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Constructing Bridges between Computational Tools in Heterogeneous and Homogeneous Catalysis

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ABSTRACT: Better catalysts are needed to address numerous challenges faced by humanity. In this perspective, we review concepts and tools in theoretical and computational chemistry that can help to accelerate the rational design of homogeneous and heterogeneous catalysts. In particular, we focus on the following three topics: 1) identification of key intermediates and transition states in a reaction using the energetic span model, 2) disentanglement of factors influencing the relative stability of the key species using energy decomposition analysis and the activation strain model, and 3) discovery of new catalysts using volcano relationships. To facilitate wider use of these techniques across different areas, we illustrate their potentials and pitfalls when applied to the study of homogeneous and heterogeneous catalysts.

KEYWORDS: catalysis, computational chemistry, energetic span model, energy decomposition analysis, activation strain model, volcano relationships, rational design, catalyst engineering.

1. INTRODUCTION

In the early decades of the twenty-first century, humanity is facing global challenges related to large increases in the world's population (projected to reach 9.7 billion by 2050),¹ with impacts on energy demands, water resources and food accessibility. Catalysis can contribute to solutions for some of these challenges in environmentally and economically sustainable ways. However, we have only a few decades to develop new or better heterogeneous, homogeneous or bio-catalysts before it is too late to address these challenges. Two main approaches are currently used to develop catalysts. One of them is the well-established “trial-and-error” approach;^{2,3} the other follows the more ambitious “rational design” or “catalyst engineering” paradigm.^{4,5}

Although engineering catalysts with desired activity and selectivity sounds appealing, in practice this process requires a detailed understanding of reaction mechanisms^{6,7} to build structure-performance relationships that can be used as guidelines to develop better or new catalysts. Such detailed information is difficult to deduce from experiments, because it involves the characterization of the atomic structures of rare and/or short-lived species, such as reaction intermediates, and the determination of activation barriers by kinetic experiments.^{8,9} At the same time, precise structural information about the considered species is readily available in atomic simulations, which makes computational catalysis a privileged tool for understanding reaction mechanisms^{10,11} and, ultimately, for rational catalyst design.^{12,13}

Engineering of highly active catalysts is driven by a few guidelines. In the beginning of the twentieth century, Sabatier formulated the principle that an ideal catalyst for a given reaction should bind the involved reacting species not too strongly and not too weakly. After almost a century of intense research, this principle crystallized in the understanding that an ideal catalyst

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3 should have a smooth reaction energy profile without a too stable (low-energy) intermediate or
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5 without a transition state that is too high in energy. These considerations, which can be applied to
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7 any heterogeneous, homogenous or enzymatic catalyst, have spurred the development of a solid
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9 theoretical foundation for interpretation of the raw numbers originating from atomic simulations,
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11 in a way that leads to rationalization and eventually predictions of catalytic behavior. At the
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13 same time, there is a historical gap between computational scientists working on homogeneous
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15 catalysis and those working on heterogeneous catalysis due to intrinsic differences between the
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17 geometric and electronic structures of the active sites of homogeneous and heterogeneous
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19 catalysts. The approaches to catalyst design developed by these two communities have been
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21 different, and today the reactivity of homogeneous and heterogeneous catalysts is usually
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23 rationalized through different sets of fundamental properties. For example, reactivity of
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25 homogeneous catalysts is often described in terms of steric or electronic factors. The former arise
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27 from forces (normally non-bonding) between parts of the molecule; the latter capture electronic
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29 effects transmitted along the chemical bonds.¹⁴ Other conceptual schemes popular in
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31 homogeneous catalysis involve the analysis of frontier orbitals, such as the energy and shape of
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33 the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO analysis), the
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35 conservation of orbital symmetry, or the isolobal analogy theory.¹⁴⁻¹⁶ These parameters are
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37 mostly considered irrelevant in the reactivity of heterogeneous catalysts, however. Indeed, in
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39 heterogeneous catalysis, there are usually no bulky ligands that could cause significant steric
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41 repulsion. The energy of the highest occupied electronic state is also usually found to be a
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43 suboptimal descriptor of a heterogeneous catalyst's electronic structure. Instead, reactivity of
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45 heterogeneous catalysts is described through the position of band centers with respect to the
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47 Fermi level^{17,18} or through the binding strength of various atomic species, often C or O, with the
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3 catalyst.^{19,20} Naturally, homogeneous catalysts do not have bands and will interact with high-spin
4 single atoms, such as C or O, in a very peculiar way. These descriptors are thus not very useful
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6 for applications in homogenous catalysis.
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11 Nevertheless, in recent years a few computational groups have started to export some of the
12 concepts and tools from homogeneous catalysis to heterogeneous catalysis and vice versa. The
13 scope of this perspective is to highlight these concepts and tools by briefly summarizing their
14 main applications in the original field and then by providing exemplary applications in the other
15 field. As non exhaustive examples, we choose energy decomposition analysis^{21,22} and the
16 energetic span model,^{23,24} developed by the homogeneous catalysis community, as well as the
17 concept of volcano relationships,^{25,26} which has already led to the discovery of several
18 heterogeneous catalysts. We hope that this perspective will foster further efforts to construct
19 bridges connecting the two fields of computational catalysis and that it will stimulate the
20 development of tools to analyze emerging catalytic systems that close the gap between
21 heterogeneous and homogeneous catalysis.
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36 37 **2. ENERGETIC SPAN MODEL (ESM)** 38 39

