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Computational catalyst screening: Scaling, bond-order and catalysis

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ABSTRACT

The design of new and better heterogeneous catalysts needed to accommodate the growing demand for energy from renewable sources is an important challenge for coming generations. Most surface catalyzed processes involve a large number of complex reaction networks and the energetics ultimately defines the turn-over-frequency and the selectivity of the process. In order not to get lost in the large quantities of data, simplification schemes that still contain the key elements of the reaction are required. Adsorption and transition state scaling relations constitutes such a scheme that not only maps the reaction relevant information in terms of few parameters but also provides an efficient way of screening for new materials in a continuous multi-dimensional energy space. As with all relations they impose certain restrictions on what can be achieved and in this paper, I show why these limitations exist and how we can change the behavior through an energy-resolved approach that still maintains the screening capabilities needed in computational catalysis.

1. Introduction

Understanding the atomic-level details behind the factors that drive any chemical reaction is necessary if one wants to expand the applicability of advanced density functional theory (DFT) calculations into a predictive tool for catalysis. DFT provides the perfect foundation for rapidly getting insight into changes in reaction energetics on different surfaces and surface structures.

The analysis of data from DFT has over the last several decades provided enormous insight into reaction mechanisms, surface kinetics, and reaction rates [1–15]. The gained insights have helped develop model approaches that can relate adsorption energies and activation energies of complex reactions on complex surface structures. Since all chemical reactions are described entirely by the energetics, this approach enables a mapping of the many energetic parameters defining the catalytic rate of the reaction onto a space spanned by a limited set of energies. Such energy considerations have been known in the field of catalysis for many years; the prime example being the Sabatier volcano, which state that catalyst activity depends on some reaction specific energy descriptor [16].

However, the Sabatier volcano is only a qualitative tool in catalysis and it provides very limited insight into how one can optimize or find a better catalyst.

The introduction of scaling relations for adsorption and activation energies have provided the necessary atomic-level understanding for the origin and interpretation of the Sabatier volcano and when combined with DFT it has become an extremely powerful tool suitable for large screening studies [17–20].

Scaling relations can be defined as a class of relations that describe how the structure of a reactant in the gas phase is affected by the interaction with a surface structure [21,22]. The relations do not care whether the reactant is in its equilibrium or in a transition state structure and as such they are therefore much more general than for example the much used Brønsted–Evans–Polanyi relations for transition state energies [23–25]. These energy scaling relations were first formulated and used for screening purposes in 2005 as part of a collaborative project on direct methane to methanol catalysis between the Center for Atomic-scale Materials Design at the Technical University of Denmark and Haldor Topsøe A/S and then published in 2007 as a descriptive model for a set of simple reactions [21].

Since the original paper several research groups have taken interest in scaling as an approach in computational catalysis and many studies have looked for limitations of these relations [26–29]. However, despite the intense research, the fundamental essence of the scaling relations remains unchallenged.

The adsorption and transition state scaling relations have been shown to play an instrumental role in describing the catalytic rate and selectivity of surface catalyzed reactions and aid in the screening for new catalysts. However, the relations also define limitations set by the surface electronic structure and it will require a whole new set of paradigms to perturb or change the scaling behavior [30,31]. Such paradigms or examples have already been

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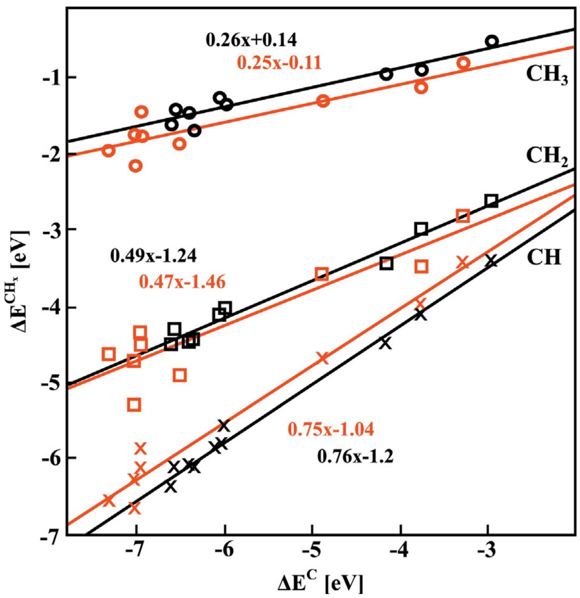

Fig. 1. Calculated CH_x, $x = 1, 2, 3$ adsorption energies plotted against C adsorption energies on close-packed fcc(1 1 1) (black) and stepped fcc(2 1 1) (red) metal surfaces. The solid lines represent linear fits to the individual data points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Adapted from [21].

outlined in the literature but without providing an actual approach to address them [32,33].

