Computational Catalyst Screening: Scaling, Bond-order and Catalysis

Frank Abild-Pedersen*

*SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator
Laboratory, Menlo Park, CA 94025, USA.*

**Email: abild@slac.stanford.edu*

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 states 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 HaldorTopsøe 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 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 CO₂ 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.

2.1 Scaling relations and the surface electronic structure

In the original paper[21], it was shown that for hydrogencontaining 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

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

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

In Figure 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.

Figure 1. Calculated $CH_x, x = 1,2,3$ adsorption energies plotted against C adsorption energies on close-packed fcc(111) (black) and stepped fcc(211) (red) metal surfaces. The solid lines represent linear fits to the individual data points. Adapted from [21].

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

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

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

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

In this particular case the system, $AH_{x_{max}}$ will behave as an 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

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

The close connection between electron density and coupling in the d -band model relates 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 Figure 1.

Equation (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 be treated separately and depending on the bond strength i.e. how reactive the underlying surface is, the adsorbate bond ordering can be estimated. This defines the overall bond strength as a sum of individual scaling terms such that

$$\gamma_s = \sum_{j=1}^{N_{surf}} (1 - \sum_{i=1}^{N_{frag}} \gamma_i) \quad (5)$$

where N_{surf} is the number of surface-bonded atoms in the complex and N_{frag} is the number of atoms or molecular fragments attached to each of these surface-bonded atoms.[22] In this way, the structural information is contained in the normalized bond order since the γ_i 's are different for various elemental atoms such as e.g. C, N, and O.

The γ_s given by Eq. (5) assumes that the structure of the adsorbate defined by the γ_i 's is independent of the interaction with the surface. This assumption is in most cases not true since partial or full bond dissociation is possible when the adsorbate-surface bond strength increases. Hence, γ_s , and through that the γ_i 's, becomes an explicit function of the interaction energies ΔE_i and therefore depends on the reactivity of the surface as expected. In Figure 2, I have plotted adsorption energies of a number of CH_xCH_2 species as a function of the carbon binding energy. One can clearly see how the noble metals are unable to break the intrinsic bonds in the adsorbates and therefore displays a different scaling behavior than the more reactive metals. Hence, it is important to stress that

Figure 2. Calculated $CH_xCH_2, x = 1,2,3$ adsorption energies plotted against C adsorption energies on close-packed fcc(111) (black) and stepped fcc(211) (red) metal surfaces. The solid lines represent linear fits to the points assuming a fixed sloped as given by Eq. (5). The figure clearly defines two carbon binding energy regions, $\Delta E^C < -5eV$, where the intrinsic C-C double bond can be broken and $\Delta E^C > -5eV$, where the C-C double bond is stronger than the carbon-metal bond. Adapted from [22].

whenever we explicitly talk about linear scaling relations it has been assumed that the γ_i 's are independent of ΔE_i .

Clearly, scaling relations are limited to interactions that are purely electronic in nature, in other words scaling in its original form was never intended to describe systems in which long-range dispersion forces like van der Waals interactions are important or cases in which electro-static interactions are significant. Therefore, care has to be taken whenever reactions with adsorbates of extended molecular structure, high surface coverage, hydrogen bonding networks or promoters are considered.

2.2 Scaling relations and kinetics

In the following, I will try to elucidate how scaling relates to the kinetics of a reaction. The concept of scaling, as defined by Eq. (5), easily extends to adsorbate systems that have been pushed far away from their equilibrium structure.

If we let $(A - B)_{eq}$ be a simple di-atomic molecule in its equilibrium structure in vacuum, then for each $(A - B)_d$, where the index d designates a change from its equilibrium structure, there is a well-defined scaling termper surface bonded fragment given by Eq. (5). Hence,for that fixed structure a single scaling relation defining the adsorption energetics as a function of changes in the surface electronic structure exists such that for our di-atomic system

$$\Delta E^{A-B_d} = \gamma_s^A \Delta E^A + \gamma_s^B \Delta E^B + \xi^{A-B_d} \quad (6)$$

where $\gamma_s = \gamma_s^A + \gamma_s^B$ and ξ^{A-B_d} is the intercept at the zero interaction limit, i.e. $\Delta E^A = \Delta E^B = 0$. It is noted, that the same arguments can be generalized to situations where A and B are molecular fragments instead of single atoms.

