Supporting Information: "General Screening of Surface Alloys for Catalysis"

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1 Implementation of the Model

A Python implementation of the model can be accessed at http://www.bitbucket.org/ mmmontemore/surfep. This includes fitting parameters in a human-readable form and template files to build structures.

2 Error Distributions

The distribution of errors for the adsorption energies are shown in Figure S1.



Figure S1: Histograms of errors for predicting adsorption energies for the model described in the main text. a) Absolute errors; b) percent errors.



Figure S2: Histograms of errors for predicting adsorption energies for the model described in the main text, separated by adsorption site. The sites are ordered from weakest average binding (top) to strongest average binding (hollow). a) Absolute errors; b) percent errors.



Figure S3: Histograms of errors for predicting adsorption energies for the model described in the main text, separated by adsorbate. The adsorbates are ordered from weakest average binding (K) to strongest average binding (C). a) Absolute errors; b) percent errors.

In all cases, the MAPE is roughly 5 to 10%, while the MAE varies much more widely. The MAE is higher for cases where adsorption is stronger. We also tested a separation of data points across different metals. For adsorption energies of OH adsorbed on an alloy that includes Au, the MAE is 0.175 eV, while for alloys that include Ti the MAE increases to 0.251 eV. This is expected, as Ti binds OH more strongly than Au. The MAPE is much more constant: 8.3% for the Au data points and 7.8% for the Ti data points.

3 Model Equation and Tested Features

In addition to the tight-binding coupling elements, the features we tested were the dorbital radius r_d , idealized d-band filling f_d (which is equivalent to the group for the set of metals we consider here), the atomic number, atomic radius, covalent radius, electron affinity, electronegativity, heat of fusion, period, specific heat, heat of vaporization, thermal conductivity, melting point, electrical conductivity, and thermal expansion coefficient. The final model equation, written out explicitly, is:

$$E_{\rm ads} = a_1 + a_2(b_1 + b_2 f_{d,n} + b_3 \sigma_n + b_4 V_{pd}^2) + a_3(b_5 + b_6 V_{pd}^2) + a_4(b_7 + b_8 f_{d,n})f_d + a_5(b_7 + b_8 f_{d,n}).$$
(1)

4 Model Validation on Experimental Data

To show that our model can be used to predict experimentally measured catalytic performance, we extracted data from previous work and used it to construct volcano plots based on our efficient predictions. As shown in Figure S4, our adsorption energy predictions are accurate enough to rationalize and predict experimental trends in catalytic performance. Our calculations also closely match the trends in previous DFT calculations of these systems, which results in volcano plots that look very similar to previous work.^{1–3}



Figure S4: a-c) Volcano plots where experimental reaction rates are plotted against efficient predictions created using our final model. b-d) The accuracy of these volcano plots for predicting the experimental rates. The reactions are a,d) ammonia decomposition,⁴ b,e) the oxygen reduction reaction on Pt overlayers on other metal surfaces,³ and c,f) the oxygen reduction reaction on Pt_3M_1 alloys,² which we modeled as Pt/M/Pt sandwiches as this mimics the structure determined experimentally.

5 Application of the Model to Stepped Surfaces

In addition to the fitting described in detail in the main text, we fit our framework to a database of more than 5000 H adsorption energies on a Ag(211) surface substitutionally doped with most other d-block metals.⁵ Similar to previous work on this data set, non-physical data points were removed (e.g., those consisting of significant surface reconstruction). We also removed metals considered in the previous work but not in the current work, such as Cd. We fit directly from the underlying features, $f_{d,n}$, σ_n , V_{pd}^2 , to the adsorption energies. These features were averaged over the surface atoms comprising the adsorption site for the H atom in each case. Fitting was performed separately for each dopant present in the adsorption site, but all site types (top, bridge, hollow) were fit together. Because this is a large data set, we used only 60% of the data for fitting and

used 40% of the data as test data. The training and test RMSE values were both 0.10 eV (see Figure S5). These errors are quite insensitive to the size of the test-train split as well as the random seed for the test-train split. While a more sophisticated fitting process and more careful consideration of the structure may improve the accuracy, this relatively simple test demonstrates that our model can be applied to other geometries and remain accurate enough to be useful.

We performed some simple comparisons between the fitting parameters here and those in the main text, but did not find close correspondence. This may be partly due to differences in the fitting process and the computational setup. It is possible that changes in geometry could be accounted for by correctly incorporating additional features, such as the orbitalwise coordination number,⁶ which would be similar to the V_{pd}^2 feature we use here.

This dataset was created using different computational parameters than those in the main text, as detailed previously.⁵ Briefly, the PBE⁷ exchange-correlation functional was used with the Tkatchenko-Scheffler method⁸ for van der Waals interactions. The (211) surface was modeled with 4 layers along the (111) direction and 4 atoms along the step edge. Atoms in the bottom of these 4 layers were fixed at their bulk positions. The k-point mesh was $7 \times 7 \times 1$, and the energy cutoff was 400 eV. Spin polarization was not used.



