

Probing the Coverage Dependence of Site and Adsorbate Configurational Correlations on (111) Surfaces of Late Transition Metals

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Abstract

Correlations between adsorption energies allow for the prediction of a large set of adsorption energies from a few quantum-chemical calculations, enabling quick evaluations of the catalytic activity of surfaces for multistep reactions. A critical question is whether these correlations – initially established at low coverage on geometrically similar surfaces – are useful at high coverage and in various geometric environments, which are the relevant industrial conditions of real catalysts. To answer this question, we use density functional theory to calculate almost 900 adsorption energies of several atomic adsorbates on late transition metal fcc (111) surfaces at a variety of coverages and configurations. We observe strict requirements of the geometric similarity between adsorption sites for the existence of correlations in adsorption energies. We also find that the introduction of higher coverages generally weakens and changes the correlations. We use our results to assess a simple model constructed from previously discovered scaling relationships and discuss their ramifications on catalyst discovery as well as strategies to incorporate this coverage dependence.

Keywords: density functional theory, scaling relationships, coverage, adsorption

Introduction

Substantial progress has been made in identifying key descriptors that dominate observed trends in adsorption on late transition metal and alloy surfaces. These descriptors include the effects of strain,¹ ligand effects,² ensemble effects,³ geometric structure,⁴ and coverage.⁵ Adsorbate-adsorbate interactions can have a significant effect on reactivity.^{6,7} A majority of these descriptors can be understood by simple linear correlations with features of the electronic structure, such as the *d*-band center, width, and filling. The existence of linear correlations with common electronic structure descriptors leads to linear correlations between the adsorption properties of different adsorbates – or scaling relationships – on metal,^{8,9}

oxide, nitride, and sulfide surfaces.¹⁰

Since their discovery, linear scaling relationships have been employed in a large number of studies that simplifies our understanding of the activity and selectivity of catalysts. Linear scaling relationships have been used to determine activity limitations for oxygen evolution,^{11,12} ammonia synthesis,^{13,14} and CO₂ reduction.¹⁵ They have been used to construct activity volcanoes of hydrogen halide oxidation,¹⁶ formic acid decomposition,¹⁷ hydrogen chloride oxidation,¹⁸ and hydrogen cyanide production.¹⁹ They have been used to understand selectivity in hydrogen peroxide production²⁰ and synthesis gas conversion.²¹ They have been employed to use simple molecules to predict adsorption energies of more complex, molecular species involved in glycerol decomposition^{22,23} and methanol electrooxidation.²⁴ Their existence has also been observed in large amount of desulfurization reactions.^{25,26}

While we note the above examples testifies to the robustness of linear scaling relationships, we also comment that a majority of these relationships are constructed at a single, low coverage and single surface facet.²⁷ Hence, major gaps in our understanding of the configurational correlations and scaling relations limit our ability to use correlations to evaluate the catalytic activity of surfaces at experimental conditions, which often include complex surfaces and high coverages. For example, the configurational correlations depend strongly on there being substantially similar geometric environments and electronic structure/property relationships for comparison.²⁸ Thus, it is unclear to what extent the knowledge of the behavior of one site can be a good indicator of behavior on another site. The existence of such configurational correlations would allow for the prediction of adsorption behavior on an experimentally relevant surface containing many sites of varied geometries. It has also not been demonstrated whether correlations between different adsorbates persist at higher coverages, which is often the relevant environment at experimental conditions.

Our goal in this article is predict whether the same simple, empirical linear scaling relationships, which have been proven to be effective at low coverage and a single surface, can be used at high coverage at a variety of geometrically different sites (different binding sites,

facets, etc). We do this by performing over 900 density functional theory (DFT) calculations of the adsorption of a number of atomic adsorbates on a variety of metals, sites, coverages, and configurations. We find that strong correlations in adsorption energies require similar geometric environments, and that a key ingredient in the breakdown of correlations between geometrically different sites is higher coverage. We also find that in almost all cases that correlations between different atomic adsorbates are coverage dependent. We use our results to assess a simple model constructed from previously discovered scaling relationships and discuss their ramifications on catalyst discovery as well as strategies to incorporate this coverage dependence.

