values calculated at 400 eV are given in parentheses. For the 3x3 unit cell, "hopping" diffusion has a barrier of 0.99 eV (0.99 eV) and substitution has a barrier of 0.74 eV (0.74 eV). For the 2x2 unit cell, hopping had a barrier of 1.03 eV (1.03 eV) and substitution 1.06 eV (0.98 eV). The mean error in these calculations (0.02 eV) and maximum deviation (0.08 eV) are sufficiently small that no conclusions of this study will be affected by the energy cutoff choice.

Surface coverage effects

In addition to the calculations performed in the 3x3 unit cell (1/9 monolayer, ML) presented in the main text, we performed the same calculations at 1/4 ML in a 2x2 surface unit cell. The binding energies of metal adatoms (Tables S2 and S3 of the Supplementary Information) were generally slightly destabilized by the increased coverage in the 2x2 unit cell. The average destabilization in the smaller unit cell of the fcc(111) and hcp(0001) facets (0.08 eV, standard deviation (s.d.) 0.08 eV) was marginally larger than the average destabilization on the fcc(100) facets (0.05 eV, s.d. 0.05 eV). The hopping diffusion barriers at 1/4 ML are provided in Tables S4 and S5. *Hopping* barriers on the fcc(111) and hcp(0001) surfaces were relatively unchanged by the surface coverage: all calculated differences were 0.1 eV or less (either increasing or decreasing), and the average change was calculated to be 0.0 eV, indicating that changing the unit cell size does not introduce any bias toward increasing or decreasing activation barriers for hopping events. A similar conclusion can be reached for hopping on the fcc(100) surfaces.

The energies of *substitution* at 1/4 ML are given in Tables S6 and S7. Again, no general trend is observed for the changes to smaller unit cells in either geometry, as the average difference between the 1/9 ML and 1/4 ML energetics is less than 0.01 eV. The activation energy barriers for adatom substitution at 1/4 ML are given in Tables S8-S10. In this case, we observe an interesting difference in coverage effects between the fcc(111)/hcp(0001) surfaces and the fcc(100) surfaces. The increased coverage from 1/9 ML to 1/4 ML caused a general increase in substitutional barrier for the fcc(100) surfaces: the magnitude of this change ranged from 0.0 eV to 0.5 eV, and averaged 0.2 eV. In contrast, the increased coverage on the fcc(111) and hcp(0001) surfaces led to a general decrease in activation energy barrier averaging -0.2 eV. Both these trends occur relatively uniformly for all bimetallic surfaces considered, rather than being dominated by one or two specific metal adatoms/host slabs.

We believe these seemingly contradictory behaviors arise from a combination of two factors, one which destabilizes the transition state and another which stabilizes it. First, we anticipate that increased adatom coverage should constrain the movement of underlying surface atoms, which is critical for enabling these substitution events. This effect should increase the activation energy barrier for substitution events. We find that this additional constraint is more pronounced on the (100) surfaces, since movement of surface atoms is much freer at low coverages on these open surfaces (due to both geometric effects as well as having eight-fold coordinated surface atoms) than on the close-packed (111)/(0001) surfaces (which have nine-fold coordinated surface atoms in a tight hexagonal surface arrangement). Our calculations support this assertion (as a representative example, distances in parentheses are given for Pd substitution into Pt): in general, surface atoms move by small amounts (~ 0.1 Å) to accommodate substitution in the

(111)/(0001) surfaces within a 3x3 unit cell, and by slightly smaller amounts (~ 0.05 Å) in the 2x2 unit cell. In contrast, (100) surface atoms move much more (> 0.2 Å) in the 3x3 unit cell and by a substantially reduced amount (~ 0.1 Å) in the 2x2 unit cell. This suggests that increasing coverage should restrict movement more on the (100) facets and have a relatively large destabilizing effect on the substitution transition states relative to the same effects on the close-packed (111) surfaces. In contrast to the destabilizing effect of reduced surface mobility, we also note a stabilizing effect of increased surface coverage by observing that metal adatoms are far below their preferred coordination number: those on (100) surfaces are bound to four atoms and those on (111)/(0001) surfaces are bound to three, both of which are substantially lower than the preferred bulk coordination of 12. Changing conditions from low to high surface coverage therefore puts more undercoordinated atoms in close proximity to the transition state for substitution. Since the transition state involves the movement of two particularly undercoordinated metal atoms (the adatom and the displaced surface atom) rather than just one undercoordinated adatom in the initial/final states, we believe that the transition state will be stabilized more by this high-coverage effect than either the initial or final states; this lowers the activation energy barrier. Further, we expect this stabilization effect should be larger on the (111)/(0001) surfaces than on the (100) surfaces since the adatoms are more undercoordinated on the close-packed facets and would therefore have stronger interactions with the transition state (in addition to proximity effects introduced by the smaller surface unit cell geometry in the close-packed hexagonal geometry relative to the more open (100) geometry). We observe a change in the preferred mechanism on the close-packed geometries, as this transition state stabilization substantially lowers the energy of asymmetric substitution (i.e. fcc-to-fcc or hcp-to-hcp substitution) and makes those mechanisms

preferred to the symmetric substitution preferred in the lower coverage case in the 3x3 unit cell (Tables S1 and S8). As a result, this stabilization effect dominates the close-packed surfaces (relative to the small destabilization from lost surface mobility) and leads to a net decrease in activation energy. The smaller stabilization effect on the (100) surfaces (relative to the large destabilization from lost surface mobility) leads to the net increase in substitution barrier.

Supplementary Tables

Table S1: Calculated "*hopping*" diffusion rate constants on fcc(111) and hcp(0001) surfaces, 3x3 unit cell. Rate constants are calculated assuming an Arrhenius expression (i.e., $\alpha * \exp(-E_a/k_B T)$ with a constant pre-exponential factor of 10^{13} site^{-1} s^{-1}. Values were then converted to a per-area basis using a factor of sites per geometric area, and converted to the meter scale (i.e., multiply rate per site by the overall factor $\frac{4\sqrt{3}}{3a^2} * \frac{site}{Å^2} * \frac{10^{20} Å^2}{m^2}$, where a is the lattice constant of the given metal in Å). All tabulated values therefore have units of m^{-2}s^{-1}.

300 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	9.1E+21	1.1E+22	6.6E+20	2.0E+23	3.1E+23	2.9E+26	2.2E+25	8.2E+28	2.7E+30	1.8E+29
	Ru	2.8E+20	8.8E+21	2.7E+22	1.9E+25	4.8E+27	3.6E+29	6.5E+27	3.3E+30	1.3E+31	2.1E+30
	Ir	5.9E+19	2.1E+26	1.2E+25	7.8E+27	8.4E+27	2.1E+29	2.6E+28	4.3E+29	3.1E+30	5.4E+29
	Rh	2.5E+24	2.0E+28	8.2E+27	2.6E+29	1.3E+29	1.3E+30	5.3E+29	1.6E+30	7.9E+30	2.1E+30
	Pt	4.1E+24	1.6E+28	9.0E+25	1.6E+28	3.1E+27	5.2E+28	2.0E+28	2.0E+29	1.9E+30	1.8E+29
	Pd	1.7E+31	2.5E+30	1.4E+30	1.9E+30	5.3E+29	1.5E+30	6.5E+29	1.5E+30	5.8E+30	1.5E+30
	Ni	1.1E+31	1.0E+31	2.7E+31	2.5E+31	1.3E+31	1.4E+31	7.9E+30	1.0E+31	3.3E+31	1.5E+31
	Au	2.9E+30	8.3E+30	1.6E+30	2.4E+30	7.6E+29	1.7E+30	9.4E+29	1.1E+30	4.5E+30	1.3E+30
	Ag	1.8E+31	4.4E+31	1.5E+31	3.1E+31	1.8E+31	1.7E+31	1.1E+31	5.4E+30	1.1E+31	5.8E+30
	Cu	9.5E+31	8.6E+31	1.0E+31	5.6E+31	4.0E+31	3.9E+31	2.8E+31	1.5E+31	3.3E+31	1.9E+31