Figure 3. Calculated $N - N$ binding energies for three fixed structures $d = 1.55\text{\AA}, 1.85\text{\AA}, 2.30\text{\AA}$ as a function of the N binding energy on stepped fcc(211) metal surfaces. Solid lines show linear fits to the points.

In Figure 3 we have plotted the adsorption energy of di-nitrogen, $(N - N)_d$, as a function of the adsorption energy of a single N atom on a number of fcc(211) transition metal surfaces for a number of different d 's, where d in this case is the $N - N$ bond distance.

One can clearly see how well the linear correlations given by Eq. (6) describe the data and hence how such an approach provides an easy way to obtain information about adsorption of reactants away from their equilibrium structure using only $\Delta E^A = \Delta E^B = \Delta E^N$.

In accordance with Eq. (1), Eq. (6) can be generalized to an n -dimensional space and fixed structure r , such that

$$\Delta E(r, \{\Delta E^1, \dots, \Delta E^n\}) = \sum_{i=1}^n \gamma_s^i(r) \Delta E^i + \xi(r, \{\Delta E^1, \dots, \Delta E^n\})$$

$$= \bar{\gamma}_s \bar{\epsilon} + \xi(r, \bar{\epsilon}) \quad (7)$$

where $\bar{\gamma}_s$ and $\bar{\epsilon}$ are n -dimensional scaling- and energy-vectors, respectively. It is now clear that BEP relations or any linear scaling between transition state energies and reaction dependent energies is a scaling relation that explicitly assumes that the transition state structure is a fixed entity independent of the surface interaction. However, it is known that the geometry of the transition state can vary significantly as one move from noble to more reactive surfaces and hence Eq. (7) can only be an approximation to the real transition state energies as a function of surface reactivity. Nevertheless, theoretical modeling over the last decade has shown clearly that linear approximations describe transition state energies with surprisingly high accuracy[47]— question is, why is that?

The answer really lies in the fact that scaling holds for any fixed structure along the reaction path as shown in Figure 3 and as we shall see this means that bond-order conservation as defined by Eq. (2) is still valid.

Lets assume that scaling holds throughout an elementary step reaction then from Eq. (7) we find that for the transition state energy[48]

$$\frac{dE^{ts}(\bar{\epsilon})}{d\epsilon_i} = \gamma_s^i(\bar{\epsilon}) + \left(\bar{\epsilon} \frac{\partial \gamma_s^i(\bar{\epsilon})}{\partial \epsilon_i} + \frac{\partial \xi(\bar{\epsilon})}{\partial \epsilon_i} \right) \quad (8)$$

where the last term in parenthesis has to vanish in the transition state. The vanishing of this term is a consequence of linear scaling and it also brings upon an interpretation of the scaling parameters γ and ξ . To first order in the energy parameter ϵ_i , the resulting strain of the system and the effective change $\partial \xi$ is compensated by the change in reactivity $\partial \gamma$, which is equivalent to bond order conservation.

A further consequence of the simple scaling behavior is that curvature given by the second derivative of $E^{ts}(\bar{\epsilon})$ with respect to ϵ_i becomes very restricted within the relevant energy region. In fact, the curvature varies so little that a linear approximation provides a more than reasonable fit to the points as seen in Figure 4 and this justifies the extensive use of linear transition state scaling relations when interpreting kinetics of chemical reactions.

Even though transition states can be described with a reasonable accuracy using the linear approach in Eq. (7) we will nevertheless push the transition state scaling a bit further and try and develop a scheme in which the actual functional form of $E^{ts}(\bar{\epsilon})$ can be derived.

I will briefly sketch the idea behind, but for a more detailed description of the approach I refer to reference [48].

Figure 4. The figure displays calculated transition state energies for di-nitrogen splitting on fcc(211) metal surfaces (solid points), a linear fit to all the points (dotted line), and the from Eq. (10) derived functional form for the transition state (solid line) as a function of the nitrogen

binding energies. The dashed lines represent the maximum and minimum slope that the transition state can have and define the limits of $E^{ts}(\bar{\epsilon})$. The dot-dashed line shows the curvature variation of $E^{ts}(\bar{\epsilon})$. Adapted from [48].