Methods

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP)^{29,30} with the Perdew-Burke-Ernzerhof (PBE)^{31,32} generalized gradient approximation (GGA) exchange-correlation functional. Details of the electronic and atomic structure parameters are provided in the supporting information. Table 1 summarizes combinations of adsorbates, surfaces, coverages, and sites we tested in this work, totaling to 896 adsorption energies. All surfaces we tested were (111) surface of late transition metals that naturally exist in the fcc crystal structure. All calculations were not spin polarized – hence, Ni and Co were not chosen in this study. We ensured all relaxed structures did not include major surface reconstruction or desorption of adsorbates. Adsorption energies were calculated using the equation shown below,

$$\Delta E_{ads}(eV/A) = \frac{1}{n} \cdot (E_{slab,ads} - (E_{slab} + n \cdot E_{ads}^{gas})), \quad (1)$$

where $\Delta E_{ads}(eV/A)$ is the adsorption energy of species A normalized by the number of adsorbates n per slab. $E_{slab,ads}$ is the total energy of the slab with adsorbates, and E_{slab} is the total energy of the clean slab. E_{ads}^{gas} is the total energy of the atomic adsorbate calculated

in a $8 \times 9 \times 10$ Å box.

Table 1: The combinations of adsorbate, surface, coverage, and sites we tested in this work. This totaled to 896 adsorption energies.

Adsorbates	Surfaces	Coverages	Sites
H, C, N, O	Cu, Rh, Pd, Ag	0.25 ML, 0.5 ML	fcc, hcp
F, S, Cl, Br	Ir, Pt, Au	0.75 ML, 1.0 ML	bridge, ontop

Though researchers use scaling relationships to study the adsorption of reaction intermediates with varying degrees of hydrogenation, we chose to study correlations between only atomic adsorbates. We do this for two reasons. First, our aim is to make general conclusions on scaling relationships as a whole, and a recent communication from Medlin has shown that the existence of scaling relationships relies on similar HOMO energies, thereby unifying adsorption of both molecular and atomic species.³³ We will further connect our results to scaling relationships by recasting the simple model found in the original letter⁸ on scaling relationships in the discussion section.

Second, we focus on systems where through-space adsorbate-adsorbate interactions, which include van der Waals, dipole-dipole, and hydrogen bonding, are minimal. Instead, we focus on the coverage induced changes to the adsorption energy through modifications of the surface electronic structure. This mechanism has been elaborated in number of studies for atomic adsorption and shows that the prominent adsorbate-adsorbate interactions exist indirectly through modifications to the surface projected *d*-states.^{34–36} The PBE functional does not explicitly or accurately include effects from dispersion (van der Waals bonding). To determine if these were important, we have performed sample calculations with dispersion turned on using the DFT+D approach.³⁷ The details and analysis of these calculations can be found in the supporting information, and the end result is that dispersion effects do not change the main conclusions drawn from calculations that neglect dispersion in this work.

Results

Our first goal is to determine whether simple linear correlations can allow adsorption on one site to predict adsorption on a geometrically different site. In experimental conditions, adsorption happens on complex surfaces that include a wide variety of geometric environments. Geometric differences between adsorption sites can take on many different forms. Very geometrically different sites may include adsorption sites on different surface facets, including adsorption on terraces, step edges, and kinks, which are characterized by a variety of coordinations of both the surface metal species and adsorbate. Studies have shown that the presence of surface reconstructions, which is a mechanism of reducing geometric similarity, eliminates the presence of correlations between atomic species.^{9,28} On a smaller scale, geometrically different sites can simply include adsorption at different sites on a single surface. We rationalize that if correlations at varying coverages are weak between adsorption energies on different adsorption sites on single, close packed facet, it is unlikely that correlations will exist between adsorption energies on the myriad of possible sites on real catalysts in experimental conditions.