600 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	1.2E+27	1.3E+27	3.1E+26	5.4E+27	6.8E+27	2.1E+29	5.8E+28	3.5E+30	2.0E+31	5.1E+30
	Ru	2.1E+26	1.2E+27	2.0E+27	5.4E+28	8.7E+29	7.5E+30	1.0E+30	2.3E+31	4.5E+31	1.8E+31
	Ir	9.5E+25	1.8E+29	4.3E+28	1.1E+30	1.1E+30	5.7E+30	2.0E+30	8.1E+30	2.2E+31	9.1E+30
	Rh	2.0E+28	1.7E+30	1.1E+30	6.4E+30	4.4E+30	1.5E+31	9.1E+30	1.6E+31	3.5E+31	1.8E+31
	Pt	2.4E+28	1.5E+30	1.1E+29	1.5E+30	6.7E+29	2.8E+30	1.7E+30	5.4E+30	1.7E+31	5.2E+30
	Pd	5.0E+31	1.9E+31	1.4E+31	1.7E+31	8.8E+30	1.5E+31	9.8E+30	1.5E+31	2.9E+31	1.5E+31
	Ni	4.5E+31	4.4E+31	7.0E+31	6.9E+31	4.9E+31	5.2E+31	3.8E+31	4.3E+31	7.9E+31	5.3E+31
	Au	1.9E+31	3.3E+31	1.4E+31	1.8E+31	1.0E+31	1.5E+31	1.1E+31	1.2E+31	2.5E+31	1.3E+31
	Ag	4.9E+31	7.7E+31	4.5E+31	6.4E+31	4.9E+31	4.8E+31	3.9E+31	2.7E+31	3.8E+31	2.8E+31
	Cu	1.3E+32	1.2E+32	4.2E+31	9.9E+31	8.4E+31	8.3E+31	7.0E+31	5.0E+31	7.6E+31	5.7E+31

Table S2: Calculated "*hopping*" diffusion rate constants on fcc(100) surfaces, 3x3 unit cell. Rate constants are calculated assuming an Arrhenius expression (i.e., $\alpha * \exp(-E_a/k_B T)$ with a constant pre-exponential factor of 10^{13} site^{-1} s^{-1}. Values were then converted to a per-area basis using a factor of sites per geometric area, and converted to the meter scale (i.e., multiply rate per site by the overall factor $\frac{2}{a^2} * \frac{site}{Å^2} * \frac{10^{20} Å^2}{m^2}$, where a is the lattice constant of the given metal in Å). All tabulated values therefore have units of m^{-2}s^{-1}.

300 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	1.4E+03	5.0E+12	9.2E+11	2.7E+15	1.6E+16	3.5E+18	1.7E+18	1.5E+23	3.5E+24	1.3E+21
	Rh	7.4E+02	2.5E+13	7.0E+10	5.3E+15	7.6E+15	3.8E+19	8.7E+18	7.5E+22	6.0E+24	6.2E+21
	Pt	3.0E-01	4.2E+11	2.3E+09	6.2E+13	7.9E+14	3.3E+18	4.5E+16	1.9E+22	5.6E+23	7.1E+19
	Pd	1.1E+04	2.6E+13	4.6E+09	7.7E+14	3.1E+15	6.1E+19	5.9E+15	1.2E+22	8.9E+23	4.8E+20
	Ni	6.2E+09	3.1E+16	1.2E+12	1.2E+17	3.0E+16	9.7E+20	7.4E+19	5.9E+23	1.4E+26	2.5E+23
	Au	5.7E+12	6.6E+11	4.0E+06	2.7E+11	6.5E+12	2.4E+17	1.2E+15	8.6E+21	2.1E+23	1.7E+19
	Ag	2.3E+20	8.1E+16	8.9E+10	4.1E+14	5.0E+14	5.1E+18	7.7E+17	7.4E+22	2.7E+24	1.1E+22
	Cu	4.5E+18	3.6E+17	4.7E+12	5.7E+16	1.2E+16	2.9E+20	6.8E+18	1.4E+23	3.4E+25	6.3E+22

600 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	4.3E+17	2.6E+22	1.1E+22	6.0E+23	1.4E+24	2.2E+25	1.5E+25	4.4E+27	2.2E+28	4.1E+26
	Rh	3.2E+17	5.8E+22	3.1E+21	8.5E+23	1.0E+24	7.2E+25	3.4E+25	3.2E+27	2.9E+28	9.2E+26
	Pt	6.1E+15	7.3E+21	5.3E+20	8.9E+22	3.2E+23	2.0E+25	2.4E+24	1.6E+27	8.4E+27	9.5E+25
	Pd	1.2E+18	5.7E+22	7.7E+20	3.1E+23	6.3E+23	8.8E+25	8.7E+23	1.2E+27	1.1E+28	2.5E+26
	Ni	1.0E+21	2.2E+24	1.4E+22	4.3E+24	2.2E+24	4.0E+26	1.1E+26	9.7E+27	1.5E+29	6.3E+27
	Au	2.6E+22	8.7E+21	2.2E+19	5.6E+21	2.7E+22	5.2E+24	3.6E+23	9.9E+26	4.9E+27	4.4E+25
	Ag	1.6E+26	3.1E+24	3.2E+21	2.2E+23	2.4E+23	2.4E+25	9.4E+24	2.9E+27	1.8E+28	1.1E+27
	Cu	2.6E+25	7.4E+24	2.7E+22	2.9E+24	1.3E+24	2.1E+26	3.2E+25	4.6E+27	7.2E+28	3.1E+27

