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Scaling Properties of Adsorption Energies for Hydrogen-Containing Molecules on Transition-Metal Surfaces

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Density functional theory calculations are presented for CHx, x = 0, 1, 2, 3, NHx, x = 0, 1, 2, OHx, x = 0, 1, and SHx, x = 0, 1 adsorption on a range of close-packed and stepped transition-metal surfaces. We find that the adsorption energy of any of the molecules considered scales approximately with the adsorption energy of the central, C, N, O, or S atom, the scaling constant depending only on x. A model is proposed to understand this behavior. The scaling model is developed into a general framework for estimating the reaction energies for hydrogenation and dehydrogenation reactions.

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The formation of a bond between a molecule and a metal surface is an important phenomenon in a number of processes including heterogeneous catalysis [1], contact formation in molecular electronics [2], and anchoring of biomolecules to solids for sensors and other biomedical applications [3]. The adsorption energy is a key quantity describing the strength of the interaction of molecules with the surface. The adsorption energy can be measured by advanced surface science techniques [4–6]. Alternatively, density functional theory (DFT) offers the possibility of calculating adsorption energies with reasonable accuracy [7–11]. While both experiments and DFT calculations are feasible for a limited number of systems, they can hardly be performed in detail for all potentially interesting adsorption systems. There is therefore a need for simple models with the ability to estimate bond energies in a first screening of interesting systems. A successful model will also expose the important factors determining the strength of an adsorbate-surface bond. In the present Letter we will develop such a model for hydrogen-containing molecules.

We use DFT calculations to derive a number of correlations between adsorption energies, and we then present a model to explain them. The model shows how the adsorbate valency, together with the properties of the d electrons of the surface, determines the adsorption energy. We further develop the scaling model into a method for estimating hydrogenation or dehydrogenation reaction energies for organic molecules on transition-metal surfaces. The model is tested against full DFT calculations for reactions of hydrocarbons, alcohols, thiols, and amino acids.

First, we present results of extensive DFT calculations of the adsorption energies of CHx, x = 0, 1, 2, 3, NHx, x = 0, 1, 2, OHx, x = 0, 1, and SHx, x = 0, 1 on a range of close-packed and stepped metal surfaces. The study involves the close-packed fcc(111), fcc(100), hcp(0001), and bcc(110) surfaces, and the stepped fcc(211) and bcc(210) surfaces. Each of the surfaces is modeled by a (2 × 2) or a (1 × 2) surface unit cell for the close-packed and stepped surfaces, respectively. Each slab has a thickness of three layers in the direction perpendicular to the close-packed surface. These slabs are thick enough to capture the trends in the chemisorption energetics. The adsorbates and the topmost layer are allowed to relax fully in all configurations, and in the case of Fe, Ni, and Co, spin polarization is taken into account. The binding energies of the different species have been taken for the most stable adsorption sites on all surfaces. The RPBE functional [12] in the generalized gradient approximation is used to describe exchange and correlation effects. The calculational method and setup is described in Ref. [13].

Figure 1 summarizes the results of the DFT calculations. We find for all the molecules studied that the adsorption energy of molecule AHx is linearly correlated with the adsorption energy of atom A:

$\Delta E^{AH} = \gamma \Delta E^A + \xi$.

(1)

There is some scatter around the linear relations, but we note that while the adsorption energies vary by several electron volts over the range of metals considered here, the mean absolute error (MAE) is only 0.13 eV. Some of this scatter is related to differences in adsorption sites for adsorbates with different amounts of hydrogen. CHx, for instance, typically prefers a onefold adsorption site on the close-packed surfaces while C prefers the threefold site. If we were to use the adsorption energy of C in the onefold adsorption site as the reference, the quality of the correlation becomes significantly better (MAE = 0.06 eV); see Fig. 2. We also find that when we use a reference with the same configuration as the molecule of interest, the scaling behavior includes alloys with the same accuracy as for the elemental metals (Fig. 2).

The main observation from Figs. 1 and 2 is that the slope of the linear relationship $\gamma$ in Eq. (1) is given to a good approximation by the number of H atoms in AHx as $\gamma(x) = (x_{\text{max}} - x)/x_{\text{max}}$, where $x_{\text{max}}$ is the maximum number of H atoms that can bond to the central atom A ($x_{\text{max}} = 4$ for
and 2 must therefore have a more general explanation that includes the argument above for CH, CH₂, and CH₃ as a special case.