Hence, we look at correlations between adsorption energies on the fcc, hcp, bridge, and ontop sites, which contain correlations between sites of varying degrees of geometric similarity. For example, the fcc and hcp sites are very similar, and differ only in the second layer. The fcc and bridge sites are less similar; the fcc site contains three directly bonding atoms, whereas the bridge site only has two atoms. We first analyze whether adsorption energies at the fcc site are correlated with those at the hcp site, which are the geometrically most similar sites. Figure 1 (a) shows strong correlations between the fcc and hcp site for all systems. This suggests that conclusions drawn from adsorption energies on the fcc site should hold for the hcp site. The fact that this correlation is independent of metal surface, the adsorbate, or coverage indicates the robustness of correlations of adsorption energies on geometrically similar sites.

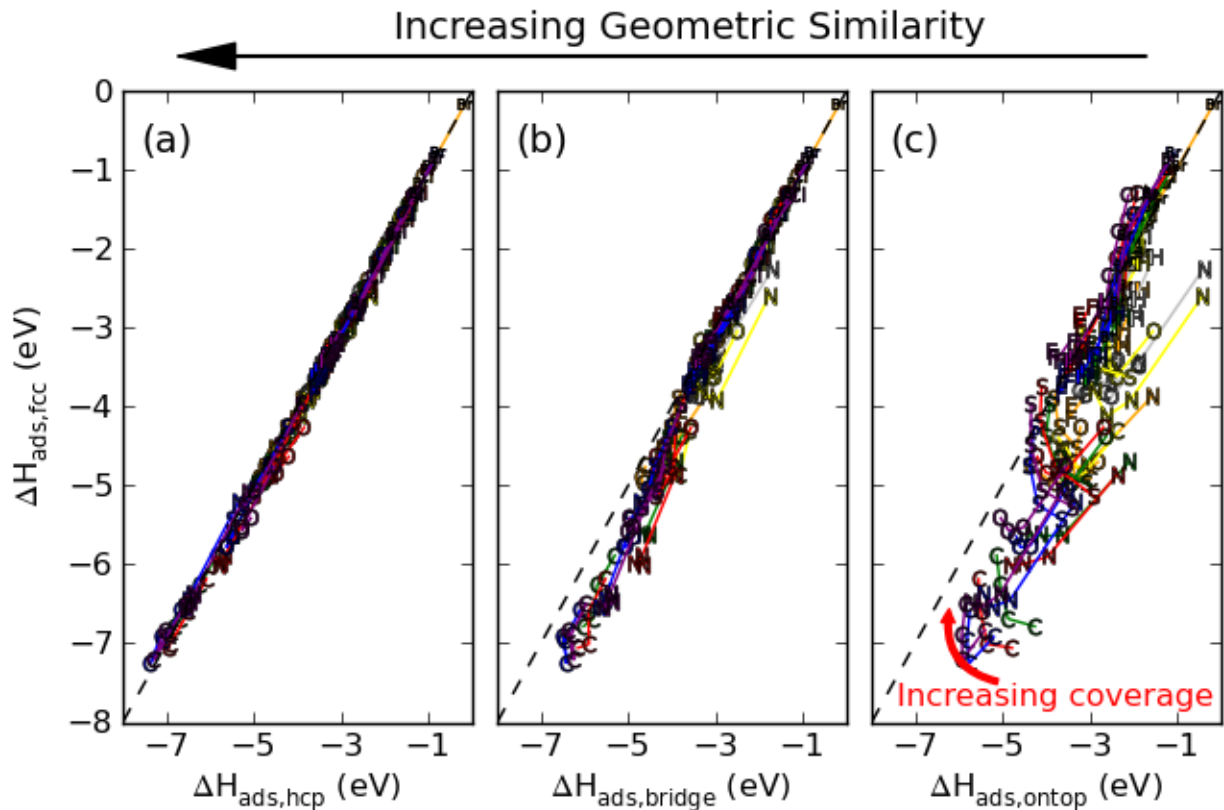


Figure 1: Coverage dependent configurational correlations between the fcc and hcp (a), bridge (b), and ontop (c) adsorption sites. Adsorbates are indicated by the letter of their marker. Each line is the coverage dependence of adsorption on a single surfaces. Surfaces are Cu (orange), Ag (silver), Au (yellow), Pd (green), Pt (red), Rh (blue), and Ir (purple). In (c), the parametric coverage dependence of strongly adsorbed correlations is highlighted by the red arrow.