Table S3: Calculated activation energy barriers for *substitution* of adatoms into fcc(111) and hcp(0001) surfaces, 3x3 unit cell. Four values are given for each substitution: the first letter denotes the original position of the adatom, and the second letter denotes the final position of the displaced surface atom. Sites are represented as: fcc (f), hcp (h). For example, an adatom in the fcc position displacing a surface atom to an hcp position would be denoted by "f-h". "X" denotes that an event was not found to occur. The most favorable pathway (with the lowest transition state energy) is bolded for each host slab-adatom combination. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	f-f: 3.75 f-h: 3.27 **h-f: 3.80** h-h: 4.17	f-f: X **f-h: 3.08** h-f: 3.65 h-h: 4.08	f-f: X f-h: 2.83 h-f: 3.48 **h-h: 3.42**	f-f: X **f-h: 3.08** h-f: 3.58 h-h: 3.57	f-f: X **f-h: 3.11** h-f: 3.56 h-h: 3.56	f-f: X h-f: 3.53 h-f: 3.89 **h-h: 3.83**	f-f: X **f-h: 3.30** h-f: 3.68 h-h: 3.64	f-f: 3.91 **f-h: 3.81** h-f: 4.05 h-h: X	f-f: 4.40 f-h: 4.26 h-f: 4.45 **h-h: 4.31**	f-f: 4.04 f-h: 3.88 h-f: 4.16 **h-h: 3.99**
	Ru	f-f: X f-h: 1.78 **h-f: 2.18** h-h: 2.19	f-f: 2.16 f-h: 1.68 **h-f: 2.19** h-h: 2.36	f-f: X f-h: 1.66 **h-f: 2.08** h-h: 2.30	f-f: X **f-h: 1.88** h-f: 2.31 h-h: 2.43	f-f: X f-h: 2.04 h-f: 2.28 **h-h: 2.23**	f-f: X f-h: 2.40 h-f: 2.62 **h-h: 2.51**	f-f: X **f-h: 2.19** h-f: 2.43 h-h: 2.57	f-f: 2.71 f-h: 2.54 h-f: 2.73 **h-h: 2.55**	f-f: 3.00 **f-h: 2.81** h-f: 3.00 h-h: 2.82	f-f: 2.71 f-h: 2.59 h-f: 2.75 **h-h: 2.62**
	Ir	f-f: 2.00 **f-h: 1.53** h-f: 1.71 h-h: 2.06	f-f: 2.21 **f-h: 1.75** h-f: 1.90 h-h: 2.21	f-f: 2.13 **f-h: 1.62** h-f: 1.69 h-h: 2.03	f-f: X f-h: 2.09 **h-f: 2.13** h-h: 2.41	f-f: 2.61 **f-h: 2.18** h-f: 2.12 h-h: 2.46	f-f: X **f-h: 2.67** h-f: 2.63 h-h: 2.83	f-f: 2.79 f-h: 2.39 **h-f: 2.37** h-h: 2.67	f-f: 2.98 **f-h: 2.69** h-f: 2.67 h-h: X	f-f: 3.06 f-h: 3.00 h-f: 3.03 **h-h: 2.97**	f-f: 2.67 **f-h: 2.66** h-f: 2.65 h-h: X
	Rh	f-f: X f-h: 1.08 **h-f: 1.20** h-h: 1.20	f-f: 1.36 f-h: 1.36 **h-f: 1.47** h-h: 1.47	f-f: X f-h: 1.37 **h-f: 1.39** h-h: 1.57	f-f: 1.91 f-h: 1.71 **h-f: 1.74** h-h: 1.93	f-f: X **f-h: 1.81** h-f: 1.82 h-h: X	f-f: 2.21 **f-h: 2.16** h-f: 2.18 h-h: 2.32	f-f: X f-h: 1.87 **h-f: 1.87** h-h: X	f-f: 2.47 **f-h: 2.21** h-f: 2.25 h-h: 2.34	f-f: 2.51 **f-h: 2.43** h-f: 2.49 h-h: X	f-f: X **f-h: 2.13** h-f: 2.14 h-h: 2.33
	Pt	f-f: 0.69 **f-h: 0.68** h-f: 0.58 h-h: 0.58	f-f: 1.26 f-h: 1.25 **h-f: 1.13** h-h: 1.14	f-f: 1.11 **f-h: 1.10** h-f: 0.94 h-h: 0.94	f-f: 1.51 f-h: 1.51 **h-f: 1.33** h-h: 1.63	f-f: 1.79 f-h: 1.54 **h-f: 1.37** h-h: 1.70	f-f: 2.06 f-h: 1.97 **h-f: 1.78** h-h: X	f-f: 1.58 f-h: 1.59 **h-f: 1.49** h-h: X	f-f: X f-h: 1.93 **h-f: 1.82** h-h: 2.09	**f-f: 2.12** f-h: 2.19 h-f: 2.09 h-h: 2.16	f-f: 2.04 f-h: 1.83 **h-f: 1.73** h-h: X
	Pd	f-f: X **f-h: 0.61** h-f: 0.63 h-h: 0.61	f-f: 1.13 **f-h: 1.12** h-f: 1.16 h-h: 1.17	**f-f: 1.01** f-h: 1.01 h-f: 1.00 h-h: 0.97	**f-f: 1.28** f-h: 1.30 h-f: 1.26 h-h: 1.24	f-f: 1.31 **f-h: 1.31** h-f: 1.27 h-h: 1.27	f-f: 1.65 **f-h: 1.59** h-f: 1.54 h-h: 1.60	f-f: 1.45 **f-h: 1.35** h-f: 1.45 h-h: 1.45	f-f: 1.71 f-h: 1.59 h-f: 1.56 **h-h: 1.54**	f-f: 1.78 f-h: 1.79 **h-f: 1.76** h-h: 1.88	f-f: 1.50 **f-h: 1.50** h-f: 1.47 h-h: X
	Ni	f-f: 1.06 f-h: 1.05 h-f: 1.09 **h-h: 1.09**	f-f: 1.58 f-h: 1.45 **h-f: 1.47** h-h: 1.47	**f-f: 1.29** f-h: 1.30 h-f: 1.31 h-h: 1.31	**f-f: 1.49** f-h: 1.50 h-f: 1.50 h-h: 1.63	f-f: 1.55 f-h: 1.53 h-f: 1.52 **h-h: 1.50**	f-f: 1.83 **f-h: 1.82** h-f: 1.81 h-h: 1.80	f-f: 1.83 f-h: 1.70 **h-f: 1.69** h-h: 1.84	f-f: 1.91 **f-h: 1.89** h-f: 1.89 h-h: 1.87	f-f: 2.16 **f-h: 2.14** h-f: 2.15 h-h: 2.14	f-f: 1.95 f-h: 1.94 h-f: 1.94 **h-h: 1.93**
	Au	f-f: 0.35 **f-h: 0.34** h-f: 0.30 h-h: 0.31	f-f: 0.65 **f-h: 0.64** h-f: 1.02 h-h: 0.97	**f-f: 0.59** f-h: 0.65 h-f: 0.59 h-h: 0.58	f-f: 0.77 f-h: 0.81 h-f: 0.73 **h-h: 0.69**	**f-f: 0.83** f-h: 0.85 h-f: 0.79 h-h: 0.78	f-f: 1.14 f-h: 1.00 h-f: 0.94 **h-h: 0.93**	**f-f: 0.71** f-h: 0.74 h-f: 0.69 h-h: 0.74	f-f: 0.95 **f-h: 0.85** h-f: 0.82 h-h: 0.96	f-f: 1.03 f-h: 0.96 **h-f: 0.93** h-h: 1.05	**f-f: 0.75** f-h: 0.77 h-f: 0.75 h-h: 0.74
	Ag	f-f: 0.71 f-h: 0.71 h-f: 0.69 **h-h: 0.68**	f-f: 0.81 f-h: 0.81 h-f: 0.79 **h-h: 0.78**	**f-f: 0.68** f-h: 0.69 h-f: 0.67 h-h: 0.66	f-f: 0.78 f-h: 0.79 **h-f: 0.76** h-h: 0.76	**f-f: 0.81** f-h: 0.83 h-f: 0.80 h-h: 0.79	**f-f: 0.95** f-h: 0.98 h-f: 0.96 h-h: 0.93	f-f: 0.86 f-h: 0.85 **h-f: 0.83** h-h: 0.85	f-f: 0.98 **f-h: 0.92** h-f: 0.91 h-h: 0.97	f-f: 1.06 **f-h: 1.01** h-f: 1.01 h-h: 1.06	f-f: 0.90 **f-h: 0.88** h-f: 0.88 h-h: 0.90
	Cu	f-f: 0.89 f-h: 0.88 h-f: 0.86 **h-h: 0.86**	f-f: 1.00 f-h: 1.01 h-f: 0.97 **h-h: 0.97**	**f-f: 0.86** f-h: 0.86 h-f: 0.83 h-h: X	f-f: 1.23 f-h: 1.03 h-f: 1.01 **h-h: 0.99**	**f-f: 1.06** f-h: 1.07 h-f: 1.06 h-h: X	f-f: 1.31 f-h: 1.30 **h-f: 1.28** h-h: 1.28	f-f: 1.19 f-h: 1.21 h-f: 1.18 **h-h: 1.16**	f-f: 1.29 **f-h: 1.29** h-f: 1.28 h-h: 1.28	f-f: 1.46 f-h: 1.46 **h-f: 1.45** h-h: 1.45	f-f: 1.39 **f-h: 1.31** h-f: 1.30 h-h: 1.38

Table S4: Calculated *substitution* rate constants on fcc(111) and hcp(0001) surfaces, 3x3 unit cell. All table values are in $m^{-2}s^{-1}$. Details of rate constant calculations are in the caption of Table S1.

300 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	2.4E-32	1.2E-29	5.0E-26	1.6E-28	2.5E-28	6.8E-33	1.0E-29	6.5E-35	4.8E-41	1.5E-35
	Ru	3.6E-05	2.6E-05	1.9E-03	1.9E-06	4.8E-06	1.1E-10	1.2E-08	1.9E-11	7.1E-16	1.5E-12
	Ir	1.1E+04	2.2E+00	6.5E+03	2.5E-04	3.5E-05	1.8E-13	2.0E-08	9.4E-14	5.9E-19	3.1E-13
	Rh	1.2E+12	3.5E+07	6.1E+08	8.4E+02	5.4E+01	9.6E-05	5.8E+00	1.2E-05	2.3E-09	3.0E-04
	Pt	5.1E+20	5.9E+11	5.6E+13	9.1E+07	1.9E+06	3.5E+00	1.2E+06	1.1E+00	3.6E-04	1.5E+02
	Pd	8.5E+21	9.9E+12	1.8E+15	5.3E+10	1.5E+10	2.9E+05	3.6E+09	3.0E+05	2.0E+02	1.1E+07
	Ni	9.1E+13	4.1E+07	2.1E+10	1.1E+07	4.3E+06	4.6E+01	5.0E+03	3.3E+00	1.9E-04	4.5E-01
	Au	2.2E+26	2.3E+21	1.6E+22	2.5E+19	1.3E+18	3.3E+15	1.5E+20	7.6E+17	2.1E+16	3.7E+19
	Ag	2.5E+20	7.0E+18	4.7E+20	8.9E+18	2.9E+18	1.3E+16	8.7E+17	5.1E+16	1.4E+15	1.9E+17
	Cu	5.3E+17	5.3E+15	7.2E+17	1.2E+15	2.4E+14	2.5E+10	3.0E+12	4.0E+10	6.1E+07	1.6E+10

600 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	1.9E+00	4.2E+01	2.7E+03	1.5E+02	1.9E+02	1.0E+00	4.0E+01	9.8E-02	8.5E-05	4.7E-02
	Ru	7.4E+13	6.3E+13	5.4E+14	1.7E+13	2.7E+13	1.3E+11	1.4E+12	5.5E+10	3.3E+08	1.5E+10
	Ir	1.3E+18	1.9E+16	1.0E+18	2.0E+14	7.3E+13	5.3E+09	1.7E+12	3.8E+09	9.5E+06	6.9E+09
	Rh	1.4E+22	7.4E+19	3.1E+20	3.6E+17	9.2E+16	1.2E+14	3.0E+16	4.4E+13	5.9E+11	2.2E+14
	Pt	2.7E+26	9.3E+21	9.0E+22	1.1E+20	1.7E+19	2.3E+16	1.3E+19	1.3E+16	2.3E+14	1.5E+17
	Pd	1.1E+27	3.8E+22	5.2E+23	2.8E+21	1.5E+21	6.6E+18	7.3E+20	6.7E+18	1.7E+17	4.0E+19
	Ni	1.3E+23	8.8E+19	2.0E+21	4.5E+19	2.8E+19	9.3E+16	9.7E+17	2.5E+16	1.9E+14	9.2E+15
	Au	1.7E+29	5.5E+26	1.4E+27	5.8E+25	1.3E+25	6.6E+23	1.4E+26	1.0E+25	1.7E+24	7.0E+25
	Ag	1.8E+26	3.0E+25	2.5E+26	3.4E+25	2.0E+25	1.3E+24	1.1E+25	2.6E+24	4.2E+23	5.0E+24
	Cu	9.6E+24	9.6E+23	1.1E+25	4.6E+23	2.0E+23	2.1E+21	2.3E+22	2.6E+21	1.0E+20	1.7E+21

Table S5: Calculated *substitution* rate constants on fcc(100) surfaces, 3x3 unit cell. All table values are in $m^{-2}s^{-1}$. Details of rate constant calculations are in the caption of Table S2.

