

Scaling relationships for adsorption energies of C₂ hydrocarbons on transition metal surfaces

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ABSTRACT

Using density functional theory calculations we show that the adsorption energies for C₂H_x-type adsorbates on transition metal surfaces scale with each other according to a simple bond order conservation model. This observation generalizes some recently recognized adsorption energy scaling laws for AH_x-type adsorbates to unsaturated hydrocarbons and establishes a coherent simplified description of saturated as well as unsaturated hydrocarbons adsorbed on transition metal surfaces. A number of potential applications are discussed. We apply the model to the dehydrogenation of ethane over pure transition metal catalysts. Comparison with the corresponding full density functional theory calculations shows excellent agreement.

KEYWORDS: Adsorption, Catalysis, Computational chemistry, Reaction engineering, Selectivity

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INTRODUCTION

Modern society is heavily dependent on fossil hydrocarbons, both as an energy resource and perhaps almost equally importantly as a provider of the basic building blocks for a multitude of derived chemicals and materials. Most of the important industrial processes for the selective transformations of hydrocarbons are dependent on catalysts to facilitate the reactions. Significant examples of such processes include the catalytic steam cracking of hydrocarbons,¹ alkene hydrogenation,^{2,3} steam and CO₂ reforming,⁴ and Fischer-Tropsch synthesis.⁵ To describe such reactions in detail, knowledge is required of the involved hydrocarbon species, both in the reaction mixture and adsorbed on the catalytic surface. To acquire this knowledge of the adsorbed species over a single catalyst surface represents a significant challenge, and to achieve this over a larger range of interesting materials requires an even greater effort and is in many cases simply intractable.

In order to build a molecular level understanding of surface catalyzed processes, it is essential to have the surface reaction energetics from which thermodynamic and kinetic studies can progress. To this end, the adsorption energy is a key quantity, describing the strength of the interaction between a molecule and a surface. Density functional theory (DFT) offers the possibility of calculating adsorption energies with reasonable accuracy at an acceptable computational cost, and over the past two decades this approach has enjoyed considerable success.^{6,7,8,9,10} DFT thus provides a method by which analysis of reaction pathways concerning a specific reaction over a single surface can be obtained within reasonable time. In a few cases this has led to the full understanding of all relevant reaction steps for a given catalytic reaction over a given catalytic surface, with the Haber-Bosch ammonia synthesis over ruthenium surfaces as the perhaps most elaborate example.¹¹ Such detailed calculations at present cannot however, be performed for a large number of potentially interesting catalytic surfaces for a particular reaction. Whereas a limited number of pure transition metal surfaces are now accessible, the computational screening of for example alloy catalysts exhibits a complexity requiring orders of magnitude more computational time than what is currently accessible practically. Simple models to

estimate adsorption and reaction energies with good accuracy and with the ability to reproduce the chemical trends observed with higher level computational methods (or careful experiments) are therefore highly desirable.^{12,13,14,15} We here present a step in this direction for the case of hydrocarbon species.

Recently, it was shown that the adsorption energies of hydrogenated sulfur, oxygen, nitrogen, and carbon atoms on a number of transition metal surfaces scale approximately with the adsorption energy of the surface-bonded atom alone.¹⁶ It has also been shown that the scaling relations can be extended from transition metal surfaces to the surfaces of compounds such as nitrides, oxides, and sulfides.¹⁷ Furthermore, it has also been demonstrated that the use of these scaling relationships in combination with a thermodynamic analysis can lead to considerable insight into a number of industrially important catalytic processes.¹⁸ Such use of the scaling relations relies on the fact that if we have calculated the energy, $\Delta E_{M1}^{AH_x}$, of the reaction intermediate AH_x on one metal, M1, we can estimate the energy, $\Delta E_{M2}^{AH_x}$, of the same intermediate on another metal, M2, from the adsorption energies of atom A on the two metals as:

$$\Delta E_{M2}^{AH_x} = \Delta E_{M1}^{AH_x} + \gamma(x)(\Delta E_{M2}^A - \Delta E_{M1}^A), \quad \text{Eq. 1}$$