Figure S5: a) Parity plot for the predictions on stepped surfaces. Black points are the training set; red points are the test set. b) Histogram of the model's test-set errors.

6 Explanation of Adsorption Energy Difference

Due to its structure, the model allows differences in adsorption energy to be rationalized. For example, we can explain why the FeCu surface mentioned in the main text and shown in Figure S10 has a weaker adsorption energy for N than a pure Fe surface. In these two cases, all contributions are quite similar except the p-band contribution, as captured by the predicted n_p value and its coefficient (Figure S6).



Figure S6: Contributions to the adsorption energy of N, as predicted by the model on an FeCu surface (Figure S10) and to an fcc(111) Fe surface.

7 N and O Adsorption Energies as Related to NO

Decomposition



Figure S7: Predicted N and O adsorption energies for the 1.6×10^7 sites described in the main text. The location of the predicted maximum activity for NO decomposition is indicated.

8 Possible Improvements to Model Accuracy

For bridge and hollow sites, we calculate site properties as a simple, unweighted average over the properties of each atom in the site. In some cases, we may expect that a weighted average would improve the accuracy, particularly when one of the atoms in the site binds the adsorbate much more strongly and induces an asymmetric adsorption geometry. In previous work, we tested some other ways to weight the various atoms in a site but found that these had little effect on the overall accuracy.⁹ In any case, our current framework gives reasonable results, as evidenced by the accuracy of our model, even in alloy sites. This may be due to partial compensation effects, as movement towards a bridge or top site of a pure metal surface often will result in decreased stability, and this may partially compensate the increase in stability due to stronger bonding to a reactive atom. Further, the reasonable accuracy we obtain may be partly because adsorbates in a hollow site with very reactive atoms and very inert atoms can relax all the way to top or bridge sites with only reactive atoms, and we use the final site for fitting the model. When screening, this effect can be easily accounted for by checking predicted adsorption energies in neighboring sites. If a neighboring bridge or top site is much more stable than the hollow site, the hollow site should be considered unstable.

We use a single set of fitting parameters for each adsorbate and site, regardless of the elements in the surface. We performed some simple tests to see if separate adsorbate fitting parameters for different groups of hosts (e.g., late transition metals vs. early transition metals) would improve the accuracy. These simple tests suggest that this may reduce the error by 5 to 15%, although more data would be needed for a rigorous test.

Fitting directly from the structures to the adsorption energies, without fitting to electronic structure parameters, reduces the errors to an RMSE of 0.35 eV and an MAE

of 0.25. Previous work has also seen lower errors for direct fitting.¹⁰ This alternative model is thus has roughly 15% lower error than the text in our main text, although it is more difficult to fit and less interpretable. Hence, both approaches may be more useful in different situations.

9 Brief Comparison to Previous Work

Previous work with a smaller dataset of alloy surfaces in two configurations (a 1% impurity and an overlayer structure) was able to predict the d-band center with RMSEs of 0.18 and 0.19 eV for each structure.¹¹ This is comparable to our RMSE of 0.19 eV for the d-band center. Each configuration was fit separately with different features using a nonlinear model. 6 features were used in each case. The top feature in both feature sets was the host metal's group, which is closely related to our top feature for predicting the dband center, $f_{d,n}$. This previous study did not directly address other electronic structure features or adsorption. Another previous study considered six adsorbates (C, CH, CO, H, O, OH) on alloys of nine late transition metals in the fcc(211) structure.¹² Linear regression was used on non-linear combinations of features. The features included band properties, which require an DFT calculation of the density of states for each new surface. There is some similarity in some features between this work and ours, as they included V_{ad}^2 , the d-band center, and the s-p band filling. They also included nearest neighbor distances and the d-orbital radius, which are related to our feature V_{pd}^2 . The RMSEs were found to be 0.17 to 0.24 eV, somewhat less than our overall error of 0.41 eV. Another previous study considered $\mathrm{C_1-C_2}$ species on alloys in three configurations, featuring combinations of 12 host metals and 3 guest metals.¹³ This study allows DFT calculations for species on a particular surface to be combined in order to make predictions for other species. The MAE was 0.19 eV, somewhat smaller than our overall MAE of 0.29. Finally, previous work has used active learning and nonlinear models to predict H and CO adsorption energies on different sites of various surface facets of bulk intermetallics, with no substitutional doping. 14 A very large dataset with thousands of points was needed to gain an accurate

model. The RMSEs were 0.46 and 0.41 eV, similar to that of our model.

In summary, while these studies have various strengths and weaknesses, our model is much more general and data-efficient than these previous approaches, allowing for increased reusability. Specifically, we consider a wider array of adsorbates and possible arrangements of surface dopants, and generally consider a wider array of metals. Our model also allows adsorption energy predictions directly from the structure with no quantum chemical calculations, which makes it several orders of magnitude faster than strategies that require DFT calculations. We also have a simple model that is interpretable and has few features. Our errors are typically 1 to 2 times larger than this previous work, though direct comparison of numbers can be difficult due to differences in datasets.