300 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	1.6E+23	1.7E+24	4.5E+27	1.4E+21	4.8E+20	1.4E+15	1.4E+17	2.4E+15	7.6E+10	2.4E+12
	Rh	1.8E+23	1.6E+18	2.2E+20	3.0E+16	2.2E+17	5.0E+12	5.5E+15	2.4E+13	2.5E+09	2.8E+11
	Pt	2.0E+31	3.2E+26	2.1E+28	3.5E+23	7.3E+23	4.2E+18	2.4E+21	1.3E+19	3.8E+15	5.6E+17
	Pd	1.3E+31	4.1E+22	1.3E+24	2.2E+20	4.8E+19	1.5E+16	1.9E+19	3.9E+15	5.5E+12	8.9E+16
	Ni	5.3E+19	1.2E+15	1.4E+16	3.1E+14	3.5E+14	8.3E+11	5.0E+14	3.1E+12	3.0E+09	6.5E+11
	Au	2.1E+30	4.3E+26	7.7E+27	3.9E+25	2.3E+26	2.4E+24	1.3E+27	3.8E+25	1.5E+24	5.0E+25
	Ag	1.7E+25	3.4E+23	1.9E+24	1.1E+23	9.6E+22	4.3E+21	1.9E+24	6.5E+20	3.8E+20	3.4E+22
	Cu	8.3E+22	7.6E+19	4.7E+19	5.5E+18	2.8E+18	1.3E+17	8.9E+18	1.3E+17	8.4E+15	3.6E+17

600 K		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	4.6E+27	1.5E+28	7.8E+29	4.3E+26	2.5E+26	4.3E+23	4.3E+24	5.7E+23	3.2E+21	1.8E+22
	Rh	5.0E+27	1.5E+25	1.7E+26	2.0E+24	5.5E+24	2.6E+22	8.6E+23	5.7E+22	5.8E+20	6.2E+21
	Pt	5.0E+31	2.0E+29	1.6E+30	6.7E+27	9.6E+27	2.3E+25	5.5E+26	4.1E+25	6.9E+23	8.4E+24
	Pd	4.0E+31	2.3E+27	1.3E+28	1.7E+26	7.8E+25	1.4E+24	5.0E+25	7.1E+23	2.7E+22	3.4E+24
	Ni	9.2E+25	4.4E+23	1.5E+24	2.2E+23	2.4E+23	1.2E+22	2.8E+23	2.2E+22	6.9E+20	1.0E+22
	Au	1.6E+31	2.2E+29	9.4E+29	6.7E+28	1.6E+29	1.7E+28	3.9E+29	6.6E+28	1.3E+28	7.6E+28
	Ag	4.5E+28	6.3E+27	1.5E+28	3.5E+27	3.3E+27	7.1E+26	1.5E+28	2.7E+26	2.1E+26	2.0E+27
	Cu	3.5E+27	1.1E+26	8.4E+25	2.9E+25	2.1E+25	4.4E+24	3.7E+25	4.5E+24	1.1E+24	7.3E+24

Table S6: Calculated binding energies of adatoms in bridge (b; when stable), fcc (f), and hcp (h) sites of fcc(111) and hcp(0001) surfaces, 2x2 unit cell; for each host slab-adatom combination, the most stable site is shown in bold. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	f: -5.79 **h: -6.18**	f: -5.36 **h: -5.87**	f: -6.21 **h: -6.77**	f: -5.01 **h: -5.51**	f: -5.29 **h: -5.76**	f: -3.53 **h: -3.86**	f: -4.22 **h: -4.54**	f: -3.14 **h: -3.24**	f: -2.42 **h: -2.46**	f: -3.07 **h: -3.16**
	Ru	f: -5.59 **h: -5.96**	f: -5.06 **h: -5.44**	f: -5.74 **h: -6.13**	f: -4.68 **h: -5.06**	f: -5.01 **h: -5.23**	f: -3.43 **h: -3.54**	f: -4.10 **h: -4.31**	f: -3.09 **h: -3.10**	f: -2.44 **h: -2.44**	f: -3.05 **h: -3.09**
	Ir	f: -5.33 **h: -5.37**	f: -4.80 **h: -4.90**	f: -5.34 **h: -5.35**	f: -4.55 **h: -4.58**	**f: -4.77** h: -4.70	**f: -3.37** h: -3.32	f: -4.14 **h: -4.15**	**f: -2.80** h: -2.73	**f: -2.35** h: -2.32	**f: -3.08** h: -3.05
	Rh	f: -5.18 **h: -5.25**	f: -4.57 **h: -4.65**	f: -5.15 **h: -5.18**	f: -4.30 **h: -4.33**	**f: -4.69** h: -4.63	**f: -3.19** h: -3.15	**f: -3.91** h: -3.90	**f: -2.86** h: -2.80	**f: -2.33** h: -2.31	**f: -2.97** h: -2.94
	Pt	**f: -4.50** h: -4.39	**f: -4.43** h: -4.36	**f: -4.70** h: -4.54	**f: -4.11** h: -3.99	**f: -4.39** h: -4.22	**f: -3.08** h: -2.98	**f: -3.96** h: -3.89	**f: -2.67** h: -2.59	**f: -2.39** h: -2.36	**f: -3.09** h: -3.04
	Pd	b: -3.85 **f: -3.91** h: -3.88	f: -3.98 **h: -3.99**	**f: -4.23** h: -4.14	**f: -3.59** h: -3.52	**f: -4.04** h: -3.96	**f: -2.72** h: -2.67	**f: -3.57** h: -3.54	**f: -2.61** h: -2.57	**f: -2.26** h: -2.24	**f: -2.82** h: -2.79
	Ni	f: -4.02 **h: -4.07**	f: -4.43 **h: -4.46**	f: -4.95 **h: -4.96**	**f: -4.14** h: -4.14	**f: -4.60** h: -4.56	**f: -3.11** h: -3.08	**f: -3.69** h: -3.68	**f: -2.85** h: -2.83	**f: -2.27** h: -2.26	**f: -2.83** h: -2.81
	Au	**f: -2.55** h: -2.50	**f: -2.91** h: -2.86	**f: -3.39** h: -3.30	**f: -3.08** h: -3.01	**f: -3.69** h: -3.61	**f: -2.61** h: -2.56	**f: -3.06** h: -3.02	**f: -2.31** h: -2.30	**f: -1.99** h: -1.98	**f: -2.54** h: -2.52
	Ag	**f: -1.97** h: -1.95	**f: -2.48** h: -2.46	**b: -3.22** f: -3.21 h: -3.18	**f: -2.84** h: -2.81	**f: -3.72** h: -3.70	**f: -2.51** h: -2.49	**f: -2.71** h: -2.70	**f: -2.49** h: -2.48	**f: -1.90** h: -1.90	**f: -2.31** h: -2.30
	Cu	b: -2.78 **f: -2.78** h: -2.76	**f: -3.27** h: -3.24	b: -4.18 **f: -4.21** h: -4.17	**f: -3.60** h: -3.57	**f: -4.39** h: -4.36	**f: -2.98** h: -2.96	**f: -3.23** h: -3.21	**f: -2.79** h: -2.79	**f: -2.14** h: -2.14	**f: -2.64** h: -2.63