where

$$\gamma(x) = \frac{x}{x_{max}}, \quad \text{Eq. 2}$$

is the valence parameter describing the slope of the scaling relation between AH_x and A, and x_{max} is the maximum number of hydrogen atoms required to provide sufficient electrons to fulfill the octet rule for A. The simple expression for the valence parameter can be viewed as a result of AH_x obtaining full bond order when interacting with a metal surface. Even though the full adsorption energy of AH_x on a given transition metal is not proportional to the surface-adsorbate bond order, the variations between adsorption on different transition metals are.¹⁶ The model circumvents the need to carry out a full calculation for every reaction intermediate on every metal. Originally, it was suggested that scaling relations are not limited to only the class of hydrogenated atom adsorbates, but that they are also valid

for other saturated compounds. For example hydrogenation or dehydrogenation reaction energies of hydrocarbons, alcohols, amino acids, and thiols with one adsorbate-surface bond were shown to be estimated well based on the simple hydrogenated atom model.¹⁶ In the present paper we extend the model from hydrogenated atoms to adsorbates with one or more internal double and triple bonds and explicitly show that the scaling relations hold for a broad class of C_2 intermediates, namely C_2H_x ($x=0,1,2,3,4,5,6$) species on different transition metal surfaces. This opens up the possibility for using scaling relations for the study of trends underlying a number of important industrial hydrogenation and dehydrogenation reactions involving unsaturated hydrocarbon species.

The study has been carried out on close-packed fcc(111), hcp(0001), and bcc(110) surfaces and the stepped fcc{211} and hcp{10 $\bar{1}$ 5} surfaces. After presentation of the model we will demonstrate an application to the dehydrogenation of ethane, where the only input is the carbon binding energy on each metal in question. In order to verify the obtained results, the model predictions are tested against full DFT calculations.

COMPUTATIONAL DETAILS

The surface DFT calculations were carried out with the Dacapo code¹⁹ which uses a plane wave basis to describe the valence electrons and Vanderbilt ultrasoft pseudo-potentials²⁰ to represent the ionic cores. The plane wave expansion of the valence states was cut-off at an energy of 340 eV. All calculations were performed with the Revised Perdew-Burke-Ernzerhof (RPBE) generalized gradient approximation functional.²¹ The self-consistent electron density was determined by iterative diagonalization of the Kohn-Sham Hamiltonian, with the occupation of the Kohn-Sham states being smeared according to a Fermi-Dirac distribution with a smearing factor of $k_B T = 0.1$ eV, and Pulay mixing of the resulting electron density.²² All energies have been extrapolated to an electronic temperature of $k_B T = 0$ eV. Slabs consisting of three close-packed layers and separated by 11 Å of vacuum were periodically repeated with a 2x2 surface unit cell for the closed packed and a 1x2 unit cell

for the stepped surfaces, respectively. A Monkhorst-Pack k -point sampling of $4 \times 4 \times 1$ was applied.²³ In the case of Ni, Co, and Fe the calculations were spin polarized. The reported adsorption energies (E_x^*) are defined with reference to a neutral molecule or fragment of species x in isolation ($E_x^{isolated}$) and the clean metal surface (E_{metal}) in question:

$$E_x^* = E_{x/metal} - E_x^{isolated} - E_{metal} . \quad \text{Eq. 3}$$

THE MODEL

In the following we describe the bond order conservation model for hydrocarbon species on transition metals and how the model is parameterized. Subsequently, results obtained with the model are compared to full density functional theory calculations.

The bond order parameters, λ_i , of the individual bonds that the atom A participates in can be normalized, $\gamma_i = \lambda_i/x_{max}$, such that the sum is unity when A has reached its maximal bond order (satisfies the octet rule):

$$\sum_i^K \gamma_i = 1 \quad \text{Eq. 4}$$

where K is the number of covalent bonds that atom A forms. The normalized bond orders, γ_i , we also refer to as the individual bond valence parameters, since they resemble the valence parameter of the adsorbate-surface bond defined in Eq. 2. For an atom A with bonds saturated by hydrogen $AH_{x_{max}}$ Eq. 4 implies that:

$$\sum_i^{x_{max}} \gamma_i = x_{max} \cdot \gamma_H = 1 \Leftrightarrow \gamma_H = 1/x_{max} , \quad \text{Eq. 5}$$