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41 Catalytic reactions follow mechanisms mostly composed by several steps: the reactants are
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43 by transition states (Figure 1).
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Figure 1. The catalytic cycle and energy profile of a model reaction. I = intermediates, TS = transition states.

Each catalytic cycle can be translated into an energy profile by reporting the energy of all the species relative to the initial state. To this extent, the reaction will be characterized by a free energy change (ΔG) that describes the thermochemistry of the reaction from reactants to products, and by the activation barrier ($\Delta E^\ddagger$, $\Delta G^\ddagger$) for the single reaction step connecting each intermediate to the following transition state. The energetic span model (ESM) is a conceptual tool developed to connect the energy profile derived from electronic-structure calculations to an experimentally accessible quantity, the turnover frequency (TOF). The latter is defined as the number of productive cycles (N) per unit of catalyst $[C_t]$ and time (t) as described in Eq. 1:

$$TOF = \frac{1}{[C_t]} \frac{dN}{dt} \quad (\text{Eq. 1})$$

Christiansen described how to derive the TOF from the rate constants of forward and reverse single steps, thereby developing the first kinetic model for catalytic cycles.²⁷ Later, Amatore and Jutand²⁸ derived the maximum rate of the catalytic cycle ($r_{\max}$) and TOF as a function of the total concentration of the catalytic species ($[C_t]$), an experimentally known quantity (Eq. 2a-c).

From the Arrhenius rate law, $r_{\max}$ can be expressed as

$$r_{\max} = [C_x] A e^{-\frac{\Delta E_x^\ddagger}{RT}}, \quad (\text{Eq.2a})$$

where $[C_x]$ is the concentration of the intermediate preceding the rate-determining transition state and $\Delta E_x^\ddagger$ is the corresponding energy barrier. Based on the Boltzmann distribution and the assumption that the concentration of all other intermediates is negligible relative to the concentration of the most stable intermediates in the catalytic cycle (the resting state), the concentration of each intermediate can be expressed as a function of the total concentration of the catalyst and of the energy of this intermediate relative to the resting state,

$$[C_x] \approx [C_t] A e^{-\frac{\Delta E_x}{RT}}. \quad (\text{Eq.2b})$$

When Eq. 2a and 2b are combined, $r_{\max}$ becomes

$$r_{\max} \approx [C_t] A e^{-\frac{(\Delta E_x^\ddagger + \Delta E_x)}{RT}} \quad (\text{Eq.2c})$$

and the corresponding TOF becomes

$$TOF = \frac{r_{\max}}{[C_t]} \approx A e^{-\frac{(\Delta E_x^\ddagger + \Delta E_x)}{RT}} = A e^{-\frac{\delta E}{RT}}, \quad (\text{Eq. 2d})$$

where δE is defined as the energetic span of the cycle, i.e., the energy difference between the points of highest and lowest energy along the reaction profile corresponding to the complete catalytic cycle (Figure 1).

Eq. 2d implies that the smaller the energy span is, the faster the catalysis will be. However, Eq. 2d is accurate only under stoichiometric conditions or for reactions at equilibrium, i.e., at $\Delta G=0$. In fact, in the latter case, the starting point of the second cycle will be at the same energy as for the first cycle and the same equations can be applied.

In 2006, Kozuch and Shaik extended the kinetic model by taking into account the energy balance at the end of the cycle, i.e., the thermochemistry of the reaction, ΔG .^{23,24} To evaluate the energy span of the cycle, δE , they proposed to calculate the energy span, δE_{jk} , between all transition states (TS_k) and intermediates (I_j) along the catalytic cycle (see Figure 2) as laid out in Eq. 3:

$$\begin{cases} \delta E_{jk} = G(TS_k) - G(I_j) & \text{if } k > j \\ \delta E_{jk} = G(TS_k) - G(I_j) - |\Delta G| & \text{if } k \leq j \end{cases} \quad (\text{Eq. 3})$$

In this relation, if $k > j$, then TS_k appears after I_j in the energy profile (Figure 2a) and δE_{jk} is equal to the difference in energy between them; if $k \leq j$, then TS_k appears before I_j (Figure 2b) and δE_{jk} is obtained by subtracting $|\Delta G|$ from this energy difference.