Table S7: Calculated binding energies of adatoms in fourfold hollow sites of fcc(100) surfaces, 2x2 unit cell. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	-7.01	-6.09	-6.64	-5.62	-5.74	-4.08	-4.94	-3.43	-2.90	-3.80
	Rh	-6.40	-5.52	-6.14	-5.08	-5.36	-3.67	-4.47	-3.27	-2.67	-3.43
	Pt	-6.16	-5.42	-5.86	-4.97	-5.18	-3.65	-4.62	-3.20	-2.82	-3.67
	Pd	-5.11	-4.72	-5.11	-4.25	-4.66	-3.15	-4.07	-3.03	-2.56	-3.24
	Ni	-5.12	-5.14	-5.88	-4.83	-5.27	-3.55	-4.16	-3.23	-2.51	-3.16
	Au	-3.45	-3.77	-4.50	-3.95	-4.48	-3.18	-3.74	-2.78	-2.37	-3.07
	Ag	-2.35	-2.97	-4.02	-3.46	-4.35	-2.93	-3.17	-2.81	-2.12	-2.62
	Cu	-3.27	-3.79	-5.06	-4.26	-5.04	-3.41	-3.70	-3.13	-2.33	-2.91

Table S8: Calculated "*hopping*" diffusion barriers on fcc(111) and hcp(0001) surfaces, 2x2 unit cell. Barriers are calculated as the difference between the transition state energy for movement between sites and the energy of the most stable binding configuration. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	0.64	0.61	0.79	0.61	0.56	0.37	0.43	0.16	0.09	0.17
	Ru	0.73	0.64	0.60	0.44	0.23	0.14	0.28	0.09	0.06	0.11
	Ir	0.68	0.32	0.31	0.19	0.24	0.17	0.19	0.14	0.10	0.15
	Rh	0.47	0.22	0.22	0.14	0.19	0.13	0.15	0.13	0.08	0.12
	Pt	0.23	0.23	0.31	0.27	0.32	0.21	0.26	0.16	0.11	0.18
	Pd	0.08	0.11	0.16	0.16	0.17	0.13	0.16	0.12	0.09	0.12
	Ni	0.06	0.06	0.04	0.03	0.08	0.07	0.08	0.07	0.04	0.06
	Au	0.09	0.06	0.14	0.12	0.15	0.12	0.15	0.12	0.09	0.13
	Ag	0.05	0.04	0.04	0.05	0.05	0.06	0.08	0.09	0.06	0.08
	Cu	0.02	0.03	0.04	0.03	0.03	0.03	0.05	0.06	0.04	0.05

Table S9: Calculated "*hopping*" diffusion barriers for an adatom moving between fourfold hollow sites of fcc(100) surfaces, 2x2 unit cell. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	1.69	1.13	1.24	1.06	1.04	0.82	0.87	0.54	0.46	0.68
	Rh	1.60	1.07	1.25	0.99	0.99	0.75	0.80	0.54	0.44	0.62
	Pt	2.06	1.31	1.63	1.29	1.13	0.85	1.00	0.58	0.51	0.75
	Pd	1.66	1.11	1.46	1.11	1.03	0.74	0.90	0.59	0.49	0.68
	Ni	1.33	0.89	1.19	0.88	0.96	0.67	0.74	0.50	0.36	0.53
	Au	1.11	1.19	1.64	1.31	1.16	0.88	1.03	0.56	0.52	0.75
	Ag	0.69	0.87	1.36	1.10	1.07	0.80	0.85	0.54	0.45	0.60
	Cu	0.78	0.82	1.26	0.99	0.97	0.70	0.81	0.51	0.38	0.55

Table S10: Calculated *energy of substitution* for metal adatoms into fcc(111) and hcp(0001) surfaces, 2x2 unit cell. The substitution energy is calculated as the difference in energy between the final state (adatom substituted into surface, with one host slab atom moved to the surface in an adjacent hollow site) and the initial state (adatom in a hollow site). Negative values signify favorable (exothermic) substitution. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	0.00	0.63	0.58	0.54	0.84	1.16	1.74	1.87	2.00	1.47
	Ru	-0.84	0.00	-0.11	0.64	0.29	0.73	1.04	1.24	1.44	0.97
	Ir	-1.27	-0.03	0.00	0.81	0.89	1.27	1.41	1.81	1.84	1.42
	Rh	-1.87	-0.70	-0.86	0.00	0.24	0.69	0.53	1.03	1.17	1.06
	Pt	-2.59	-0.84	-1.12	-0.31	0.00	0.59	0.27	0.57	0.57	0.61
	Pd	-2.95	-1.15	-1.69	-0.83	-0.70	0.00	-0.25	0.26	0.36	0.11
	Ni	-2.31	-0.63	-1.19	-0.38	-0.30	0.27	0.00	0.47	0.72	0.39
	Au	-1.74	-1.27	-1.68	-1.13	-0.91	-0.45	-0.64	0.00	0.04	-0.22
	Ag	-1.39	-1.29	-1.87	-1.34	-1.17	-0.68	-0.75	-0.13	0.00	-0.23
	Cu	-1.78	-1.33	-1.82	-1.08	-0.89	-0.27	-0.65	0.11	0.27	0.00

Table S11: Calculated *energy of substitution* for metal adatoms into fcc(100) surfaces, 2x2 unit cell. The substitution energy is calculated as the difference in energy between the final state (adatom substituted into surface, with one host slab atom moved to the surface in an adjacent hollow site) and the initial state (adatom in a hollow site). Negative values signify favorable (exothermic) substitution. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	-0.57	0.07	0.00	0.39	0.56	0.83	0.60	1.11	1.21	0.89
	Rh	-1.14	-0.34	-0.48	0.00	0.09	0.47	0.26	0.72	0.90	0.52
	Pt	-1.25	-0.41	-0.56	-0.17	0.00	0.25	0.20	0.48	0.50	0.36
	Pd	-1.80	-0.66	-1.00	-0.49	-0.41	0.00	-0.10	0.20	0.35	0.13
	Ni	-1.39	-0.38	-0.63	-0.16	-0.03	0.39	0.00	0.69	0.85	0.34
	Au	-0.98	-0.73	-0.81	-0.60	-0.45	-0.30	-0.31	0.00	-0.06	-0.08
	Ag	-1.01	-0.92	-1.07	-0.80	-0.59	-0.38	-0.39	0.00	0.00	-0.07
	Cu	-1.52	-1.03	-1.07	-0.66	-0.45	-0.12	-0.38	0.28	0.37	0.00