We will base our analysis on the d-band model which has been used quite successfully to understand trends in adsorption energies from one transition metal to the next [8,15–19]. According to the d-band model, it is useful to think of the formation of the adsorbate-surface bond as taking place in two steps. First, we let the adsorbate states interact with the transition metal sp states, and then we include the extra contribution from the coupling to the d states:

$$\Delta E = \Delta E_{sp} + \Delta E_d. \quad (2)$$

The coupling to the metal sp states usually contributes the largest part of the bonding and involves considerable hybridization and charge transfer. In terms of variations from one transition metal to the next it can, however, be considered to be essentially a constant; the sp bands are broad, and all the transition metals have one sp electron per metal atom in the metallic state [20]. According to the d-band model, the main contribution to the variations in bond energy from one transition metal to the next comes from the coupling to the metal d states; the d states form narrow bands of states close to the Fermi level, and the width and energy of the d bands vary substantially between transition metals. According to the d-band model, all the variations among the metals observed in Fig. 1 should therefore be given by $\Delta E_d$. That means that the x dependence of $\Delta E_{d}^{AH_{\alpha}}(x)$ must be given by the d coupling alone: Let us assume for the moment that the d coupling for AH₃ is proportional to the valency parameter $\gamma$ defined above:

$$\Delta E_d^{AH_{\alpha}} = \gamma(x) \Delta E_d^A \quad (3)$$

Using Eq. (1), this will lead to the kind of relationship in Fig. 1. We can write the adsorption energy of molecule AH₃ in terms of the adsorption energy of molecule A as

FIG. 1 (color). Adsorption energies of CHₙ intermediates (crosses: $x = 1$; circles: $x = 2$; triangles: $x = 3$), NHₙ intermediates (circles: $x = 1$; triangles: $x = 2$), OH, and SH intermediates plotted against adsorption energies of C, N, O, and S, respectively. The adsorption energy of molecule A is defined as the total energy of A adsorbed in the lowest energy position outside the surface minus the sum of the total energies of A in vacuum and the clean surface. The data points represent results for close-packed (black) and stepped (red) surfaces on various transition-metal surfaces. In addition, data points for metals in the fcc(100) structure (blue) have been included for OHₓ.

FIG. 2 (color). Binding energies of CH₃ plotted against the binding energies of C for adsorption in the most stable sites (triangles) and in the case where both CH₃ and C have been fixed in the on-top site (squares).

$A = C$, $x_{\text{max}} = 3$ for $A = N$, and $x_{\text{max}} = 2$ for $A = O, S$.

Since $(x_{\text{max}} - x)$ is the valency of the AHₓ molecule, we conclude that for the four families of molecules considered the slope only depends on the valency of the adsorbate. In the following we will consider a model that allows us to understand the origin of this effect.

For some of the considered systems, simple valency or bond-counting arguments [14] can explain the results: Comparing CH, CH₂, and CH₃ on the close-packed surfaces, we generally find CH (with a valency of 3) to prefer threefold adsorption sites, CH₂ (valency of 2) to prefer twofold adsorption, and CH₃ (valency of 1) to prefer one-fold adsorption. The implication of these trends is that unsaturated bonds on the carbon atom form bonds to surface metal atoms; in effect, each unsaturated $sp^3$ hybrid on the central C atom binds independently to the d states of the nearest neighbor metal atoms, consistent with the slopes in Fig. 1. However, this picture cannot include adsorbed atomic C. Adsorbed C also adsorbs in a threefold site (neglecting long range reconstructions), but it does not have four bonds as would be needed to explain all the C data in Fig. 1. We also note that the overall scaling behavior is independent of the adsorption geometry and hence the details of the bonding; see Fig. 2. The scaling in Figs. 1 and 2 must therefore have a more general explanation that includes the argument above for CH, CH₂, and CH₃ as a special case.
\[ \Delta E_{\text{AH}} = \Delta E_d^{\text{hyb}} + \Delta E_{\text{sp}}^{\text{hyb}} = \gamma(x) \Delta E_d^A + \Delta E_{\text{sp}}^{\text{hyb}}, \]
\[ = \gamma(x) \Delta E^A + \xi, \quad (4) \]

where \( \xi = \Delta E_{\text{sp}}^{\text{hyb}} - \gamma(x) \Delta E_d^A \) is independent of the metal in question. The parameter \( \gamma \) can be read off Fig. 1 for each \( \Delta \text{AH}/A \) combination; see Eq. (1). The parameter \( \xi \) can be obtained from calculations on any transition metal. In the following all model data presented are obtained using Pt(111) as the reference system.

The basic question remains, why the coupling to the \( d \) states should scale with the valency of the adsorbate as in Eq. (1). We cannot provide a general rigorous proof of the scaling, Eq. (1), and most likely no such proof exists—the scatter in Fig. 1 indicates that the linear relationship is only approximate. What we will do, however, is show that Eq. (1) should hold approximately for the kind of systems investigated in Fig. 1.