Figure 2. Schematic representation of two scenarios for calculating the energy span. a) The transition state, TS_k , follows intermediate I_j . b) The transition state, TS_k , precedes intermediate I_j .

The highest δE_{jk} determined by Eq. 3 is defined as the energy span of the catalytic cycle, δE , and the corresponding combination of states (j and k) are defined as the TOF-determining intermediate (TDI) and the TOF-determining transition state (TDTS).

Although this model takes into account the difference in free energy between products and reactants, which is independent of the catalyst, the energy of both intermediates and transition states depends strongly on the catalyst and thus δE depends on the catalyst. Given these dependences, identification of the states defining δE , i.e., the TOF-determining states for the reaction, is the key factor in understanding which catalyst features should be changed to reduce δE , and thus which catalyst features should be manipulated during the design of new catalysts with higher TOF. If other transition states (TS_n , ...) or intermediates (I_m , ...) have energies similar to TS_k or I_j , they should be included in the TOF calculation:²⁴

$$TOF = \frac{1}{1+e^{-b}} A e^{\frac{-\delta E}{RT}} \quad (\text{Eq. 4})$$

$$b = (TS_k - I_j \{-\Delta G\}) - (TS_n - I_m \{-\Delta G\})$$

As consequence of this reformulation, the TOF will be lowered by increasing the number of combinations between extreme intermediates and transition states with similar energies in the cycle to the point that it will be halved if there are two combinations of states yielding the same δE . In any case, a fundamental consequence of ESM is the clarification that neither one reaction step nor one transition state possesses all the kinetic information to determine the efficiency of a catalyst. Technically speaking, great accuracy in the calculation of the energetic profile is required to obtain a precise and trustworthy TOF value that can be compared with experimental results.

Figure 3. In the case of two competing reaction pathways (red and green lines), TDI may be from one pathway and TDS from another. Reproduced with permission from Ref. 29.

In addition, the correct calculation of the energetic span for a given reaction may require calculating several feasible reaction pathways to assemble the operative one. Indeed, TDI and TDS are the pair of states that maximize the energy span value within the operative reaction pathway. For example, analysis of the energy profile of Figure 3 indicates that the thermodynamic sink of the catalytic cycle is intermediate I_2 on the red pathway. However, the most likely evolution of this intermediate toward products does not occur via the high energy

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3 transition state TS'_3 . Rather, it occurs via reverse conversion of I'_2 to I_1 , followed by evolution of
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5 I_1 to products via transition state TS_3 , which is the TDTS, as indicated in Figure 3.
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8 In the field of homogeneous catalysis, ESM has been successfully applied to a large number
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10 of different transition-metal catalyzed reactions including cross-coupling,^{30–32} hydrogenation,^{33,34}
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12 hydrosilylation, amination,³⁵ cycloaddition,³⁶ and olefin metathesis.^{37,38} In the following, we
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14 describe exemplary applications of the model to demonstrate its capabilities to discern alternative
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16 mechanistic hypotheses and to provide new insights into the factors that control the catalytic
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18 cycle.
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22 Application of ESM in homogeneous computational catalysis started with Shaik's pioneering
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24 work on transition-metal catalyzed cross-coupling reactions. Even though the basic mechanism
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26 of this reaction consists of only three generic steps, i.e., oxidative addition, transmetallation or
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28 substitution, and reductive elimination, many factors (metal identity, ligand landscape, an
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30 organo-reagent coupling partner involved in the transmetallation step, etc.) can play key roles in
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32 determining the efficiency of the catalytic cycle and, especially, the identity of the rate-
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34 determining states.
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38 For example, let us consider the cross-coupling between an anhydride and an organozinc
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40 compound catalyzed by a nickel bipyridyl complex reported by Martin.³¹ Experimental results
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42 revealed that the rate of the reaction had first-order dependency on the catalyst concentration and
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44 zero-order dependency on the anhydride concentration. The span model allowed the observed
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46 kinetics to be rationalized, highlighting the crucial importance of identifying the rate-determining
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48 states.^{29,31}
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Figure 4. Computed free energy profiles versus the reaction coordinate of the full Ni cycle. Reproduced with permission from Ref. 31.