Table S12: Calculated activation energy *barriers for substitution* of adatoms into fcc(111) and hcp(0001) surfaces, 2x2 unit cell. Four values are given for each substitution: the first letter denotes the original position of the adatom, and the second letter denotes the final position of the displaced surface atom. Sites are represented as: fcc (f), hcp (h). For example, an adatom in the fcc position displacing a surface atom to an hcp position would be denoted by "f-h". "X" denotes that an event was not found to occur. For each combination of host slab and adatom, the most favorable pathway (with the lowest transition state energy) is bolded. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	f-f: 3.39 f-h: 2.48 **h-f: 2.88** h-h: 3.53	f-f: 3.37 **f-h: 2.48** h-f: 3.59 h-h: 3.76	f-f: X f-h: 2.47 h-f: 3.51 **h-h: 2.97**	f-f: X f-h: 3.14 h-f: 3.70 **h-h: 3.20**	f-f: X f-h: 3.19 **h-f: 3.62** h-h: X	f-f: X f-h: 3.39 **h-f: 3.46** h-h: X	f-f: X f-h: 3.42 h-f: 3.81 h-h: 3.36	**f-f: 3.53** f-h: 3.82 h-f: 4.05 h-h: 3.91	f-f: X f-h: 4.08 h-f: 4.31 **h-h: 4.12**	f-f: X **f-h: 3.88** h-f: 4.14 h-h: X
	Ru	f-f: X f-h: 2.05 h-f: 2.13 **h-h: 1.92**	f-f: 2.36 f-h: 2.01 **h-f: 2.39** h-h: 2.50	f-f: X f-h: 2.09 h-f: 2.49 **h-h: 2.36**	f-f: 2.51 f-h: 2.14 h-f: 2.77 **h-h: 2.34**	f-f: X f-h: 2.34 h-f: 2.67 **h-h: 2.45**	f-f: X f-h: 2.58 h-f: 2.85 **h-h: 2.64**	f-f: 2.57 f-h: 2.51 h-f: 2.81 **h-h: 2.69**	f-f: 2.81 f-h: 2.80 h-f: 2.98 **h-h: 2.69**	f-f: 3.04 f-h: 2.91 h-f: 3.08 **h-h: 2.90**	f-f: 2.87 **f-h: 2.83** h-f: 2.97 h-h: X
	Ir	f-f: X **f-h: 1.67** h-f: 1.24 h-h: 1.74	f-f: 2.10 **f-h: 1.40** h-f: 2.13 h-h: 2.06	f-f: 1.85 f-h: 1.62 **h-f: 1.63** h-h: 1.77	f-f: 2.30 **f-h: 2.09** h-f: 2.38 h-h: 2.21	f-f: 2.29 f-h: 2.45 h-f: 2.54 **h-h: 2.07**	f-f: 2.71 f-h: 2.80 h-f: 2.85 **h-h: 2.54**	f-f: 2.70 f-h: 2.71 **h-f: 2.52** h-h: 2.58	f-f: 2.70 f-h: 2.91 h-f: 3.01 **h-h: 2.51**	f-f: 2.96 f-h: 3.05 h-f: 3.17 **h-h: 2.83**	f-f: 2.93 f-h: 2.94 h-f: 3.05 **h-h: 2.78**
	Rh	f-f: X f-h: 1.02 h-f: 1.00 **h-h: 0.85**	f-f: 1.46 f-h: 1.46 h-f: 1.47 **h-h: 1.31**	f-f: 1.44 f-h: 1.47 h-f: 1.44 **h-h: 1.39**	f-f: 1.91 f-h: 1.75 h-f: 1.78 **h-h: 1.73**	f-f: 1.84 f-h: 1.90 h-f: 1.69 **h-h: 1.64**	f-f: 2.25 f-h: 2.15 h-f: 2.20 **h-h: 2.02**	**f-f: 1.85** f-h: 2.01 h-f: 2.01 h-h: 1.87	f-f: 2.09 f-h: 2.22 h-f: 2.27 **h-h: 1.97**	f-f: 2.38 f-h: 2.36 h-f: 2.42 **h-h: 2.26**	f-f: 2.30 f-h: 2.27 h-f: 2.30 **h-h: 2.18**
	Pt	**f-f: 0.13** f-h: 0.47 h-f: 0.34 h-h: 0.13	**f-f: 1.04** f-h: 1.16 h-f: 1.03 h-h: 1.09	**f-f: 0.81** f-h: 1.06 h-f: 0.87 h-h: 0.73	**f-f: 1.17** f-h: 1.43 h-f: 1.21 h-h: 1.17	**f-f: 1.05** f-h: 1.43 h-f: 1.27 h-h: 1.02	**f-f: 1.40** f-h: 1.68 h-f: 1.54 h-h: 1.39	f-f: 1.51 f-h: 1.48 **h-f: 1.40** h-h: X	**f-f: 1.36** f-h: 1.60 h-f: 1.59 h-h: 1.37	**f-f: 1.61** f-h: 1.76 h-f: 1.73 h-h: 1.65	**f-f: 1.61** f-h: 1.63 h-f: 1.61 h-h: 1.65
	Pd	f-f: X **f-h: 0.52** h-f: 0.54 h-h: 0.53	f-f: 0.93 f-h: 1.01 h-f: 1.00 **h-h: 0.93**	f-f: X f-h: 0.93 h-f: 0.88 **h-h: 0.70**	**f-f: 1.13** f-h: 1.19 h-f: 1.12 h-h: 1.08	**f-f: 1.06** f-h: 1.18 h-f: 1.14 h-h: 1.05	**f-f: 1.34** f-h: 1.41 h-f: 1.36 h-h: 1.35	**f-f: 1.27** f-h: 1.32 h-f: 1.28 h-h: 1.33	**f-f: 1.29** f-h: 1.40 h-f: 1.38 h-h: 1.31	**f-f: 1.53** f-h: 1.53 h-f: 1.51 h-h: 1.55	**f-f: 1.40** f-h: 1.43 h-f: 1.41 h-h: 1.46
	Ni	f-f: 0.37 f-h: 0.46 h-f: 0.47 **h-h: 0.37**	**f-f: 0.99** f-h: 1.07 h-f: 1.06 h-h: 1.05	**f-f: 0.73** f-h: 0.84 h-f: 0.74 h-h: 0.84	f-f: X f-h: 1.10 **h-f: 1.09** h-h: 1.19	**f-f: 1.05** f-h: 1.07 h-f: 1.07 h-h: 1.02	**f-f: 1.39** f-h: 1.40 h-f: 1.39 h-h: 1.38	f-f: 1.54 f-h: 1.46 **h-f: 1.45** h-h: 1.52	**f-f: 1.44** f-h: 1.48 h-f: 1.48 h-h: X	f-f: 1.69 f-h: 1.69 h-f: 1.70 **h-h: 1.65**	**f-f: 1.61** f-h: 1.65 h-f: 1.65 h-h: 1.68
	Au	f-f: 0.24 f-h: 0.28 h-f: 0.23 **h-h: 0.14**	**f-f: 0.39** f-h: 0.53 h-f: 0.49 h-h: 0.35	**f-f: 0.35** f-h: 0.71 h-f: 0.63 h-h: 0.31	**f-f: 0.62** f-h: 0.85 h-f: 0.78 h-h: 0.59	**f-f: 0.52** f-h: 0.84 h-f: 0.77 h-h: 0.54	**f-f: 0.78** f-h: 0.96 h-f: 0.90 h-h: 0.74	**f-f: 0.59** f-h: 0.73 h-f: 0.69 h-h: 0.72	**f-f: 0.57** f-h: 0.76 h-f: 0.74 h-h: 0.63	**f-f: 0.69** f-h: 0.78 h-f: 0.76 h-h: 0.72	**f-f: 0.67** f-h: 0.70 h-f: 0.68 h-h: 0.69
	Ag	f-f: 0.51 f-h: 0.56 h-f: 0.53 **h-h: 0.50**	**f-f: 0.61** f-h: 0.67 h-f: 0.65 h-h: 0.59	f-f: 0.48 **f-h: 0.45** h-f: 0.64 h-h: 0.44	f-f: 0.71 f-h: 0.77 **h-f: 0.61** h-h: 0.66	**f-f: 0.56** f-h: 0.77 h-f: 0.75 h-h: 0.53	f-f: 0.81 f-h: 0.90 h-f: 0.88 **h-h: 0.78**	**f-f: 0.82** f-h: 0.83 h-f: 0.82 h-h: 0.81	**f-f: 0.73** f-h: 0.83 h-f: 0.82 h-h: 0.73	**f-f: 0.81** f-h: 0.86 h-f: 0.86 h-h: 0.82	**f-f: 0.81** f-h: 0.83 h-f: 0.83 h-h: 0.81
	Cu	f-f: 0.39 f-h: 0.44 h-f: 0.40 **h-h: 0.36**	**f-f: 0.58** f-h: 0.64 h-f: 0.56 h-h: 0.56	**f-f: 0.38** f-h: 0.54 h-f: 0.51 h-h: 0.35	f-f: 0.78 f-h: 0.75 **h-f: 0.64** h-h: 0.64	f-f: 0.64 f-h: 0.75 **h-f: 0.55** h-h: 0.56	**f-f: 0.94** f-h: 0.97 h-f: 0.95 h-h: X	**f-f: 0.99** f-h: 1.01 h-f: 1.00 h-h: 0.98	f-f: 0.92 f-h: 0.97 h-f: 0.95 **h-h: 0.91**	f-f: 1.11 f-h: 1.09 **h-f: 1.08** h-h: 1.11	**f-f: 1.03** f-h: 1.07 h-f: 1.06 h-h: 1.03

Table S13: Calculated *minimum activation energy barriers* for *substitution* of adatoms into fcc(111) or hcp(0001) surfaces, 2x2 unit cell. Barriers are calculated as the difference in energy between the lowest energy transition state (of the considered combinations of fcc-fcc, fcc-hcp, hcp-fcc, hcp-hcp) and the lowest energy initial state. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Re	2.87	2.99	2.97	3.20	3.62	3.46	3.36	3.63	4.12	3.97
	Ru	1.92	2.39	2.36	2.34	2.45	2.64	2.69	2.69	2.90	2.86
	Ir	1.24	1.66	1.63	2.12	2.14	2.60	2.52	2.57	2.86	2.81
	Rh	0.85	1.31	1.39	1.73	1.70	2.06	1.85	2.03	2.29	2.21
	Pt	0.13	1.04	0.81	1.17	1.05	1.40	1.48	1.36	1.61	1.61
	Pd	0.52	0.93	0.79	1.13	1.06	1.34	1.27	1.29	1.53	1.40
	Ni	0.37	1.01	0.74	1.09	1.05	1.39	1.46	1.44	1.66	1.61
	Au	0.19	0.39	0.35	0.62	0.52	0.78	0.59	0.57	0.69	0.67
	Ag	0.51	0.61	0.45	0.65	0.56	0.81	0.82	0.73	0.81	0.81
	Cu	0.37	0.58	0.38	0.67	0.58	0.94	0.99	0.92	1.08	1.03

Table S14: Calculated activation energy *barriers* for *substitution* of adatoms into fcc(100) surfaces, 2x2 unit cell. All values in eV.