When the molecule $AH_{x_{max}}$ approaches a metal surface then Eq. 4 implies that no covalent bonds between the surface and the molecule will form. In the following we will work with the hypothesis that any under-coordinated atom or molecular fragment bound to a surface, will form a bond with the surface such that Eq. 4 will be satisfied, corresponding to the surface bond leading to full saturation of

A. Hence, for the adsorbed species AH_x , where $x \leq x_{\max}$ we have for the surface-adsorbate valence parameter, γ_s :

$$\gamma_s + x\gamma_H = 1 \Leftrightarrow \gamma_s = 1 - x\gamma_H = \frac{x_{\max} - x}{x_{\max}}, \quad \text{Eq. 6}$$

which is the bond order conservation derivation of Eq. 2.

In general for each atom A, which is bound to K other atoms or fragments in addition to the surface, we find:

$$\gamma_s = 1 - \sum_{i=1}^K \gamma_i, \quad \text{Eq. 7}$$

Now for any molecule with L surface-bonded atoms, we would expect that:

$$\gamma_s = \sum_{j=1}^L \left(1 - \sum_{i=1}^{K_j} \gamma_i \right). \quad \text{Eq. 8}$$

Hence for hydrocarbon species, C_nH_m , $m \in [0; 2n + 2]$ with only σ intra-molecular bonds, and where all the carbon atoms attain their full bond order by interacting with the surface the surface-bond valence parameter is defined as

$$\gamma_s = \sum_{j=1}^n \left(1 - \sum_{i=1}^{K_j} 1/4 \right) = n - \sum_{j=1}^n \sum_{i=1}^{K_j} 1/4 = n - M/4. \quad \text{Eq. 9}$$

where $M = \sum_{j=1}^n \sum_{i=1}^{K_j} 1$ is the total number of internal single bonds. The expression in Eq. 9 is generally

applicable for unsaturated hydrocarbons (where all carbon atoms with incomplete bond order are in contact with the surface), provided that M is redefined more generally as the sum of bond orders,

$M = \sum_{j=1}^n \sum_{i=1}^{K_j} \lambda_i$. The scaling behavior is determined only by the atoms in contact with the surface, thus

for the case of molecules which have atoms with incomplete bond order that are not in contact with the surface (which frequently happens during reactions), the index n in Eq. 9 and in the definition of M should only run over the surface bonded atoms.

In order to apply the relationship in Eq. 9, we must address the crucial question of how one determines the bond valence parameters of the adsorbed species through consideration of just the gas-phase species and consequently the scaling (valence) parameter. To do this we must clearly extend the current model¹⁶ beyond counting just the H atoms that are present, to consider both the σ -bonding and π -bonding present in the molecule. For the case where one carbon atom is fully saturated it is fairly straightforward to count each σ bond present in the gas phase species in a similar fashion as we do for the C_1 species (where we count H atoms or simply the number of bonds). However, for the unsaturated species one needs to take into account the presence of the π -bonds and the reactivity of the metal substrate and its corresponding ability to cleave π -bonds (double and triple bonds). This is in fact analogous to organometallic chemistry where we can separate the metals into noble and reactive subgroups where σ and di- σ complexes are formed.

The simplest case to consider is that of an unsaturated fragment binding to a noble metal surface. In this situation we consider the reactivity of the metal to be such that it cannot break the π -bonding, this leads the bond order of the central atoms to be the same as in the gas-phase species. However, it becomes more complicated when considering an unsaturated fragment bonding to a reactive metal. Here we will consider all of the π -bonds to be broken, leaving a C-C bond order of one. This approach can be justified by examining the local density of states (LDOS) for the gas-phase species and the adsorbed molecular species on different metals. Furthermore, examination of the LDOS allows us to broadly define which metals can be considered reactive and which are to be considered noble towards the adsorption of a given fragment. These points are clarified in the following discussion, which closely follows the arguments presented by Nilsson and Pettersson.²⁴