The full energetic profile shown in Figure 4 depicts the low-energy pathway connecting the reactant species, i.e. the anhydride and the organozinc compound, to the coupling product. The first transition state, represented by the oxidative addition of anhydride to nickel (TS_{OA}) is the free-energy maximum of the whole catalytic cycle; the corresponding product is the free energy minimum (**2** in Figure 4). The identification of TDI is straightforward since it coincides with the lowest-energy species; on the contrary, the identification of TDTS requires careful analysis of the reaction profile. In fact, defining TS_{OA} as TDTS based on its absolute energy is incorrect.

Since TDI comes after TS_{OA} , the corresponding energy span is calculated as $\delta E = G(\text{TS}_{\text{LS}}) - G(\mathbf{2}) - \Delta G_{\text{rx}}$, where ΔG_{rx} is the overall change in the free energy of the reaction (Figure 4) according to Eq. 3. On the contrary, the last TS of the cycle, the ligand substitution TS (TS_{LS}), appears after TDI, with the corresponding energy span simply calculated as the difference in free energy, $\delta E = G(\text{TS}_{\text{LS}}) - G(\mathbf{2})$. The combination of states $\mathbf{2}$ and TS_{LS} in Figure 4 maximizes δE , indicating that the ligand substitution is the TDTS of the cycle. Identifying the two TOF-determining states makes possible affirmation that the rate of the reaction depends only on the catalyst concentration and that no dependency from the anhydride concentration should be expected (since no free anhydride is involved in TDI and TDTS), in agreement with experimental results. In sum, ESM allowed the authors to rationalize the intriguing dependencies of the reaction rate on the concentration of the reagents and to identify the two critical species of the cycle, thus providing the basis for the possible design of better performing catalysts.

Kozuch and Martin exploited the span model to rationalize the experimentally observed³⁹ inefficiency of the Pd catalyst bearing the PMe_3 ligand instead of the larger PPh_3 and PtBu_3 ones in the Suzuki-Miyaura cross-coupling reaction. They derived the turnover number (TON) by including the formation of intermediates along deactivation pathways in the analysis.⁴⁰ As TON is a measure of the expected life time of a catalyst, it can be calculated from the energetic span and the energy barrier for deactivation (see⁴⁰ for further details):

$$TON \approx e^{\frac{(-\delta E + TS_d - I_x)}{RT}} \quad (\text{Eq. 5})$$

When the catalyst includes the small phosphine PMe_3 , the catalyst can precipitate into a very stable trans-diphosphine species outside the catalytic cycle. The TON calculated by taking into account the formation of this trans-diphosphine species explains the basically nonexistent activity of this catalyst, even though it has quite a good TOF.

ESM also quantitatively describes how important each intermediate and transition state is to the reaction rate. In early papers, the degree of rate control, X , was defined as the normalized influence of a rate constant on the overall reaction rate when all other rate and equilibrium constants remained constant.⁴¹ Within the framework of ESM, this quantity is redefined for a given state along the catalytic cycle as follows:

$$X_{TOF,i} = \left| \frac{1}{TOF} \frac{\partial TOF}{\partial E_i} \right| \quad (\text{Eq.6})$$

The larger X_{TOF} is, the higher the influence of the corresponding state on the TOF. Li et al. calculated X_{TOF} for each species participating in the lanthanum-catalyzed bicyclic oligomerization of acetylene to naphthalene.⁴² Their reported mechanism consists of more than 24 states among intermediates and transition states. The calculation of X_{TOF} allowed them to easily recognize TDI and TDTS, given that these states are the ones that maximize δE , i.e., they have an X_{TOF} close to one.

Similarly, Wang et al. referred to the calculation of X_{TOF} and δE to rationalize the activity and the enantioselectivity of [4+3] cycloaddition between vinylcarbenoids and dienes catalyzed by rhodium complexes.⁴³ Using ESM, they not only identified TDI and TDTS in a complex mechanistic scenario, but they also rationalized the effect of substitution on the X_{TOF} of the different species and, consequently, on the stereoselectivity of the reaction.

Until now, reactions occurring on heterogeneous catalysts have been seldom analyzed using ESM, although this possibility was initially suggested by Kozuch and Shaik.⁴⁴ Namely, they used ESM to analyze the $N_2 + 3H_2 \leftrightarrow 2NH_3$ reaction under various conditions to explain why different catalysts are needed for NH_3 synthesis and decomposition. However, to perform such analysis the authors had to use “gross” simplifications for the reasons outlined below.