Let us rewrite the complex total energy in Eq. (7) such that

$$\Delta E(r) = \Delta E^{hyb}(r) + \Delta E^{strain}(r) \quad (9)$$

where ΔE^{hyb} is the contribution from the hybridization between the surface and the adsorbate in structure r and ΔE^{strain} is the energy needed to perturb the adsorbate from its equilibrium structure to the structure defined by r .

This explicitly divides the total energy into a surface and a gas phase dependent part each of which have a much simpler form than the total energy as seen in Figure 5. The extreme points on the $\Delta E(r)$ curve are simply the energy of the adsorbed reactant and products and these are all known from the adsorption energy scaling relations as explained above. For simple molecules, $\Delta E^{strain}(r)$ is easily obtained by calculating the gas phase value of the molecule for a range of fixed structures defined by r . To obtain accurate enough values for the scaling parameters γ and ξ as a function of r we need only a couple of points along the potential energy surface and then to impose that the function $\Delta E^{hyb}(r)$ is monotonous. Knowing $\gamma_s^i(r)$ and $\xi(r)$ for all r , we can then calculate $\Delta E(r, \bar{\epsilon})$ through Eq. (7) for any value of the vector $\bar{\epsilon}$ and obtain $E^{ts}(\bar{\epsilon})$ as

$$E^{ts}(\bar{\epsilon}) = \max_r [\Delta E(r, \bar{\epsilon})] \quad (10)$$

Figure 5. The figure displays the three terms in Eq. (9); the energy needed to strain di-nitrogen from its equilibrium structure, $\Delta E^{strain}(r)$ (solid line), the energy of the strained structure due to interaction with the surface, $\Delta E^{hyb}(r)$ (dotted line), and the total energy, $\Delta E(r)$ (dot-dashed line). $\Delta E^{strain}(r)$ has been obtained from calculations, $\Delta E^{hyb}(r)$ has been fitted and $\Delta E(r)$ is given through Eq. (9). The solid black squares are the calculations used to fit $\Delta E^{hyb}(r)$ and the solid circles are full DFT calculations along the reaction path. Adapted from [48].

Like with the adsorption energies, where only one calculation was needed to establish the scaling relations we have now introduced a scheme where transition state energies can be obtained knowing $\Delta E^{strain}(r)$ from simple gas phase calculations, the scaling relations for the initial and final state in the reaction, and finally at least one fixed structure calculation in the transition state region on as many surfaces as there are independent scaling parameters. The functional form obtained for di-nitrogen dissociation is shown in Figure 4 (solid black line) and it is in remarkably good agreement with calculations considering that it is based on very few adsorbate/surface calculations. This approach

introduces a significant reduction in computational time since transition state energies are among the most difficult numbers to obtain from DFT calculations.

2.3 Methane steam reforming – a reductionists approach

In the following, I will apply the results we have so far to gain understanding in catalysis. To do that I shall make the assumption that both reaction energies and transition state energies are adequately described by linear correlations as given in the general form of Eq. (7).

In catalysis there exist a number of very elaborate models to describe reaction rates and I will only focus on the simple mean-field microkinetic model that in most cases provide a reliable description of turnover rates for catalytic reactions.

In order to construct our microkinetic model we need two basic relationships:

First, one that relates the standard free energy change, ΔG_i^0 , of an elementary reaction step i , to the equilibrium constant, K_i^{eq} , of the reaction

$$K_i^{eq} = e^{-\Delta G_i^0 / k_B T} \quad (11)$$

Here k_B is Boltzmann's constant and T is the temperature in K.

Secondly, one equation that relates the standard free energy of activation, ΔG_i^{act} , to the rate constant, k_i , which follows from transition state theory as

$$k_i = \frac{k_B T}{h} e^{-\Delta G_i^{act} / k_B T} \quad (12)$$

where h is Planck's constant.