10 Model Accuracy for Activity

To check the accuracy and utility of our model, we performed a number of DFT calculations of N and H adsorption energies after the model creation process was completed. We then compared predicted activity between the model and the DFT calculations, as shown in Figure S8. The errors in predicting these adsorption energies are comparable to the errors in predicting the adsorption energies used to create the model. We also found that errors tend to be similar for similar surfaces. This demonstrates that the predictions are accurate enough to be useful in catalyst design.



Figure S8: Density plots of catalytic activity vs. cost for a large number of surface sites, as shown in main text. For some sites, DFT calculations were performed after-the-fact, and the predictions from DFT (filled circles) are compared to the predictions from the model (empty circles).

11 Simple Stability Test

Given an alloy surface $A_x B_y$ with A substitutionally doped into B, we define a simple test of the stability by comparing to the energies of the pure B surface and the bulk energies of A and B:

$$\Delta E = E(\mathbf{A}_{\mathbf{x}}\mathbf{B}_{\mathbf{y}}) - E(\mathbf{B}_{\text{surf}}) + nE(\mathbf{B}_{\text{bulk}}) - mE(\mathbf{A}_{\text{bulk}}), \qquad (2)$$

where n and m are chosen to account for the number of each element in the alloy. A more negative ΔE indicates a surface that is more likely to be stable. We calculated ΔE using bare surfaces and with N adsorbed on the surface. We calculated this quantity for several of the surfaces we used to test our N prediction model (Figure S10). As shown in Figure S10, these surfaces range significantly in their ΔE value, and several have negative ΔE values. In most cases, adsorbed N decreases the value of ΔE .



Figure S9: A simple stability test (Equation (2)) for several surfaces tested for their N adsorption properties after the model was finished.

12 Shifts in Volcano Plots

We extracted several volcano plots from previous work. To account for differences in computational setup, reference state (e.g., gas-phase O vs. gas-phase O_2), and zero-point energy (for hydrogen evolution), we shifted the volcano plots from previous work using a reference surface where the adsorption energy was available both in our dataset and in the previous work. We chose a reference surface near the top of the volcano in all cases. The shifts were (in eV): 6.17 for ammonia synthesis; 5.355 (N) and 3.678 (O) for NO decomposition; 0.043 (C) and 0.378 (O) for aqueous-phase hydrogenation; -2.680 for hydrogen evolution; 8.607 (C) and 5.608 (O) for methane oxidation; -2.446 for the oxygen reduction reaction; and 0.343 for solid oxide fuel cells.

13 Example Alloy Structure

We show an example FeCu alloy structure in Figure S10.



Figure S10: Visualization of N adsorbed on an FeCu alloy surface. The larger, orange atoms are Fe, and the smaller, yellow atoms are Cu.

The coordinates for this structure, in extended .xyz format, are:

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Lattice="7.753119 0.0 0.0 3.876559 6.714398 0.0 0.0 0.0 23.908118"

Cu	7.70024797	4.48476587	15.05579932	
Cu	5.13778686	4.47982376	15.07726788	
Cu	6.45115183	2.23438063	15.11909694	
Cu	2.55180188	-0.02125607	15.08110804	
Cu	11.61568610	6.71419540	15.07080546	
Cu	10.35840080	5.97726776	12.93564982	
Cu	3.87108294	3.71661319	12.98274740	
Cu	9.02509032	3.75182393	12.95842678	
Cu	2.57148651	1.49480461	12.96021977	
Cu	9.04530548	5.22230955	10.89899298	
Cu	6.46093248	5.22230955	10.89899298	
Cu	3.87655949	5.22230955	10.89899298	
Cu	7.75311898	2.98417689	10.89899298	
Cu	5.16874599	2.98417689	10.89899298	
Cu	2.58437299	2.98417689	10.89899298	
Cu	6.46093248	0.74604422	10.89899298	
Cu	3.87655949	0.74604422	10.89899298	
Cu	1.29218650	0.74604422	10.89899298	
Cu	7.75311898	4.47626533	8.78886127	
Cu	5.16874599	4.47626533	8.78886127	
Cu	2.58437299	4.47626533	8.78886127	
Cu	6.46093248	2.23813267	8.78886127	
Cu	3.87655949	2.23813267	8.78886127	
Cu	1.29218650	2.23813267	8.78886127	

Cu	5.16874599	0.0000000	8.78886127
Cu	2.58437299	0.0000000	8.78886127
Cu	0.0000000	0.0000000	8.78886127
Fe	10.25516736	4.55094603	15.03645731
Fe	3.92379271	2.11437934	15.02155118
Fe	9.01901148	2.24834258	15.03046670
Fe	5.17052491	0.00313573	14.94055645
Fe	7.73199910	5.99953627	13.01380524
Fe	5.21657546	5.95739343	13.00712575
Fe	6.44446359	3.71470744	13.01020565
Fe	5.18738629	1.49863943	13.03807371
Fe	7.69713983	1.51398045	13.03655389
N	2.66877264	3.01876761	15.89666948

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