

A Unified Picture of Adsorption on Transition Metals through Different Atoms

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S Supporting Information

ABSTRACT: A key issue in catalyst design is understanding how adsorption energies of surface intermediates vary across both different surfaces and various types of adsorbing atoms. In this work, we examine trends in adsorption energies of a wide variety of adsorbates that attach to transition metal surfaces through different atoms (H, C, N, O, F, S, etc.). All adsorption energies, as calculated by density functional theory, have nearly identical dependence on the metal bands (the d-band center and the number of p electrons) and the adsorbates' highest occupied molecular orbital (HOMO) energies. However, the dependence on the adsorbate–surface coupling and the d-band filling varies with the energy of the HOMO. Adsorbates with low HOMOs experience a higher level of Pauli repulsion than those with higher HOMOs. This leads to a classification of adsorbates into two groups, where adsorption energies in each group correlate. Even across the groups, adsorbates with similar HOMO energies are likely to have correlated adsorption energies.

Adsorption is a critical process in many areas of research, particularly heterogeneous catalysis. As transition metals form an important class of catalysts, understanding and predicting adsorption energies on transition metal surfaces may have an impact on a variety of chemical and energy applications. In fact, surface activity^{1–4} and selectivity^{2–5} can often be expressed in terms of a few simple adsorption energies.

Variations across adsorbates that bond through a particular type of atom can be understood based on gas-phase bond energies^{6–9} or using so-called scaling relations.^{9,10} For example, the adsorption energy of C-bound adsorbates can be predicted using the adsorption energy of C or CH₃.^{9,10} Therefore, these relations provide a general framework for understanding adsorption through any single type of atom (e.g., C or O). It is also important, however, to understand what drives differences in surface binding between these different types of atoms. Such differences are of crucial importance because many catalytic processes can be optimized by tailoring the adsorption of one type of atom relative to another. For example, to maximize activity and selectivity for synthesis gas conversion, the C and O adsorption energies must be tuned against one another.³ Further, the selectivity for ethylene epoxidation depends on the relative affinity of the surface for adsorption through C and O

atoms.^{5,11,12} Most theories of adsorption give insight into adsorption energy variations across surfaces, but do not focus on differences in behavior between different adsorbed atoms. Hence, the differences are poorly understood.

Here, we provide a unified treatment of adsorption strength when bonding to a surface through a variety of atoms, allowing an elucidation of the chemistry underlying the adsorption process. To ensure the generality of our framework, we include most of the period 2 atoms (C, N, O, F) as well as H and S. Hence, the atoms we study will be involved in the vast majority of catalytic systems. To develop and test our framework, adsorption energies and electronic structure parameters were calculated on 49 monometallic and alloy transition metal surfaces (from all groups of the d-block except 5 and 6) using density functional theory (DFT); see the Supporting Information (SI) for details and a discussion of possible effects of the methods on our results. We initially performed calculations on hexagonal surfaces at low (1/9 monolayer) coverage.

To understand trends in adsorption through different types of atoms, we considered two simple classes of adsorbates: simple monovalent species such as H, CH₃, NH₂, OH, SH, and F, as well as atoms including H, C, N, O, S, and F. Both types of adsorbates are important in surface reactions of small molecules; conceptually, the monovalent species are formed by abstraction of a single hydrogen atom from a stable molecule, while the atoms are formed by complete dehydrogenation.

By investigating the extent to which the adsorption energies of these various species are correlated with each other, we found that adsorption through different atoms can be divided into two groups: C and H are in one group, while O, N, S, and F are in the other. When the monovalent species are adsorbed in the top site (i.e., to a single surface atom), the adsorption energies within each group correlate, as shown in Figure 1a. However, species from different groups generally do not correlate (see Figure 2). The same is true for the atoms in the fcc hollow (i.e., adsorbed to three surface atoms), as shown in Figure 1b. There are some mild discrepancies in the strength and slopes of the correlations between our work and a previous study,¹³ likely because the previous study focused on atomic adsorption in the top site of Pt alloys.