The present paper is intended to give the reader a comprehensive understanding of the applicability of the scaling relations in terms of their ability to describe thermodynamic as well as kinetic properties of surface reactions. As of today we have successfully applied the scaling approach to a large variety of surface catalyzed reactions, including methane steam reforming [34], the Haber–Bosch process [35], methanol synthesis from syngas [36], and electrochemical reactions like oxygen evolution [37] and CO_2 reduction [38]. All these reactions involve simple intermediates and the possible reaction channels of the processes are limited. With the level of understanding we have developed for simple reactions our future endeavors will have to move in a direction of added complexity and here the role of scaling is still not fully established.

In this paper I will address some of these challenges and ultimately frame the energy relations in a more general form. This will allow for manipulation of the relations such that more complex catalytic systems can be studied and as an additional benefit it will establish ways to identify independent intermediate steps in a reaction that if tweaked in the right way, could enhance catalytic activity and selectivity.

1.1. Scaling relations and the surface electronic structure

In the original paper [21], it was shown that for hydrogen containing molecules, AH_x the adsorption energies $\Delta E_{ads}^{AH_x}$, scale with the adsorption energies, ΔE_{ads}^{A} of the central atom, A, as

$$\Delta E_{ads}^{AH_x} = \gamma_s \Delta E_{ads}^{A} + \xi \qquad (1)$$

where the intercept ξ and the proportionality constant, γ_s, are independent of the metal.

In Fig. 1 this is shown explicitly for CH_x species.

As we shall see later, γ_s in this formulation is a parameter that only depends on the number of H bonds in the molecule. The linear scaling relations as given by Eq. (1) are closely coupled to the underlying electronic structure of the surface and can therefore be related to approaches linking the surface reactivity and adsorption such as the *d*-band model [39,40]. The *d*-band model describes the adsorption energy by two separable terms; a coupling between the adsorbate and the de-localized surface *sp*-states and a contribution coming from the interaction with the localized surface *d*-states. On transition metals, the *sp* coupling is very similar and hence leaving the *d* coupling as the only term describing the difference between the metals.

Since all of the *sp* coupling lies within the parameter ξ in Eq. (1) then γ_s act as a simple scaling between the states of AH_x relative to the central atom A. Combining all this with the understanding gained from effective medium theory (EMT) [41,42] we can get a qualitative understanding of the relations.

In the simplest form of EMT the adsorption is approximated by the interaction with a homogeneous electron gas whose density is taken to be a spatial average, $\rho(r)$, over the surroundings such that $\Delta E = \Delta E(\rho(r))$. Usually, for a given system the function $\Delta E(\rho(r))$ will have a minimum $\rho(r) = \rho_0$, where r is the position at which the system reaches its optimum density. Clearly, the position r will be affected by an increase or a decrease in electron density thus linking the making and breaking of bonds within the system, to the adsorption geometry. To illustrate this, let ρ_0 be the optimum electron density for an atom A and let γ_i define the normalized bond order of A such that

$$\sum_{i=1}^{x_{max}} \gamma_i = 1 \qquad (2)$$

Here x_{max} is the maximum number of covalent bonds that the atom A can form with its surroundings. The actual value of x_{max} will be given by the electronic nature of the bond formed and hence becomes an explicit function of the electron density, $\rho_i < \rho_0$, stored in the bond. Let us for simplicity saturate these bonds with hydrogen, such that $\rho_i = \rho_H$ for all i, then assuming each bond contributes the same

$$\sum_{i=1}^{x_{max}} \gamma_i \rho_H = \rho_H = \frac{\rho_0}{x_{max}} \qquad (3)$$

In this particular case the system, $AH_{x_{max}}$ will behave as a noble gas with no covalent bonding to any surface. However, if we only saturate a limited number of bonds, $x < x_{max}$, then the electron density, ρ_s, required from a surface to reach a close-shelled adsorbed structure becomes

$$\rho_s = \rho_0 - \frac{x}{x_{max}} \rho_0 = \frac{x_{max} - x}{x_{max}} \rho_0 = \gamma_s \rho_0 \qquad (4)$$

The close connection between electron density and coupling in the *d*-band model relates the γ_S in Eq. (1) with the one in Eq. (4) and thus provides a simple way of estimating the adsorption energy of complex structures based on simple bond counting arguments and knowing the adsorption energy of the single element A. How well the theoretical values for γ_s agrees with the fits to the DFT calculated values is seen in Fig. 1.

Eq. (1), clearly does not set any limitations to which elements you can scale but it is the explicit link with the electron density in Eq. (4) that restricts this approach to adsorbates with similar electronic structures interacting with a well-defined surface orientation. This approach was derived explicitly for low index metal surfaces but it can easily be generalized to other structures such as metal particles [43], metal compounds (sulfides, nitrides, oxides) [44,45], and zeolites [46].

If we treat the adsorption event as an alteration of the intrinsic bond ordering in the adsorbate, then assuming that individual binding sites do not interact or at least interact in a correlated way, then our approach also allows for an understanding of multisite adsorption. Under this assumption, the interaction at each site can