First we compare the atom resolved LDOS for the molecular fragments adsorbed on Ag and Pd (which we take as representative of noble and reactive metals, respectively). Figure 1 illustrates the LDOS plot for ethene. Here it can clearly be seen that Ag does not dramatically perturb the electronic structure of the gas-phase species upon adsorption, whereas the electronic structure of ethene on Pd is

significantly distorted illustrating a strong interaction between the molecular π -orbitals and the bands of the metal d-states to form two σ -bonds. In most cases it is obvious where the separation of the metals into the two reactivity classes lies and this is often in the region of the Cu binding energy. As can be seen in Figure 2, Cu falls into the reactive class for the stepped $\{211\}$ surface, where there is a stronger adsorption energy due to the higher reactivity of the under-coordinated step sites, whereas on the $\{111\}$ surface Cu in general falls in the noble class. Again, in the case where there is ambiguity as to where exactly Cu should be placed, we can examine the LDOS to decide whether the electronic structure of the adsorbate resembles that on Ag or the one on Pd (or in fact any other metal in either class). Figure 3 illustrates the atom-resolved LDOS for C_2H_2 and C_2H adsorbed on $Cu\{111\}$ and $Cu\{211\}$. For the C_2H_2 species it can be seen that both $Cu\{111\}$ and $Cu\{211\}$ are *reactive* with respect to ethene. C_2H adsorbed on the $Cu\{111\}$ surface, however, still has the intact π^* orbital, indicating a weak interaction with the surface. This is in contrast to the $Cu\{211\}$ surface where the π^* state has disappeared. This analysis thus allows one to determine that in the case of C_2H on Cu the close-packed surface is *noble* whereas the stepped surface is *reactive*.

The difference between the *noble* and *reactive* class can furthermore be observed on the adsorption geometry of the C_2H species. Figure 4 illustrates the adsorption geometry of C_2H on $Ag\{211\}$, $Au\{211\}$, and $Cu\{211\}$. Here qualitatively different adsorption geometries are observed when moving through the metals from Ag to Au and Cu. Again, there is ambiguity as to how one should classify the borderline metals, but from inspection of the LDOS and the bond lengths the situation is clearly resolved, and in this particular case $Au\{211\}$ can be classified as *reactive* towards C_2H .

On the basis of the above discussion we can draw up well-defined regions of reactive and noble metals. The situation is clearly not black and white, and one would expect a continuous transition between the two groups. This happens to occur approximately at the Cu binding energy.

DEHYDROGENATION OF ETHANE

Using the above approach it is now possible to examine the gas phase species and identify the bonds present in the fragment, and consequently the internal bond orders required to determine the adsorbate-surface valence parameter γ for a given molecule. As can be seen from Figure 2 there is excellent agreement between the predicted slopes and the calculated energies from density functional theory. The mean absolute error (MAE) is found to be only 0.14 eV and 0.15 eV for the CH₃ and CH₂ terminated fragments, respectively. The one-line fit for C-CH step adsorption result in a slightly worse MAE for the CH terminated fragments (0.28eV). We note that for some intermediates the close-packed surface leads to stronger binding than at the step. This non-obvious behavior is observed only for the intermediates that prefer a threefold binding site over the B5 step-site (five fold coordinated site at the bottom of the step) for the first carbon (C-CH₃, C-CH₂, C-CH). The carbon descriptor is adsorbed at the B5 sites at the step and that limits the number of sites tested for the intermediates. This is why these intermediates bind stronger on the close-packed surface.

These model results show that to a first approximation a simple bond order picture allows to semi-qualitatively predict the reaction trends of transition metals through consideration of the nature of the gas-phase species alone. When this approach is coupled with relatively few calculations of the binding of carbon on transition metal surfaces to establish an adsorption model, one obtains an excellent agreement with the full DFT calculations for the adsorption energies of higher hydrocarbons. One particularly useful application of this model is in the screening of metal catalysts. In that spirit the application of the adsorption model to the full dehydrogenation of ethane will now be demonstrated.

The full dehydrogenation of ethane can be described by 6 elementary steps involving the C₂ groups. From these steps three significant routes can be found going from ethane to the formation of C₂H on the surface. In order to benchmark the scaling results and make the comparison with DFT we have taken the intercepts from the graphs in Figure 2, and used these in conjunction with the predicted slopes. An alternative approach could have been to calculate all of the species on a single metal, and to use the slopes in combination with the carbon binding energies to predict every other metal. Figure 5 depicts the

energy of each elementary reaction determined from the scaling plotted against the full DFT calculated value. If there is good agreement then an ideal slope having a 1:1 ratio should be observed. As can be seen there is excellent agreement, verified by the mean average error (MAE) being only 0.13 eV. This is particularly promising given that the accuracy of DFT is often only expected to be ± 0.2 eV.²¹ It is important to note that the scaling relations derived are in the low coverage regime and that any adsorbate-adsorbate interactions will lead to shifts in the binding energies and hence the scaling relations. However, ethane dehydrogenation is run at fairly high temperatures and a mean-field approach should therefore be adequate to describe the process. In this limit, the accuracy of the adsorption scaling model is within a useful tolerance-level, and suggests that the model may be accurate enough to be used in the search for new catalysts.²⁵