The coupling of the adsorbate states to the \( d \) band has two contributions \([15,16,21]\), \( \Delta E = \Delta E_d^{\text{hyb}} + \Delta E_d^{\text{orth}} \). The first term describes the energy change associated with the formation of bonding and antibonding states. Since the \( d \) coupling can often be described in second order perturbation theory \([8,15,21]\), we can write \( \Delta E_d^{\text{hyb}} \approx V^2_d \rho_d \), where \( V_{ad} \) is the Hamiltonian matrix element between the adsorbate and the metal \( d \) states \([21]\). If there is more than one adsorbate state, the total interaction energy will scale with the sum of contributions from the adsorbate states, \( V_{ad}^2 = \sum_i V_{ad,i}^2 \). Since we are using EMT to model the \( sp \) density contribution to the surface at the equilibrium site for \( CH_4 \) is therefore

\[ n_{\text{surf}} = \frac{(x_{\text{max}} - x)}{x_{\text{max}}} n_0 = \gamma(x) n_0, \quad (5) \]

The linear dependence on \( x \) in Eq. (5) is based on the reasonable assumption that the contribution to the electron density is the same for all \( x \) H atoms, and that the total density should add up to \( n_0 \) \([25]\). The electron density \( n \) can be viewed as a generalized bond order \([26,27]\), and the requirement that \( n = n_0 \) is then an example of bond order conservation.

Since we are using EMT to model the \( sp \) contribution to the bonding, \( n_{\text{surf}} \) denotes the \( sp \) electron density outside the surface. The decay length of \( n_{\text{surf}} \) outside the surface is given asymptotically by the work function (the energy of the Fermi level relative to vacuum). Since the \( d \) states have energies close to the Fermi level as well, their decay length is roughly the same. That means that to a first approximation \( V_{ad}^2 \) scales with \( n_{\text{surf}} \). We have therefore shown that the following relations hold approximately,

\[ \Delta E_{d}(x) \approx V_{ad}^2(x) \approx n_{\text{surf}}(x) \approx \frac{x_{\text{max}} - x}{x_{\text{max}}} = \gamma(x), \quad (6) \]

which implies Eq. (1).

Given the understanding provided above, we can try to generalize the findings in Fig. 1. For any hydrogenation or dehydrogenation reaction of molecules bonding to a transition-metal surface via C, N, O, or S atoms, we should be able to estimate the reaction energy for all transition metals given the reaction energy for just one metal. For each atom \( A_i, i = 1, \ldots, N \) bonding to the surface, we determine the change \( \Delta \gamma_i \) in the valence parameter during the reaction, and we can then estimate variation in the bond energy for the full system from the variations in the bond energies of the \( A_i \):
The change in the thiols, and amino acids. In each case, we have calculated the model to complete DFT calculations for hydrogenation reaction energy for one single metal. In Fig. 3, we compare needs to be calculated once and for all by calculating the dehydrogenation reactions plotted against the model predictions.

FIG. 3 (color). Calculated reaction energies for a series of dehydrogenation reactions plotted against the model predictions. The model data have been generated using calculated Pt(111) data as reference.

\[
\Delta E = \sum_{i=1}^{N} (\Delta \gamma_i \Delta E^{A_i} + \Delta \xi_i) = \sum_{i=1}^{N} (\Delta \gamma_i \Delta E^{A_i}) + \Delta \xi. \quad (7)
\]

The change in the \(\xi\) parameter for the particular reaction needs to be calculated once and for all by calculating the reaction energy for one single metal. In Fig. 3, we compare the model to complete DFT calculations for hydrogenation or dehydrogenation of a series of hydrocarbons, alcohols, thiols, and amino acids. In each case, we have calculated \(\Delta \xi\) from Pt(111) data. The agreement between the model and the full DFT calculations indicates that the model has the power to describe both the absolute magnitude and the trends in reaction energies for hydrogenation or dehydrogenation reactions of a number of organic molecules on transition-metal surfaces. We note that the scaling relations can easily be generalized so that the adsorption energy of any hydrogenated species \(A H_x\) is used as the reference instead of \(A\).

By combining the present model with the Brønsted-Evans-Polanyi–type correlations that have been established between activation barriers and reaction energies for surface reactions [8,10,11], it will be possible to estimate the full potential energy diagram for a surface catalyzed reaction for any transition metal on the basis of the C, N, O, and S chemisorption energies and a calculation for a single metal. We suggest that this will be a useful tool in screening for new catalysts. Such estimates can subsequently be followed up by full DFT calculations and experiments for the most interesting systems.

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[25] NH\(_3\), H\(_2\)O, and H\(_2\)S do bind weakly to the surface. This bonding by lone pairs cannot be described in the simplest EMT model. The bond lengths to the surface of the fully hydrogenated species are, however, significantly larger than for any of the less hydrogenated species, and the density contribution from the surface is small. This is therefore a small correction to the scaling picture developed here.