The correlations in Figure 1 have practical value: by performing a DFT calculation of one atom from each group (e.g., C and O), the adsorption energies of all the other atoms can

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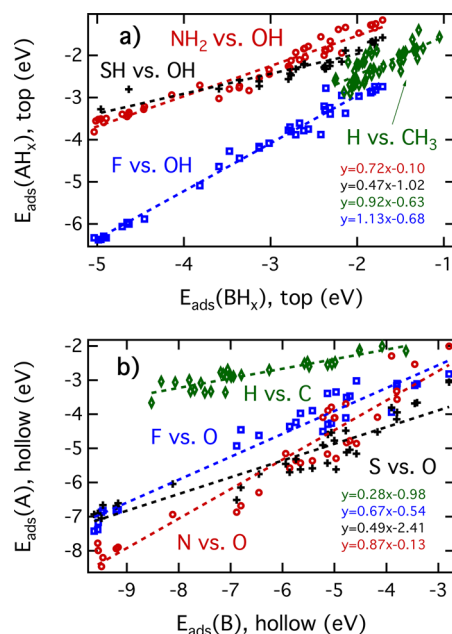


Figure 1. Correlations between the adsorption energies of (a) OH, NH₂, SH, and F in the top site; CH₃ and H in the top site; (b) O, N, S, and F in the fcc hollow; C and H in the fcc hollow. Equations of fits are inset. “A vs. B” means that the adsorption energy of A is on the vertical axis and that of B is on the horizontal axis.

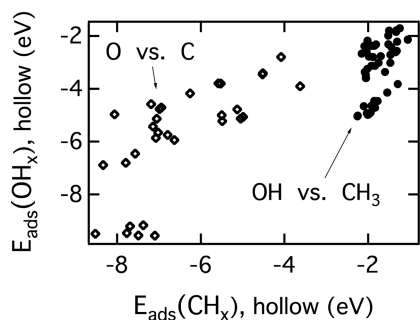


Figure 2. Relationship between adsorption energies of OH and CH₃, as well as O and C, demonstrating the lack of correlation between adsorbates from different groups.

be quickly estimated. Subsequently applying scaling relations allows the prediction of the adsorption energy of nearly all adsorbates of practical interest. Further, these correlations suggest strategies and limitations for catalyst design. For example, NO oxidation rates depend on the N and O adsorption energies.¹⁴ While there are some significant outliers from the linear trends that could allow for tuning of these energies against each other, as a first approximation only one of these adsorption energies is independent, which simplifies catalyst design but makes the optimal catalyst difficult to achieve using conventional surfaces.

Although adsorption energies correlate with bond energies to H when comparing bonding through a single type of atom,^{6,9} this correlation does not hold when comparing across different types of atoms. For example, while gas-phase bond energies can predict adsorption energy differences for OH and methoxy, they cannot predict these differences for OH and CH₃. This behavior has been seen in bonding to metal centers in organometallic complexes.¹⁵ Nevertheless, gas-phase bond energies can give insight into adsorption energies even if the adsorbing atom

changes: for the monovalent adsorbates, the slopes of the fits correlate with their gas-phase bond energies to H, such that a stronger bond leads to a steeper slope. In particular, the slopes of the NH₂, SH, F, and OH vs OH fits linearly correlate with the NH₃, H₂S, HF, and H₂O bond energies ($R^2 = 0.98$); see Figure S1. This implies that adsorbates that bond more strongly are more sensitive to variations in the surface.

We will now rationalize the grouping of the adsorbates based on electronic structure, in the framework of the d-band model.¹⁶ We begin our analysis with the monovalent adsorbates in the top site, as this ensures that changes in adsorption energy are due to the properties of a particular surface atom. Upon adsorption, adsorbate states interact with the metal bands, splitting into bonding and antibonding states. The formation and occupation of these states has a large effect on the adsorption energy. The hybridization and orthogonalization (Pauli repulsion) of adsorbate and metal states also play a significant role. The metal band centers and the surface–adsorbate coupling are often used to predict these effects.^{7,9,12,17–21} Based on this previous work, we predict the adsorption energy as