In both cases the change in Gibbs free energy is given by

$$\Delta G_i^{react} [T] = \Delta E_i^{react} + \Delta H^{0 \rightarrow T} + \Delta E_i^{ZPE} - T \Delta S_i^{react} \quad (13)$$

where ΔE_i^{react} is the reaction energy as calculated from DFT, $\Delta H^{0 \rightarrow T}$ is the enthalpy change from 0K to T, ΔE_i^{ZPE} is the change in zero point energy and ΔS_i^{react} is the change in entropy for reaction step i . To a good approximation, zero point energies, enthalpy and entropic contributions can be calculated from DFT frequencies by approximating the potentials around each vibrational mode by a harmonic potential.

Let ΔG_i^{react} denote n reaction free energies, ΔG_i^0 , and n activation free energies, ΔG_i^{act} , for a specific process. These energies can be obtained from total energy calculations using DFT but we could also utilize the scaling relations introduced earlier instead. If we let p be the number of independent single elemental adsorption energies that via scaling effectively describe ΔG_i^0 and ΔG_i^{act} for all i , then with the relations in Eq. (7) we have a linear mapping f from the continuous space spanned by these p elemental adsorption energy descriptors to the $2n$ -dimensional space spanned by the energies ΔG_i^0 and ΔG_i^{act} . The micro kinetic model can be seen as a function g that take the $2n$ values of ΔG_i^0 and ΔG_i^{act} and maps them onto a 1-dimensional space of reaction rates, such that for the

combined mapping $\mathbb{R}^p \xrightarrow{f} \mathbb{R}^{2n} \xrightarrow{g} \mathbb{R}$. Hence, $g \circ f$ is an explicit mapping from the p -dimensional descriptor space to the 1-dimensional rate space.

In many cases p can be reduced to 1 or 2 descriptors such that a simple catalytic activity map can be constructed that defines the rate in the space spanned by the descriptors. The activity map exhibits at least one maximum for the optimal descriptor values and this defines the region in which to search for optimum catalysts.

Let us look at a specific example: the steam reforming of methane. This reaction is an industrial process of major importance and it is really the first step in converting natural gas resources into valuable products like petroleum, diesel, methanol, higher alcohols, or ammonia.[49]

The elementary reaction steps in the steam reforming of methane are as follows:

If all steps except (I) and (VII) are treated as quasi-equilibrated then assuming steady state, we can write the overall rate of the reaction as

$$r = r_1 = r_7 = \left(k_1^+ P_{CH_4} - k_1^- \frac{\left(k_1^+ P_{CH_4} + k_7^- \frac{P_{CO}}{K_9} \right) \sqrt{P_{H_2}}}{\left(k_1^- \frac{\sqrt{P_{H_2}}}{K_8} + K_2 K_3 K_4 K_5 K_6^5 k_7^+ \frac{P_{H_2 O}}{P_{H_2}^{5/2}} \right) K_8} \right) \theta_*^2$$

$$= \left(\left(k_7^+ \frac{K_2 K_3 K_4 K_5 K_6^5 P_{H_2 O}}{P_{H_2}^{5/2}} \right) \frac{\left(k_1^+ P_{CH_4} + k_7^- \frac{P_{CO}}{K_9} \right)}{\left(k_1^- \frac{\sqrt{P_{H_2}}}{K_8} + K_2 K_3 K_4 K_5 K_6^5 k_7^+ \frac{P_{H_2 O}}{P_{H_2}^{5/2}} \right)} - k_7^- \frac{P_{CO}}{K_9} \right) \theta_*^2$$

where the coverage of empty sites is given by $\theta_* = \frac{1}{(1 + \sum_i \frac{\theta_i}{\theta_*})}$.

For a more detailed derivation of the rate equations for this reaction I refer to reference [34].

For the methane steam reforming process we find that when using the scaling relationships, there are only two independent variables needed to map out all equilibrium and rate constants, namely ΔE^C and ΔE^O . Hence, applying the scaling approach enables us to probe not only effects of temperature and pressure but also to what extent variations in the adsorption energies of carbon and oxygen affect the reactivity and from that we can get an idea of what to look for in an ideal catalyst.