We next investigate how decreasing the geometric similarity between sites effects correlations between adsorption energies on those sites. Figures 1 (b) and (c) show the configurational correlation between the fcc and the bridge and ontop site for a variety of materials and adsorbates. For a wide majority of surfaces and coverages, we found that the fcc site (and therefore the hcp site) is preferred over the bridge or top site for a majority of the adsorbates, with the exception of the halogens, which prefer the top site. This observation is consistent with previous findings.³⁸ Additional discussion of trends of preferential binding site can be found in the Supporting Information.

Figures 1 (b) and (c) clearly demonstrate that decreasing the geometric similarity of

sites lowers the strength of correlations of adsorption energies on those sites. We observe correlations between the fcc site and the bridge and ontop sites are weaker than those between the fcc and hcp site. Figure 1 (c) also highlights that coverage can have the opposite effects on the adsorption energies for ontop sites compared to the fcc site. This is evident in some systems with C, N, O, and S adsorbed with more negative adsorption energies. Therefore, we conclude that the introduction of higher coverages is a key ingredient in the breakdown of these correlations between geometrically different sites.

Having established that there are strict geometric requirements for strong correlations between different sites, we now investigate the quality and coverage dependence of correlations between different adsorbates. Considering our calculations include a wide variety of sites, metals, coverages, and configurations, we believe we are presenting to date the most comprehensive analysis of the robustness of correlations between different adsorbates. We divide our analysis of correlations into both same-group and same-period correlations. We use linear regression analysis to evaluate both the *strength* and *coverage-dependence* of different correlations, which is the emphasis of our investigation.

Figures 2 and 3 show correlations between adsorbates in the same Group of the periodic table. For correlations within Group 17 (halogens), we observe a similar, strong correlation between all adsorbates at low coverage, but at increasing coverages, the correlations weaken, which is highlighted by larger confidence intervals of the fits in Figure 2 (d) at high coverage. In no correlation between adsorbates does a single slope lie within the 95% confidences of the slopes at all coverages. Furthermore, in contrast to the halogen Group correlations, correlations between S and O are strong at all coverages, but the slopes still diverge at high coverages. These results suggest that when correlating same valence species, a single coverage-independent correlation is not appropriate, while high coverage correlations may not exist in certain cases.