$$E_{\text{ads}} = E_{\text{elec}} + a_1 V_{\text{ad}}^2 f + a_2 V_{\text{ad}}^2 \quad (1)$$

where V_{ad} is the matrix coupling element between the adsorbate states and the metal d states, and f is the d-band filling. The value of V_{ad} was calculated using the geometry of CH₃ in the top site; this has been shown to give good results for CH₃ and OH.¹² E_{elec} accounts for changes in the metal bands and the adsorbate’s highest occupied molecular orbital (HOMO):

$$E_{\text{elec}} = b_1 \varepsilon_a + b_2 \varepsilon_d + b_3 n_p \quad (2)$$

where ε_a is the energy of the HOMO, ε_d is the d-band center (the average energy of the metal d states relative to the Fermi energy), and n_p is the number of p electrons, determined by integration over the occupied states. (The p-band center ε_p can be used in place of n_p , but n_p strongly (and inversely) correlates with ε_p .)

There is little previous work examining how different adsorbates are affected by the various surface and adsorbate properties. Fitting eqs 1 and 2 to our DFT data indicates that the adsorption energies of all the adsorbates have nearly the same dependence on the properties in E_{elec} ; hence, constraining the fitting parameters to be the same ($b_1 = 0.42$, $b_2 = -0.22$, $b_3 = -0.98$) results in accurate predictions for all adsorbates. Differences in behavior between different adsorbate types are exclusively due to the V_{ad} terms in eq 1.

Therefore, the dependence on V_{ad} and f (more specifically, the values of a_1 and a_2) determine to which group the adsorbates belong. For C and H, a_1 is negative and a_2 is approximately zero, leading to a net stabilization when V_{ad} is increased. For O, N, S, and F, a_1 is positive and the relationship $a_2 = -0.67 a_1$ fits the data well. (This relationship was suggested by initial fitting, and we set it as a constraint in the final fitting.) This leads to a net destabilization when V_{ad} is increased for surfaces with mostly full d bands ($f > 0.67$) but a stabilization for surfaces with fairly empty—and hence more reactive—d bands ($f < 0.67$). This difference is due to the energies of the adsorbate electronic states:¹⁶ CH₃ and H have much higher ε_a values than OH, NH₂, SH, and F, as shown in Table 1. Increasing V_{ad} increases both the covalent interaction and the Pauli repulsion.¹⁷ Since it is easy for higher-energy adsorbate states in CH₃ and H to induce splitting, greater coupling to the d band leads to stronger adsorption. For the deeper states of the other adsorbates, there are two regimes: on surfaces with mostly full d bands, the Pauli repulsion

Table 1. Adsorbate-Specific Fitting Parameters and HOMO Energies (in eV)

	H	CH ₃	NH ₂	SH	OH	F
a_1	-0.48	-0.10	0.60	0.34	1.03	1.21
a_2	0	0	$-0.67a_1$	$-0.67a_1$	$-0.67a_1$	$-0.67a_1$
ϵ_a	-3.81	-4.19	-6.05	-6.21	-7.39	-10.49

dominates and greater coupling leads to weaker adsorption, while on surfaces with fairly empty d bands, the covalent interaction dominates and greater coupling leads to stronger adsorption. (Even if the adsorbate-d interactions become unfavorable, the adsorbate-sp interactions will be favorable and adsorption will still be exothermic for radical species.¹⁶) Therefore, H and CH₃ correlate because they both have high HOMO energies, while the other adsorbates correlate because they have low HOMO energies.

Equations 1 and 2, along with the relations among the fitting parameters given above, give accurate results for most surfaces, with a mean absolute error (MAE) of 0.20 eV (see Figure 3).