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3 Unlike homogeneous catalysts, heterogeneous catalysts expose a variety of active sites
4 commonly located in the vicinity of each other. Moreover, even the simplest reactions may
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6 require several active sites to be present close to each other to proceed, e.g., dissociative
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8 adsorption of hydrogen, nitrogen or oxygen, $A_2 + 2* \rightarrow 2A^*$, where * indicates a surface site
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10 available for adsorption or an already adsorbed species. This requirement greatly complicates the
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12 kinetics of surface reactions involving O_2 dissociation, such as CO oxidation.^{45,46} Naturally,
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14 these complications are not taken into account in ESM, which provides a realistic description for
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16 only single-site reactions.⁴⁷ Thus, ESM cannot be used for precise modeling of the kinetics of
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18 reactions involving heterogeneous catalysts.
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24 The second reason why ESM has not been widely used in heterogeneous catalysis is that it
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26 ultimately leads to the calculation of TOF, which is difficult to measure in heterogeneous
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28 catalysis. As mentioned before, heterogeneous catalysts often contain a multitude of various
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30 surface sites and it is difficult to determine how many of these sites are actually catalytically
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32 active. The activity of a catalyst per active site is rarely ever measured. Rather, catalytic activity
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34 is typically reported per surface area.⁴⁸ However, when experimental TOF can be measured, it
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36 can be easily converted into experimental energy span values, as was done for H_2O_2
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38 decomposition promoted by Fe^{2+} ions in $\alpha-Fe_2O_3$.⁴⁹ Moreover, simulations of heterogeneous
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40 catalysts are almost always performed on simplified catalyst models, e.g., infinite perfect
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42 periodic single crystal surfaces, whereas real catalysts are typically composed of catalyst
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44 nanoparticles attached to mesoporous support materials. This discrepancy further limits the
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46 degree of quantitative agreement between experimental and computational results. Finally, when
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48 TDTS is not previously identified, ESM requires precisely calculated energies of all the
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50 transition states in the reaction energy profile. Obtaining transition states on heterogeneous
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3 catalysts seems to be significantly more difficult than in molecular systems. The difficulty in
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5 calculating transition states in computational heterogeneous catalysis contributes to the limited
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7 application of ESM in this field.
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11 Nevertheless, for many reactions, the complicated nature of surface kinetics as well as the
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13 complicated morphology of real heterogeneous catalysts can be neglected for practical purposes.
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15 Indeed, quantitative results from experiments and simulations often differ, although they follow
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17 very similar qualitative trends. Rational design and discovery of new catalysts *in silico* relies
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19 mostly on trends in catalytic activity, rather than on precise values. This discovery process is
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21 often done using simplified “thermodynamic” volcano relationships constructed for perfect
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23 single crystal surfaces (see Section 4).
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27 Apart from some fundamental studies of cluster reactivity,^{50,51} ESM is mostly used in
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29 computational heterogeneous catalysis studies to simplify the analysis of the competing reaction
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31 pathways with complicated energy profiles. A critical advantage of ESM is that it can be used as
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33 a “black-box” tool without any *ad-hoc* adjustments, allowing researchers to focus on the
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35 chemistry of the system. For example, ESM led to the conclusion that ethylene oligomerization
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37 on Ni-containing SSZ-24 zeolite proceeds via the Cossee-Arlman mechanism, instead of via
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39 metallacycle or proton transfer mechanisms.⁵² This analysis also revealed that the TDI in the
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41 former mechanism is not the intermediate with the lowest energy.
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46 Knowing the most probable reaction pathway is important because this pathway governs the
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48 selectivity of a catalyst. For example, the analysis of various transformations of furfural on a
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50 Pd(111) surface using ESM allowed the rationalization of the change in catalytic selectivity from
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52 furan at low H coverage to fufuryl alcohol at high H coverage.⁵³ As well, the higher selectivity of
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54 Rh(111) towards 1,2-pentanediol than towards 1,5-pentanediol and 2-methyltetrahydrofuran in
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the transformation of tetrahydrofurfuryl alcohol was rationalized by comparing the respective energy spans.⁵⁴