In Figure 6, the 2 dimensional plot obtained from solving the above rate equations, is depicted and it clearly shows the expected volcano behavior. The binding energy tuples $(\Delta E^C, \Delta E^O)$ for the elemental metal surfaces are shown explicitly and at the top of the

volcano, metals like *Ru*, *Rh*, and *Ni* are found, which is in agreement with experimental observations reported in the literature.[50-53]

Figure 6. 2D mapping of the reaction rate for the methane steam reforming as a function of the carbon, ΔE^C and oxygen, ΔE^O binding energies. Simulations are done at 773K, 1bar pressure and 10% conversion. The calculated values ($\Delta E^C, \Delta E^O$) for fcc(211) elemental metals are shown explicitly on the plot. The top of the volcano is seen to be located in the vicinity of the metals *Ru*, *Rh*, and *Ni*, which are known to be among the most active metals for the reaction. Adapted from [34].

With the tools at hand one should now be able to find a catalyst that are optimal for any reaction by tuning the structure of the catalyst surface such that it binds the intermediates with just the right strength. However, even though the map in Figure 6 identifies the location of the optimum it also reveals that certain ranges on the map are unreachable for

the reaction of interest. We might think of a situation where a strong oxygen binding energy is needed but at the same time we want to avoid strong binding carbon species. Evidently there is nothing, at least not among the elemental metals, in the lower right region of the map and hence no metal catalyst will be suitable for such requirements. In a different situation we might have found the right binding energy regime but we need to stabilize one single species without stabilizing the rest to get a high selectivity towards one specific reaction product. However, because of the correlations between reaction intermediates, changing one will affect others and hence it is obvious that even though the scaling relations provides a significant reduction in the computational time needed to map out the activity volcano's it also sets limitations on what one can do.

2.4 Bond order conservation and design paradigms

This unacceptable consequence of the linear scaling relations has opened up an entirely new avenue of approaches in which intrinsic and extrinsic modifications of the system are being explored in order to derogate from the relations.[32,33] In the following I will give my view on some of these ideas, which involve surface structural engineering, coverage effects, promotion, ligand or multisite effects, and support effects, and how we can approach them without losing the predictability of energy scaling relations.

Figure 7. Calculated OH adsorption energies plotted against O adsorption energies on close-packed fcc(111) (open circles), fcc(100) (open squares), and stepped fcc(211) (crosses) metal surfaces. The lines represent linear fits to the individual data points. The lines all have approximately the same slope but are seen to shift down with decreasing metal-metal coordination at the adsorption site. Adapted from [21].

One of the central ingredients in the derivation of the scaling relations is the conservation of bonds. Consequently, if the intrinsic structure of any adsorbate remains fixed even upon interacting with a surface then the scaling vector $\bar{\gamma}_s$ is a fixed-valued entity as well. This also identifies the intercept ξ as the only parameter in the scaling relations that contains information about the surface electronic structure. Hence, for example on transition metals, when one introduces surfaces with a decreasing surface atom

coordination or for some reason the overlap of metal surface d -states around the adsorption site decreases then ξ will also tend to decrease. In Figure 7, we have plotted hydroxyl adsorption energies against oxygen binding energies on three different index surfaces to illustrate this point.

However, within a fixed surface structure (ξ constant) the variation in bond strength from one system to the next never changes by more than $\bar{\gamma}_s \bar{\Delta \epsilon}$, where $\bar{\Delta \epsilon}$ is a vector consisting of descriptor energy differences between two systems. This also means that (disregarding electro-static interactions) any surface structural changes, coverage, promotion or support effects that leaves the adsorbates in an unperturbed state never will result in deviations from the energy differences set by $\bar{\gamma}_s$ and hence adsorbate binding energies or activation energy barriers linked by the same descriptor cannot be manipulated independently.

In order for any of the approaches outlined above to have an effect they would have to be able to attack certain properties of a reaction and leave others unchanged. One such example is the activation of a surface through promoters or defects that directly interact with some of the intermediates in a reaction. In that way one might be able to selectively change the bond ordering in ways that would enhance the rate of the reaction.

The scaling method in its original linear form is not equipped to study such variations because the relations define the bond order of the adsorbate through a discrete well-defined set of scaling parameters and hence to address these questions the relations will have to be cast in a form that provides more flexibility.