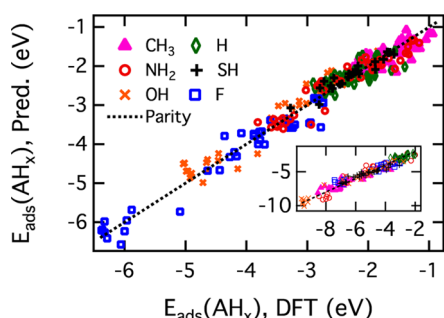


Figure 3. Parity plot for using eqs 1 and 2 to predict adsorption energies of the monovalent adsorbates as compared to the values from DFT. A single set of fitting parameters was used in eq 2, and parameters for eq 1 are in Table 1. Inset: Parity plot for using scaled values of the fitting parameters to predict atomic adsorption energies.

(The parameter values are in Table 1.) This analysis also allows predictions of differences in adsorption energy between adsorbates from the two groups based on the V_{ad} terms, as shown in Figure 4.

To apply eqs 1 and 2 to the atomic species in the fcc hollow, we employ previously developed scaling relations,¹⁰ which imply

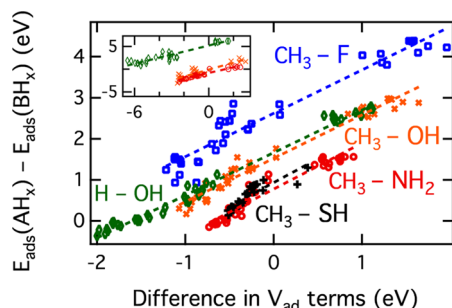


Figure 4. Adsorption energy differences for the monovalent adsorbates in the top site as a function of the differences in the V_{ad} terms in eq 1, e.g. $E_{ads}(CH_3) - E_{ads}(OH)$ as a function of $[a_1(CH_3) - a_1(OH)]V_{ad}^2 f - a_2(OH)V_{ad}^2$. Inset: Adsorption energy differences for the atoms in the fcc hollow as a function of the scaled V_{ad} terms, e.g. $E_{ads}(C) - E_{ads}(O)$ as a function of $[4a_1(CH_3) - 2a_1(OH)]V_{ad}^2 f - 2a_2(OH)V_{ad}^2$. Values for $a_i(AH_x)$ are in Table 1

that the adsorption energies of the monovalent adsorbates can be scaled by the number of dangling bonds in the atom:

$$E_{ads}(A) = \gamma E_{ads}(AH_x) + \xi \quad (3)$$

where γ is the valency of A (4 for C, 3 for N, 2 for O and S, 1 for F and H). Using eq 3, the parameters in eqs 1 and 2 can be scaled to derive expressions for atomic adsorption energies, fitting the single parameter ξ for each atom. This gives reasonable accuracy (MAE of 0.4 eV; see the inset of Figure 3), and the inset of Figure 4 shows that this scheme allows the prediction of the differences in the atomic adsorption energies with no additional fitting. Hence, the V_{ad} terms display the same qualitative behavior for the atoms as for the monovalent species: C and H are always stabilized by increased coupling, while the other atoms' behavior depends on the filling of the d band. This is consistent with the HOMO energies of the atomic species not dramatically differing from those of the hydrides, which may be required for scaling relations to hold.

Equation 1 does not rigorously demonstrate that there will be a linear relationship among the adsorption energies for the adsorbates in a particular group. However, adsorbates that have a similar dependence on surface properties should have correlated adsorption energies.¹³ Further, the nature of the transition between the two groups of adsorbates is unclear as of yet—i.e., how do adsorbates with moderate HOMO energies behave? To explore these subjects, the adsorption energies of K, Na, BH₂, SiH₃, PH₂, F, and Cl were calculated in the top sites of 15 surfaces. These calculations confirm that eqs 1 and 2 can predict adsorption energies for a variety of adsorbates with a single set of fitting parameters in eq 2 (MAE of 0.17 eV; see Figure S2 for the parity plot). They also confirm that adsorbates with a high HOMO energy are stabilized by an increase in V_{ad}^2 , while those with a low HOMO energy are destabilized on late transition metals but stabilized on early transition metals. In particular, adsorbates with high HOMO energies are modeled well by a negative a_1 value and an a_2 value of 0, while adsorbates with low HOMO energies are accurately modeled by a positive a_1 value and an a_2 value of $-0.67a_1$, which is the same behavior as that seen in Table 1. Interestingly, PH₂, which has an intermediate HOMO energy, has almost no dependence on V_{ad} , indicating that it is near the transition between the adsorbate groups.