To further showcase both the potentials and pitfalls of ESM when applied to computational heterogeneous catalysis, we used it to analyze some already published reaction energy profiles. First, we considered work on a simplified scheme describing dry reforming of methane (DRM):

on Ni(111).⁵⁵ Based on simulations, it was argued that the elementary step of methane activation,

has the highest activation energy of 1.17 eV and should be considered as the rate-limiting step in this reaction, if desorption of products is not considered (Figure 5).⁵⁵ This conclusion was in contrast to the common belief that elemental C formation,

could be the rate-limiting step. ESM revealed that neither of these processes considered in Ref. 55 determines the reaction rate. Rather, it indicates that TDTTS is the C-O bond formation (TS31 in Figure 5) via

whose energy with respect to the initial state is 0.91 eV. At the same time, two intermediate configurations, $\text{CO}^* + \text{O}^* + \text{CH}_4$ and $\text{CO}^* + \text{O}^* + \text{CH}^* + 3\text{H}^*$, have similarly low energies approximately equal to -0.7 eV, and therefore have to be considered as TDI. Here, ESM leads us to two important conclusions. First, the resulting energetic span of $\delta E \approx 1.6$ eV is significantly higher than the activation energies of methane activation or elemental carbon formation. Second, ESM shows that the elementary step of CH oxidation is not, in fact, rate limiting. Indeed, if CH^*

binding to the catalyst had been weaker, then $\text{CO}^* + \text{O}^* + \text{CH}_4$ would become the sole TDI and the reaction rate would not critically change.

Figure 5. Simplified reaction energy profile of dry reforming of methane on Ni(111) based on data in Ref. 55. The TOF-determining intermediates are $\text{CO}^* + \text{O}^* + \text{CH}_4(\text{g})$ and $\text{CO}^* + \text{O}^* + \text{CH}^* + 3\text{H}^*$; the TOF-determining transition state is $\text{CH}^* + \text{O}^* \rightarrow \text{CHO}^*$.

Due to the previously mentioned limitations, application of the ESM to reactions on heterogeneous catalysts, particularly when approximating a multi-site reaction by a single-site process, should be done carefully. To illustrate such complications, we consider methanol synthesis from CO_2 on ceria clusters supported on Cu(111) single-crystals.⁵⁶ The TDTS in this reaction is unambiguously **TS5** (Figure 6) corresponding to

where $E(\text{TDTS}) \approx -0.25$ eV. We can also consider two intermediate configurations, $\text{CO}_2^* + 2\text{H}^* + 2\text{H}_2(\text{g})$ and $\text{CO}^* + \text{H}_2\text{O}^* + 2\text{H}^* + \text{H}_2(\text{g})$, as TOF-determining intermediates with very similar energies of $E(\text{TDI}) \approx -1.2$ eV. The differences between these two intermediate states are partially caused by the

and

reactions occurring alongside the considered transformations of CO_2 . Importantly, these two side reactions occur independently on other sites. They therefore do not belong to the considered catalytic cycle, which can be simplified to

The contributions of the mentioned side reactions (Figure 6),

$$\Delta\text{E}[\text{H}_2(\text{g}) \rightarrow 2\text{H}^*] \approx 0.7 \text{ eV and } \Delta\text{E}[\text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}^*] \approx 0,$$

should therefore not be included in the energetic span analysis, although they were included in the reaction energy profile. Upon excluding the contributions of the side reactions to the energies in Figure 6, the energetic span for the first intermediate becomes

$$\begin{aligned} \delta\text{E} &= \text{E}[\text{TDTS}] - \text{E}[\text{CO}_2^* + 2\text{H}^* + 2\text{H}_2(\text{g})] - \Delta\text{E}[\text{H}_2(\text{g}) \rightarrow 2\text{H}^*] - \\ &\Delta\text{E}[\text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}^*] \approx -0.25 + 1.2 + 0.7 - 0 \text{ eV} \approx 1.65 \text{ eV}. \end{aligned}$$

In turn, the second identified intermediate does not require such corrections, and its δE value is therefore smaller:

$$\delta\text{E} \approx -0.25 + 1.2 \text{ eV} \approx 0.95 \text{ eV}.$$

Thus, TDTS of methanol synthesis from CO_2 corresponds to the

process, whereas TDI is the adsorbed CO_2^* species.

As shown above, the application of the ESM to heterogeneous catalysis requires careful separation between the main catalytic cycle and the side reactions occurring on other sites. The characteristic feature in identifying such side reactions is that they do not have a fixed place in the reaction sequence. For example, dissociative adsorption of H_2 can be moved to the beginning

of the considered reaction energy profile and water formation to its end without changing the main catalytic process.

Figure 6. Simplified reaction energy profile of CO_2 hydrogenation to methanol on $\text{CeO}_x/\text{Cu}(111)$ based on data from Ref. 56 with adsorbed species marked by "*" sign. Key intermediate and transition states are highlighted in bold, dashed arrows indicate the elementary steps of $\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^*$ and $\text{H}_2(\text{g}) \rightarrow 2\text{H}^*$.