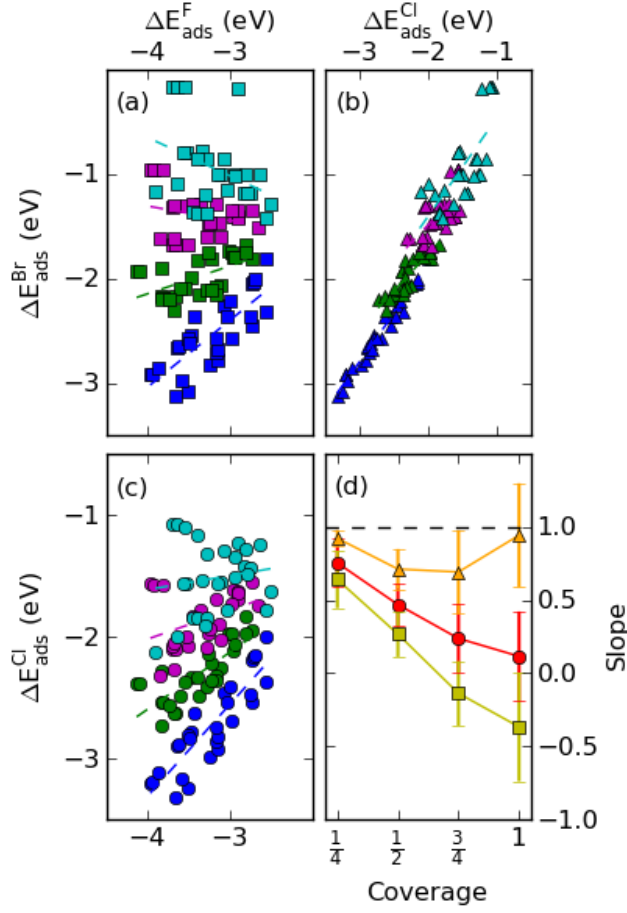


Figure 2: Adsorbate correlations between Group 17 elements (halogens) at different coverages. (a), (b), and (c) show correlations between F and Br, Cl and Br, and F and Cl respectively. In (a), (b), and (c), the correlations are at constant coverages of 0.25 ML (blue), 0.5 ML (green), 0.75 ML (magenta), and 1.0 ML (cyan). (d) shows the variation in the slope of the correlation with the 95% confidence interval of the correlations between F and Br (yellow square), Cl and Br (orange triangle), and F and Cl (red circle) at different coverages. The dashed black line is the slope predicted by Equation 3 for all correlations.

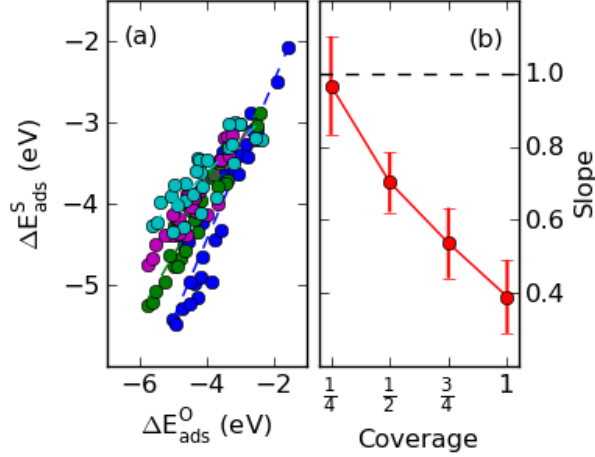


Figure 3: Adsorbate correlations between Group 16 elements at different coverages. (a) shows the correlation between O and S, respectively. In (a), the correlations at constant coverages of 0.25 ML (blue), 0.5 ML (green), 0.75 ML (magenta), and 1.0 ML (cyan). (b) shows the variation in the slope of the correlation within the 95% confidence interval of the correlations between O and S at different coverages. Dashed black line is the slope predicted by Equation 3

We next look at correlations between adsorbates of the same Period. We found that correlations with the halogens were weak. A likely reason for this is the presence of large amounts of repulsion between adsorbate states and metal d -states that leads to a breakdown in the d -band model for halogen species.³⁸ Because it has been shown that the existence of correlations between adsorption energies lies in similar correlations between the d -band and the adsorption energy, a breakdown in the d -band model for halogens would naturally weaken their correlation with less electronegative species C, N, O, and S, which have more common correlations with the d -band.⁹ Further insight into criteria for existence of correlations can be found by a recent study by Montemore and Medlin,³³ who found that similar HOMO levels between adsorbates were required to observe strong correlations between their adsorption energies. Nonetheless, our study focuses on the coverage dependence of correlations, and the question of criteria for the mere existence of correlations is outside the scope of this paper.

Figure 4 shows correlations between C, N, and O. We find that correlations between these elements are strong at all coverages, which is in agreement with correlations between C, N, and O at multiple coverages and configurations on the Pd(111) surface.⁹ We also

observe that the confidence intervals of the correlation between C and O are slightly larger than those between N and either C or O. This is most likely due to a two valence electron difference between C and O, whereas a single electron separates N from C and O. The same observation was also observed in previous work.³³

Further discussion on Figure 4 is required to determine the coverage-dependence of correlations between C, N and O. Correlations with C (Figures 4 (a) and (b)) show a monotonic change in the slope of the correlation at increasing coverages, and no single slope lies within the 95% confidence intervals of the slope at all coverages. Only the correlation between N and O is persistent enough that a common slope lies within the 95% confidence intervals of the slopes at all coverages. Furthermore, all correlations at 0.5, 0.75, and 1.0 ML show a shift away from coverages at 0.25 ML. All of this evidence suggests that correlations between the Period 2 elements of C, N, and O are also coverage dependent.