CONCLUSIONS

We have shown in this work how the scaling relationships previously identified for AH_x species can be extended to the C_2H_x species. Whereas the adsorption of these species is clearly complicated by the presence of unsaturated bonds it is shown that the level of internal saturation can be determined directly from an electronic structure analysis which classifies surfaces into a reactive (π -bond destroying) group and a noble group (on which the internal π -bonds remain). This enables the extension of the adsorption scaling model from exclusively σ -bonded adsorbates to general saturated as well as unsaturated hydrocarbons. The model has been verified to be in excellent agreement with the energetics obtained from full DFT calculations. Furthermore, the example of the dehydrogenation of ethane on both the $\{111\}$ and $\{211\}$ surfaces shows that the approach can be generally applied to a full reaction scheme comprising a number of elementary steps.

The general applicability of this model is not just limited to the C_2 species, it applies equally well to larger C_n species, provided that some knowledge of the adsorption geometries is available. For example,

if one extends the saturated chain then the scaling will continue to follow the trends determined for the CH_x species. Furthermore, the presented analysis of the adsorption of unsaturated fragments defines the general scaling for transition metal bonding of unsaturated species, and again if we substitute a hydrogen atom on these species with a saturated chain the scaling is expected to persist with unchanged slope. The intercept, however, might be different and will need to be determined in each specific case. Some complications do arise when multiple unsaturated bonds are present in the same molecule and multiple bonding points to the surface are present. The essential element, however, is still to determine the bond order parameter of each surface-bonded atom from consideration of the gas-phase species alone; once this parameter is determined the corresponding scaling relation can be predicted.

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FIGURE LEGENDS

Figure 1: Atomic orbital resolved local density of states for C_2H_4 in the gas phase and adsorbed on Ag, Cu, and Pd. The absence of the π -orbitals upon adsorption on a reactive metal (Cu, Pd) is clearly observed.

Figure 2: Adsorption energies of (a) CH_x-CH_3 ($x = 0, 1, 2$) intermediates, (b) CH_x-CH_2 ($x = 0, 1, 2$) intermediates, and (c) CH_x-CH ($x=0,1$) intermediates plotted against the adsorption energies of carbon (squares: $x = 0$; triangles: $x= 1$; circles: $x = 2$). The adsorption energy of molecule A is defined as the total energy of A adsorbed in the lowest energy position on the surface minus the sum of the total energies of the isolated neutral species A and the clean surface. The data points represent results for close-packed (black) and stepped (red) surfaces of various transition-metals.

Figure 3: Atomic orbital resolved local density of states for C_2H_2 and C_2H in the gas phase and adsorbed on Cu{211} and Cu{111}. Notice the absence of the π^* antibonding orbital for both of the C_2H_2 plots, however for the C_2H species adsorbed on Cu{111} there is still some localized π^* state present. This is due to the slightly weaker bonding interaction between the adsorbate and the lower-index surface.

Figure 4: Atomic orbital resolved local density of states for C_2H in the gas phase and adsorbed on the (211) surfaces of Ag, Au, and Cu. To the right the relaxed geometries for this species are shown with the C-C bond length indicated in Angstrom. It is observed that C_2H adsorbed on Cu and Au have the same binding motif and qualitatively the same electronic structure, whereas on Ag it has an internal bond length closer to that of the gas-phase and a less delocalized electronic structure.

Figure 5: Calculated reaction energies for a number of dehydrogenation reactions (relevant for the full dehydrogenation of ethane) plotted against the model predictions. The data points represent results for the close-packed (circles) and stepped (triangles) surfaces on a number of transition metal surfaces. The model data has been generated using the model gradients and calculated intercepts from Figure 2.