		Adatom									
		Re	Ru	Ir	Rh	Pt	Pd	Ni	Au	Ag	Cu
Host Slab	Ir	0.60	0.78	0.68	1.06	1.13	1.43	1.27	1.48	1.74	1.65
	Rh	0.66	0.87	0.90	1.13	1.21	1.41	1.22	1.38	1.54	1.46
	Pt	0.47	0.61	0.58	0.85	0.86	1.01	0.91	1.05	1.21	1.09
	Pd	0.61	0.84	0.82	0.97	0.98	1.11	0.97	1.12	1.23	1.10
	Ni	0.89	1.11	1.13	1.18	1.23	1.30	1.20	1.23	1.33	1.31
	Au	0.20	0.45	0.58	0.66	0.58	0.68	0.49	0.47	0.53	0.47
	Ag	0.48	0.63	0.70	0.77	0.75	0.82	0.67	0.74	0.75	0.68
	Cu	0.63	0.79	0.97	1.02	0.98	1.01	0.97	0.90	0.92	0.93

Supplementary Figures

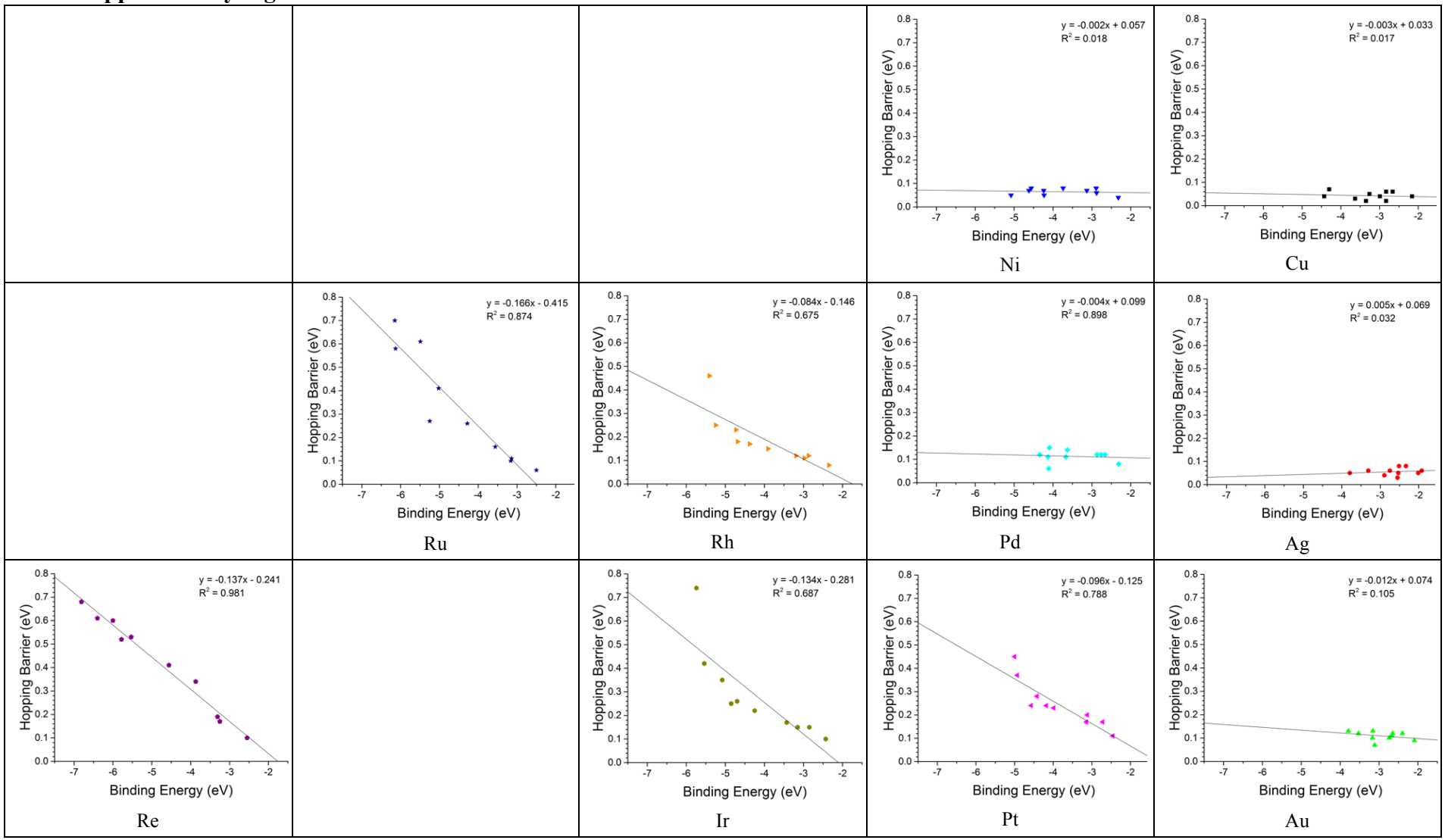

Figure S1: Correlation between adatom *hopping* diffusion barrier and adatom binding energy on fcc(111) and hcp(0001) surfaces. The label on each plot represents the *host slab* on which calculations were performed. All values were calculated in a 3x3 surface unit cell.

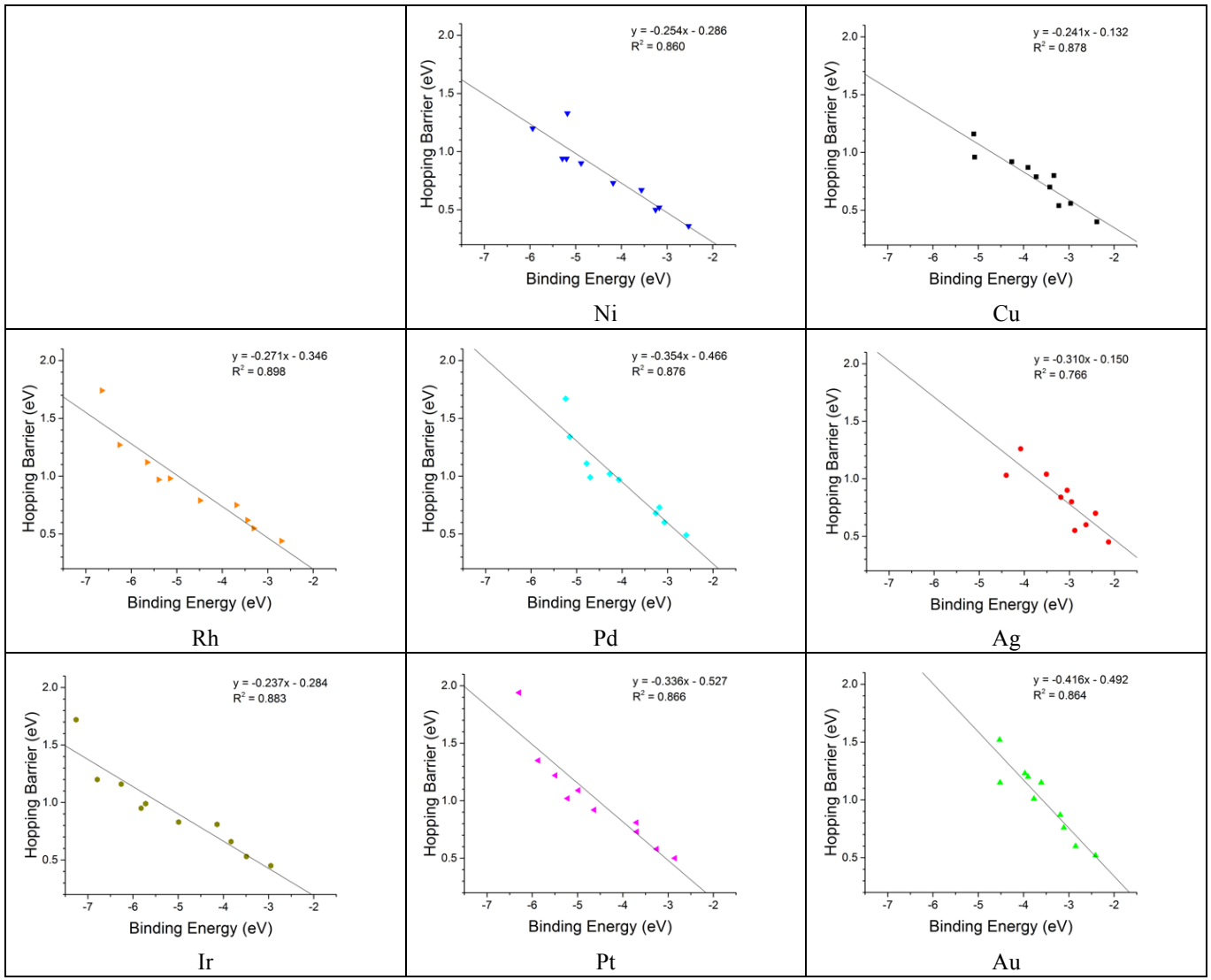

Figure S2: Correlation between adatom *hopping* diffusion barrier and adatom binding energy for fcc(100) surfaces. The label on each plot represents the host slab on which calculations were performed. All values were calculated in a 3x3 surface unit cell.