To do this let us consider a molecular structure AB adsorbed on an arbitrary surface as shown schematically in Figure 8a. If AB is fixed, i.e. that its intrinsic bond-ordering does not change by the adsorption and that it binds through A then the binding energy of AB , ΔE_{ads}^{AB} , can be written as a linear relation of the binding of A , regardless of the nature of B such that $\Delta E_{ads}^{AB} = \gamma_s \Delta E_{ads}^A + \xi$, as defined in Eq. (1).

Figure 8. Schematics showing; a, adsorption of the adsorbate AB on a surface and b, the effect that a promoter P (defect, alloying atom, add-atom, or a ligand) could have on the adsorption event.

To increase the bond strength of AB one needs to increase the interaction between constituent A and the surface but as we have argued earlier this only allows for a linear change in the binding of AB and hence the activity of the surface is limited entirely by the scaling relation.

Let us instead introduce a promoter P - it could be an alloying atom, a defect in the surface, an atom on the same surface, or under conditions of extreme spatial confinement an atom on a different surface that interacts directly with the adsorbate or through hydrogen bonding.

The presence of the promoter can affect the energetics of a reaction in many ways. If the promoter adsorbs strongly on the surface and block certain sites it can either force the

reaction to take place on different and more favorable sites or it can completely prevent certain reactions from happening in which it acts more as an inhibitor. We will focus on situations where the promoter interacts directly with the adsorbate AB through B as shown schematically in Figure 8b. Clearly, for AB to interact with the promoter it will have to perturb its bond order to fulfill Eq. (2). Furthermore, P should be of such nature that it interacts stronger with B than the surface otherwise it is not energetically favorable to form the bond. In order to say something quantitative about this it is important to recognize the resemblance between this situation and the way in which we treated transition states earlier. The perturbed structure r of AB induced by P is fully given by the energy $\bar{\epsilon}$, where the energy vector now contains information not only about the binding of A but also the binding of P to the surface. Since all of the intrinsic scaling parameters, γ_i , as defined in Eq. (5) are given by the structure of the molecule AB , but now with the modification that we allow for changes due to the interaction energy vector $\bar{\epsilon}$, then clearly the scaling parameters become functions of $\bar{\epsilon}$ such that $\gamma_i(\bar{\epsilon})$. Hence, we now have a link between the molecular structure and the interaction energy between the molecule and the surface, through A , and the interaction between the molecule and the promoter P through the adsorption of P , such that

$$\Delta E_{ads}^{AB} = \bar{\gamma}_s(\gamma_i(\bar{\epsilon}))\bar{\epsilon} + \xi(\bar{\epsilon}) \quad (14)$$

where the bond order conservation requirements given by Eq. (2) provides the limitations to how much each γ_i can vary with energy.

For this approach to work, the interaction with the promoter will have to be accounted for by scaling relations as well.

In the following, I will show that the effect of a promoter can be described equally well with scaling and that the promoter simply act as a stabilizing agent which is strongly dependent on its interaction with the surface.

Let us again look at the situation shown schematically in Figure 8b.

In the two cases where B is bound to either A or P the structure dependent non-linear adsorption energy relations can be written

$$\Delta E_{ads}^{jB} = \gamma_s \left(\gamma_i(\Delta E_{ads}^j) \right) \Delta E_{ads}^j + \xi(\Delta E_{ads}^j) \quad (15)$$

where j equals A or P , respectively. Due to the conservation of bonds, at any point along the reaction $AB^* + P^* \rightleftharpoons A^* + PB^*$ the energetics at any point along the path from initial to final state is given by

$$\Delta E_{ads}^{A-B-P} = \bar{\gamma}_s \left(\gamma_i(\Delta E_{ads}^A, \Delta E_{ads}^P) \right) [\Delta E_{ads}^A, \Delta E_{ads}^P] + \xi(\Delta E_{ads}^A, \Delta E_{ads}^P) \quad (16)$$

To estimate a promoter's ability to activate the bond between A and B and how much AB is stabilized overall we first need information about how much the promoter stabilizes B in a given configuration and then use that to estimate the latter. Using Eq. (15) we find that

$$\Delta E_{ads}^B = \Delta E_{ads}^{P-B} - \Delta E_{ads}^P = (\gamma_s \left(\gamma_i(\Delta E_{ads}^P) \right) - 1) \Delta E_{ads}^P + \xi(\Delta E_{ads}^P) \quad (17)$$