Since the value of a_1 determines an adsorbate's behavior, the difference in a_1 is a good predictor of whether two adsorbates will correlate. Further, ϵ_a correlates with a_1 , while being much easier to calculate and conceptualize. This implies that adsorbates with similar HOMO energies should correlate, while those with very different HOMO energies should not correlate. As shown in Figure 5, this is indeed the case. (The adsorbate electronegativity correlates with the HOMO, and hence it can also be used to predict whether adsorption energies will correlate, as suggested previously in studies of organometallics.¹⁵) Additionally, Figure 5 shows that the adsorbates basically form two groups, and the cutoff lies between CH₃ and PH₂, which is exactly where a_1 goes from negative to positive. Therefore, we conclude that adsorption energies are likely to correlate (1) if the adsorbates have similar a_1 (or ϵ_a) values or (2) if a_1 has the same sign.

Though our discussion above focuses only on atomic adsorption in hollow sites and monovalent adsorption in top sites for hexagonal surfaces, the trends described here also hold for other types of adsorption sites. For example, adsorption of atomic adsorbates in bridge sites and monovalent species in hollow sites follow the same correlations within groups, as shown

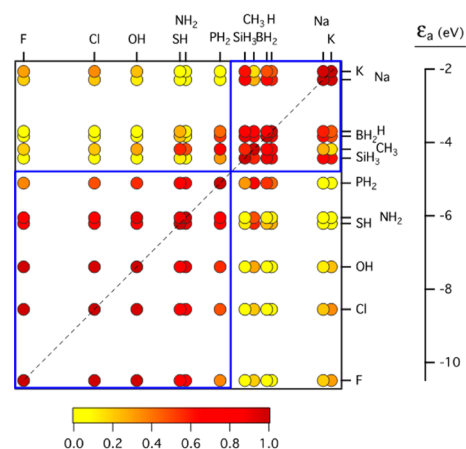


Figure 5. R^2 values for linear correlations between the adsorption energies of various adsorbates, arranged by their HOMO energies. The upper box contains adsorbates with $a_1 < 0$, while the lower box contains adsorbates with $a_1 > 0$. H's ϵ_a value has been increased slightly for display purposes only.

in the SI. This is not surprising, as correlations for the same adsorbate in different sites have been shown previously.^{22,23} The same correlations also appear to hold for monovalent adsorbates in the top sites of stepped surfaces. In fact, the correlations fall on the same lines as those for the close-packed surfaces, as shown in the SI. Therefore, our conclusions appear to be independent of the specific site and surface.

In summary, the adsorption energies of adsorbates that bind to metal surfaces through O, N, S, and F atoms are linearly correlated, and the same is true for C and H. This applies to both atomic and monovalent species. The monovalent adsorbates all have the same dependence on the HOMO energies and the metal bands, but their dependence on V_{ad} and f varies. Increased coupling stabilizes adsorbates with high HOMO energies, such as CH_3 and H. However, adsorbates with low HOMO energies, such as OH, NH_2 , SH, and F are stabilized by increased coupling on early transition metals but destabilized on late transition metals. These behaviors explain the grouping of adsorbates and allow the adsorption energies of all monovalent adsorbates to be unified into a single expression (eqs 1 and 2), with only a single adsorbate-dependent fitting parameter that correlates with the HOMO energy. An additional fitting parameter allows eqs 1 and 2 to be applied to the atomic species. Additionally, using V_{ad} and f , adsorption energies in one group can be predicted using an adsorption energy from the other group, allowing adsorption energies for all of the adsorbates to be estimated from a single calculation. For example, using the adsorption energy of CH_3 , H can be predicted using a linear correlation and OH can be predicted using V_{ad} and f .

■ ASSOCIATED CONTENT

Supporting Information

More details on the methods, the relationship between gas-phase bond energies and variations in adsorption energies, the level of correlation between the atomic species, and correlations in other sites and on stepped surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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