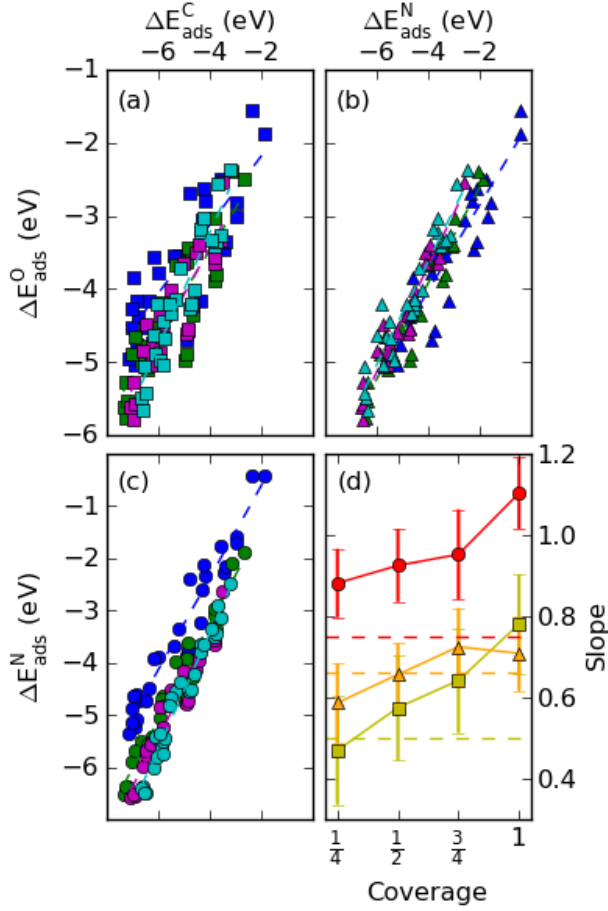


Figure 4: Adsorbate correlations between Period 2 elements at different coverages (excluding F). (a), (b), and (c) show correlations between C and O, N and O, and C and N, respectively. In (a), (b), and (c), the correlations are at constant coverages of 0.25 ML (blue), 0.5 ML (green), 0.75 ML (magenta), and 1.0 ML (cyan). (d) shows the variation in the slope of the correlation with the 95% confidence interval of the correlations between C and O (yellow square), N and O (orange triangle), and C and N (red circle) at different coverages. Dashed lines in (d) are the slopes calculated with Equation 3 to describe the scaling between C and O (yellow), N and O (orange), and C and N (red).

We herein conclude that correlations between different adsorbates require similar geometric environments for their existence and are dependent on coverage. The variety of surfaces, adsorbates, and configurations and the unprecedented number of systems studied supports the universality of this conclusion. At higher coverage, we have also observed that while almost all correlations change slope at increasing coverage, some correlations even break down. This observation is exclusive to correlations with halogens and is more notable to

correlations with F. We again cite Xin and Linic’s study of adsorption of adsorbates with almost filled valence shells on late transition metal surfaces.³⁸ Their study shows that the introduction of repulsion, brought on by highly electronegative species, leads to a breakdown of the d -band model. We hypothesize at high coverage, the repulsion effects of F, Cl, and Br become less systematic, thereby changing the d -band dependence and leading to a breakdown of the correlation. This hypothesis is supported by the fact that correlations with between electronegative species exist at high coverage.

Having established this fact, we now discuss the ramifications this conclusion has on scaling relationships as a whole, relationships between coverage and activity/selectivity trends constructed using scaling relationships, and strategies to account for these coverage dependencies when using scaling relationships.