Hence, we can now write Eq. (16) as

$$\Delta E_{ads}^{A-B-P} = \gamma_s^1 \left(\gamma_i(\Delta E_{ads}^A) \right) \Delta E_{ads}^A + \left(\gamma_s^2 \left(\gamma_i(\Delta E_{ads}^P) \right) - 1 \right) \Delta E_{ads}^P + \xi(\Delta E_{ads}^A, \Delta E_{ads}^P) \quad (18)$$

where ξ contains information about the surface and the energy required to stretch AB from its adsorption equilibrium without the promoter and Eq.(18) provides the energetics for any configuration in the reaction $AB^* + P^* \rightleftharpoons A^* + PB^*$.

Let us look at a more intuitive example where A is carbon, B is hydrogen and P is oxygen and all adsorbates are in a confined space like a zeolite or a porous structure. For simplicity we shall make a slight change from the general example above such that in the final state, hydrogen is adsorbed on the surface and not on oxygen. In the insets of Figure 9 we have shown schematically the reaction considered. Assuming that the isolated structure of CH is independent of the energy descriptor, then linear scaling will describe both the binding of CH to the surface and the binding of H to C as a function of the carbon binding energy to the surface as shown in Figure 9a. Due to the introduced confinement CH and O are able to form a hydrogen bond. This bond hardly affects the structure of CH on the surface and hence γ_s is unchanged but ξ is shifted by a constant as indicated in Figure 9b. In the final state the bond between C and H is broken and the linear scaling with the binding energy of carbon is exact and shown in Figure 9c. In the discrete picture which is what we use normally the stable configurations are then given entirely by crossings between individual scaling lines in energy space as shown by the

solid lines in Figure 9d. As we have seen in many cases this gives us no room to play and tuning the catalysis to be just right often lies in the small variations, hence we need to be able to describe these variations. The deviation from linearity, as given by Eq. (14) are shown as dot-dashed curves in Figure 9d and it is in these deviations we will find new ways to improve on today's catalysts.

The level of complexity needed to describe chemical reactions increases rapidly with the system size (number of reactants, larger molecules, number of reaction channels etc.). This makes it progressively more difficult to identify what reaction steps are dominant in determining rates and selectivity and more importantly what independent changes can be made to improve on the catalysis.

In Eq. (14) I have formulated the connection between variations in the individual γ_i 's for the intermediates in the reaction and the nature of any intrinsic or extrinsic modification of the process as a function of relevant energies for the system. To make use of this approach several issues have to be addressed computationally, such as classifying individual bond activation processes in terms of variations in γ_i 's and ξ 's, understanding how long-range dispersion forces or hydrogen bonding networks affect the stability of intermediates and activation energies, and how such weak interactions can be incorporated.

Figure 9. Schematics that shows how CH and H binding varies as E_C and the surroundings change. a; linear scaling of CH and H-C binding on an isolated surface. b; linear scaling of CH and H-C introducing a constant hydrogen bond interaction from neighboring surface. Arrows indicate the shift in ξ . c; linear scaling of C+H and H binding for dissociative adsorption of CH. d; the combined picture as given by Eq. (14). Solid lines indicate binding energy of stable (C+H) and H surface configurations assuming two discrete regimes of γ_s . Dot-dashed curves show the same stable configurations but with γ_s being a continuous function of E_C .

3. Conclusions

Tackling key challenges in catalysis requires an understanding of complex reaction networks at the atomic and electronic level. The advancement in computational chemistry over the last two decades have pushed the theoretical development aspect of heterogeneous catalysis from being entirely trial and error based to a level where we have a set of design strategies. Undoubtedly more effort still needs to be put into our fundamental understanding of these strategies but we are already in a position where we can begin to think about how to address future challenges involving reactions of increased complexity and catalyst designs of higher dimensionality. Energy scaling relations have become an established tool in heterogeneous catalysis and we have gained quite a bit of understanding and chemical intuition from these relations. Nevertheless, we still need to explore the range of the scaling relations in order to make them applicable to more demanding obstacles.

4. Acknowledgments

I acknowledge financial support from the U.S. Department of Energy (DOE), Office of Basic Energy Sciences to the SUNCAT Center for Interface Science and Catalysis.

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