3. ENERGY DECOMPOSITION ANALYSIS AND THE ACTIVATION STRAIN

MODEL (ASM)

In the previous section, we described a rigorous approach to identifying the rate-determining steps along a reaction pathway and to determining how the expected TOF of a given catalyst can be related to the energy span of the reaction. One way to engineer catalysts is to reduce the energy span by either destabilizing a too stable intermediate or by stabilizing a too high-energy transition state. To do so, it is important to have access to tools that can deconstruct the energy of the TOF-determining species. Since the introduction of molecular orbital theory, attempts to

rationalize reactivity in terms of orbital interactions became widespread. Among the most noted examples are Woodward-Hoffmann rules,^{57,58} Fukui's frontier molecular orbital theory,⁵⁹ and Marcus theory.⁶⁰ Here, we focus on a model that explains reactivity on the basis of both geometrical properties and bonding capabilities of reacting species. This energy decomposition scheme was initially developed by Morokuma²¹ and Ziegler and Rauk to analyze equilibrium structures. It can be straightforwardly used to describe the overall interaction energy of any two fragments, A and B, forming an A-B complex. The simplest version of this energy decomposition scheme assumes that the total interaction energy, E_{Tot} in Figure 7, can be decomposed into deformation energy, E_{Def} (also referred to as distortion or preparation energy in the literature), and interaction energy, E_{Int} (Figure 7). E_{Def} is the cost in energy to deform interacting fragments from their optimal geometries to the geometries they will have upon interaction. In turn, E_{Int} is the interaction energy between the deformed fragments. By definition, E_{Def} is positive and destabilizing, whereas E_{Int} is negative and stabilizing. E_{Int} can be further decomposed into other energy components with physical meaning,^{21,22} but these components are beyond the scope of this perspective.

Figure 7. Schematic representation of various contributions to total energy.

This energy decomposition analysis scheme has broad applicability in catalysis, from the study of the coordination energy of a molecule to a metal complex or to the surface of a heterogeneous catalyst, to the analysis of the activation energy of a particular elementary step. The extension of energy decomposition analysis to transition states was initially proposed by Morokuma⁶¹ and Houk⁶² to analyze transition-state geometries in organic reactions. This method was further refined by several groups^{62–64} into the model known today as the distortion/interaction or the activation strain model (ASM).⁶⁵

The idea at the foundation of these approaches is that the height of reaction barriers, $\Delta E^\ddagger$, can be decomposed as

$$\Delta E^\ddagger = \Delta E_{Strain}^\ddagger + \Delta E_{Int}^\ddagger, \quad (\text{Eq. 7})$$

where $\Delta E_{Strain}^\ddagger$ and $\Delta E_{Int}^\ddagger$ are the differences between the E_{Def} and E_{Int} values calculated for an intermediate and the following transition state (Figure 7). $\Delta E_{Strain}^\ddagger$ is mostly impacted by the strength of the bonds in the substrate involved in the catalytic event (stronger bonds lead to larger $\Delta E_{Strain}^\ddagger$), the rigidity of the reacting fragments, and any kind of structural/conformational reorganization of the reacting fragments occurring in the transition state. $\Delta E_{Int}^\ddagger$ depends on the electronic structure of the reactants and on the proper orientation of the reacting fragments as they approach each other (the larger overlap and closer proximity in the energy between the frontier orbitals of the two fragments lead to more favorable $\Delta E_{Int}^\ddagger$). Bickelhaupt^{65,66} expanded this decomposition model to the whole reaction pathway, i.e., from reactants to products including transition states, by choosing an appropriate reaction coordinate, ξ (e.g., a crucial bond distance), and calculating $\Delta E_{Strain}^\ddagger$ and $\Delta E_{Int}^\ddagger$ as the reaction coordinate changes. In homogeneous catalysis, ASM is mainly used to analyze transition states and to rationalize the

origin of a given reaction barrier and eventually to predict the structures of new or improved catalysts.^{67–69}

A prototype application of ASM is the study of the activation of the carbon-halogen bond by Pd. This reaction can occur via an oxidative-addition (OA) pathway that retains the configuration of the C atom, or via a S_N2-type pathway inverting the configuration of the C atom (see Figure 8).^{70–72}

Figure 8. Schematic representation of OA and S_N2 mechanisms for the activation of a R-X bond by Pd.

Standard electronic structure calculations indicated that activation of halomethanes by Pd is easier with heavier halogens in both the OA and S_N2 pathways.^{70–72} These calculations also confirmed the experimental result that in the presence of a naked Pd atom, the OA pathway is favored, whereas when the chloride coordinated to the Pd, i.e., when PdCl[−] is considered as a catalyst, the S_N2 pathway is favored. ASM was used to deconstruct this switch in the preferred reaction pathway.