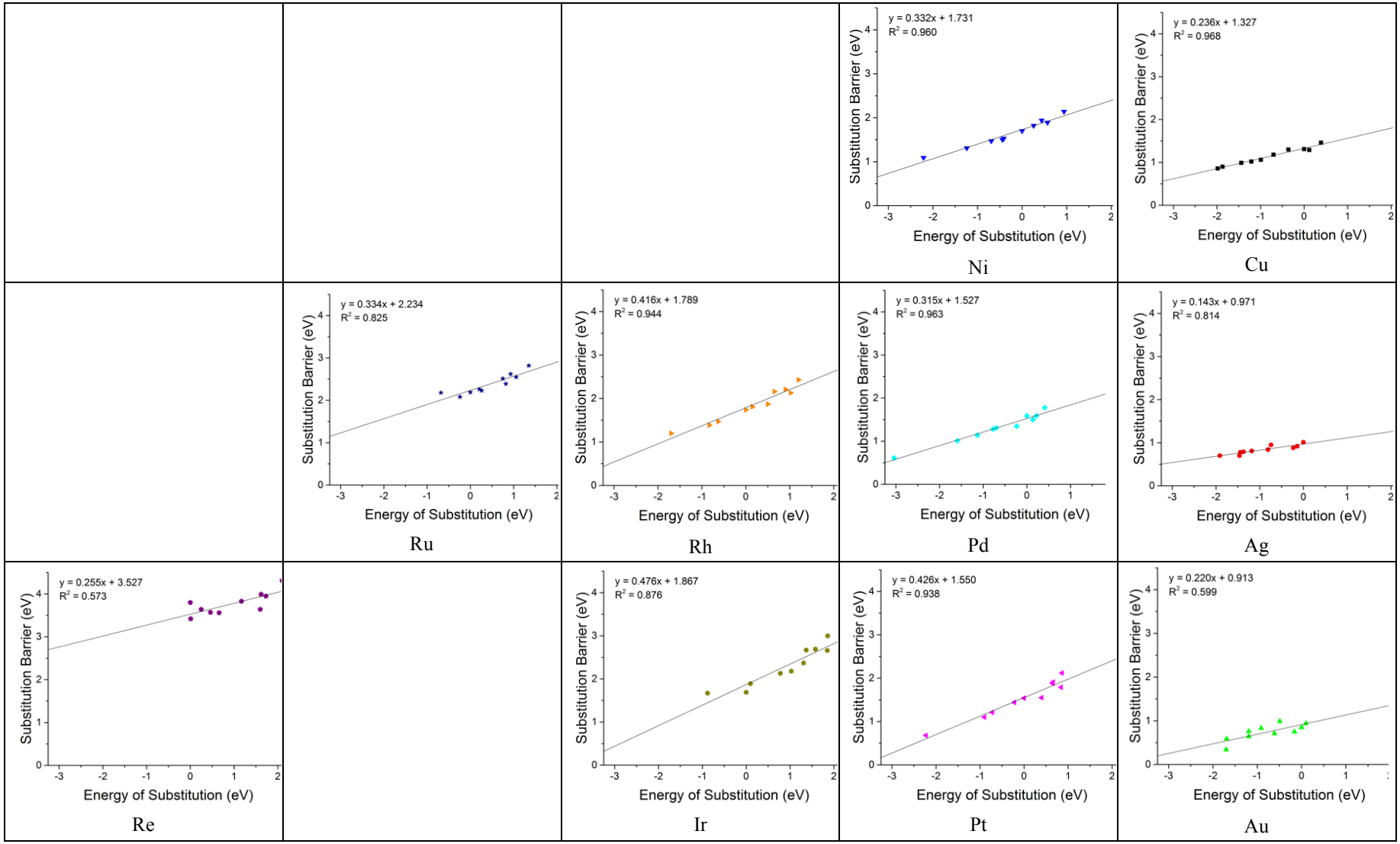

Figure S3: Correlation between adatom *substitution* barrier and energy of substitution for fcc(111) and hcp(0001) surfaces. The label on each plot represents the host slab on which calculations were performed. All values were calculated in a 3x3 surface unit cell.

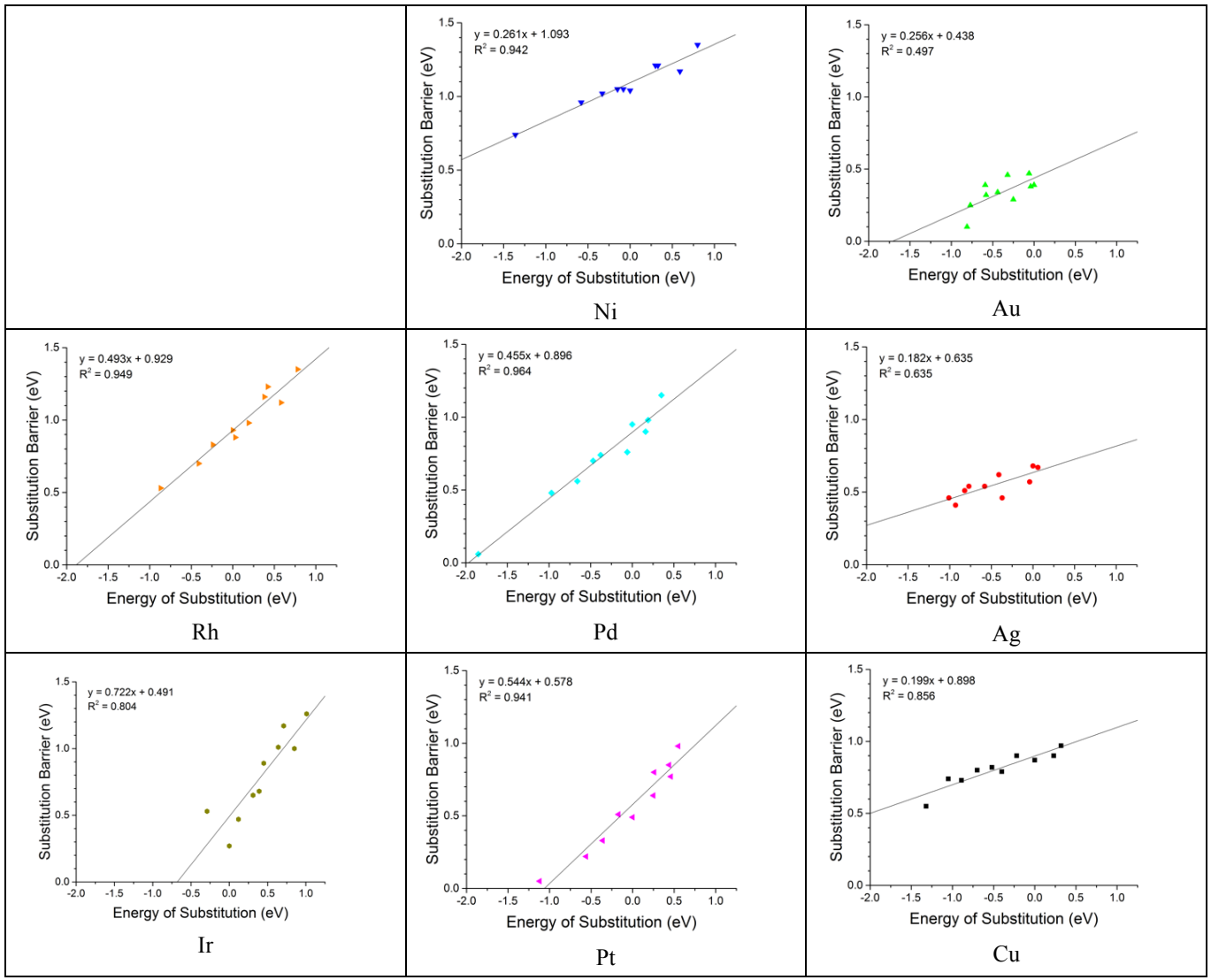

Figure S4: Correlation between adatom *substitution* barrier and energy of substitution for fcc(100) surfaces. The label on each plot represents the host slab on which calculations were performed. All values were calculated in a 3x3 surface unit cell.