Discussion

We would first like to connect our results on correlations between atomic adsorbates to scaling relationships. This would allow us to discuss our conclusions in the light of relevant chemical reactions, which often include species of varying degrees of hydrogenation/oxidation. Abild-Pederson et al. has found that the slope, γ , of scaling relationships between CH_x , NH_x , OH_x , and SH_x species is described by a simple bond counting model,

$$\gamma(x) = \frac{x_{\max} - x}{x_{\max}} \quad (2)$$

where x_{\max} is the maximum number of H atoms that can be bound to the central atom and x is the degree of hydrogenation.⁸ Because these correlations were constructed at low coverages, it is important to assess whether these relationships are valid at higher coverages. To gain insight on this question using the calculations we have already performed, we first propose scaling relationships between atomic adsorbates should have a similar physical meaning to the scaling relationships found by Abild-Pederson et al. for CH_x , NH_x , OH_x , and SH_x

at different degrees of hydrogenation. We recast Equation 2 to be in terms of number of electrons the adsorbate needs to form a complete octet of electrons,

$$\gamma(x) = \frac{8 - Y_{val}}{8 - Z_{val}} \quad (3)$$

where Y_{val} and Z_{val} are the number of valence electrons held by elements Y and Z , respectively.

We can now compare the slopes of the correlations in our work with the simple model proposed by Abild-Pederson et al. This is shown in Figures 2 (d), 3 (b), and 4 (d) where the dashed line is the slope predicted by Equation 3. At low coverage, excellent agreement is found in the S-O, C-O, and N-O correlations, while reasonable agreement is found in correlations among the halogens and between C and N. Although agreement with Equation 3 is varied, in almost all cases the introduction of higher coverages leads to larger disagreements between the slope predicted by Equation 3 and the observed slope. This demonstrates the electronic similarity of scaling relationships between atomic species at different degrees of hydrogenation and correlations between atomic elements with a different number of valence electrons. Our results are similar to a recent study that also found that correlations between atomic adsorbates of different valences can be described by simple electron counting rules grounded in completion of electron octets.³⁹ These results also suggest more complex models than Equation 2 are required to obtain accurate predictions of adsorption energies at higher coverages. We discuss the ramifications of these two points below.

The electronic similarity of our results with that of scaling relationships involving molecular species allows us to probe the effect of coverage on the types conclusions drawn using scaling relationships summarized in the introduction. The locations of activity ceilings and peaks, initially established at low coverage, will likely shift at higher coverage. Furthermore, selectivity boundaries constructed using scaling relationship will also shift as well. This sensitivity towards selectivity has recently been observed in a study that incorporated coverage and scaling relationships to study the activity landscape of CO methanation.⁴⁰ Furthermore,

the existence of poor correlations between geometrically different sites also suggest that tuning the shape and size of catalysts could lead to deviations of the scaling relationships. All of these points expand the number of materials that might be predicted to be promising candidates for synthesis.

Our results also point out that a single linear relationship oftentimes cannot capture the scaling relationships at all coverages and motivate the need for more complex models to capture the relationship between coverage, geometric complexity, and scaling relationships. Models for understanding coverage used in the past include cluster expansions,^{41,42} semi-empirical electronic structure models,⁵ and Monte Carlo simulations.⁴³ The application of such models to the relationship between coverage and scaling relationships could be helpful in accelerating our understanding between the relationship between coverage and activity and selectivity. Our results also hint that linear scaling relationships, though dependent on coverage, do indeed exist at higher coverages. Outside of the correlations involving the halogens, all other correlations at show similar 95% confidence intervals at low and high coverage. Furthermore, there seems to be a simple linear relationships between coverage and a change in the slope of the correlation. Therefore, one strategy might be to construct models that predict changes in scaling relationships at different coverages.

Conclusions

In conclusion, we have tested the robustness of correlations between adsorption energies over a wide variety of adsorbates, surfaces, coverages, and configurations and to a degree larger than we any study we are aware of. We observed that decreasing the geometric similar between adsorption sites weakens correlations between adsorption energies on the sites, and a key ingredient in this trend is increasing coverage. We also found that the introduction of higher coverages generally leads to changes in the correlations of adsorption energies of different adsorbates as well as weaker correlations in many cases. We use our results to

discuss the effect that including coverage can have on scaling relationships and consequently activity, selectivity, and materials discovery for catalytic reactions.

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Supporting Information Available

Full details of the computational setup and analysis of the computations is available. A json datafile containing all of the data in the manuscript is included in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Graphical TOC Entry