ASM analysis applied to both the starting Pd-halomethane complex and to the OA transition state revealed that the change in the strength of the Pd-halomethane interaction in the starting

complex follows the halogen electronegativity trend.^{70–72} This happens because the energy of the empty σ^* molecular orbital corresponding to the carbon-halogen bond decreases along the group, reducing the energy gap with the filled orbitals of Pd. ASM analysis of the transition state revealed that the strain energy is governed by the stretch of the carbon-halogen bond from its length at equilibrium to its length in the transition state. As a consequence, the strain energy follows the change in the strength of the carbon-halogen bond, with the highest energy penalty corresponding to the stronger $\text{H}_3\text{C-F}$ bond. Comparisons between the interaction energy and the strain energy indicated that the energy barriers are dominated by the strain energy, which explains the correlation of the energy barrier with the carbon-halogen bond energy.

ASM analysis of the $\text{S}_{\text{N}}2$ pathway revealed that the strain energy is significantly higher than that in the OA pathway due to greater distortion of the halomethane geometry in the transition state. This increase in the strain energy is not compensated by a similar increase in the interaction energy and the OA pathway is thus favored. Coordinating a Cl^- to the Pd atom, which means using PdCl^- as the catalyst, has little impact on the strain energy, while it significantly increases the interaction energy in the $\text{S}_{\text{N}}2$ transition state. This increase in the interaction energy was calculated to be large enough to counterbalance the strain energy along the $\text{S}_{\text{N}}2$ pathway and to switch the reactivity from the OA to the $\text{S}_{\text{N}}2$ pathway. In a similar way, the strain model helped to explain the trend in activity in the model $\text{S}_{\text{N}}2$ reaction of Cl^- with RCl , where $\text{R} = \text{CH}_3, \text{NH}_2, \text{OH}, \text{or F}$.⁷³ The stabilizing interaction energy increases with the electronegativity of the R group due to the lower energy of the unoccupied acceptor orbital, i.e., a stronger HOMO–LUMO orbital interaction, and the geometric strain has only a minimal contribution on the overall activation barrier.

The examples presented above show the potential of ASM to rationalize experimentally observed behaviors. The model can also be used to predict and guide experimental efforts. This is illustrated by recent work on OA of aryl-halide bonds to Au(I) complexes, leading to Au(III)(aryl)(halide) complexes, which is a difficult reaction to achieve, compared with the facile OA of aryl-halides to Pd(0).⁷⁴ Bickelhaupt showed that the energy barrier for OA of aryl-halides to Au(I) catalysts based on a linear L-Au-L geometry is due to the energy penalty associated with deformation of the linear framework into a bent framework (see Figure 9).⁷⁵ At the same time, Au(I) complexes containing chelating diphosphines with small bite angles, thus already deformed towards the bent geometry that they will assume in the oxidative addition transition state/product, perform OA of phenyl iodide to Au(I) at low temperature.^{76,77}

Figure 9. Observed reactivity for Au catalyzed by PhI OA in relation to the ligand framework. L=ligand (e.g., phosphine, PR₃)

Another prototype example of the application of ASM to guide experimental work is in the analysis of the evolution of the strain and interaction energies from the reactant to the transition state geometry. This analysis was particularly useful to rationalize the lower activation barrier for the hydrogenation of unsaturated C=X bonds (X = heteroatom) relative to C=C bonds using the ruthenium Noyori hydrogenation catalyst (see Figure 10).⁷⁸

Figure 10. ASM for the Noyori hydrogenation reaction. Reproduced with permission from Ref. 78.

Using ethylene and formaldehyde as model systems, the ASM analysis reported in Figure 11 shows that the strain energy (red curve) similarly increases for both species, whereas the interaction energies (blue curves) significantly differ. The interaction energy for ethylene increases up to $\text{H}\cdots\text{C}$ distances of approximately 1.8 Å (Figure 11a), due to the repulsion between filled orbitals on the two fragments. On the contrary, with formaldehyde (Figure 11b), the interaction energy is always stabilizing due to the formation of an intramolecular hydrogen bond between the NH group of the catalyst and the heteroatom. The stabilization provided by

this interaction term compensates for the strain energy and the reaction proceeds with a considerably lower reaction barrier.

Figure 11. a) ASM analysis of the Noyori hydrogenation reaction involving ethylene and b) formaldehyde. Reproduced with permission from Ref. 78.

ASM has mostly been used to deconstruct energy barriers in homogeneous catalysis, since localization of transition states in heterogeneous catalysis is not yet routine. Nevertheless,

implementation of better algorithms for transition-state localization, together with more easily available computational power, is making localization of transition state geometries in heterogeneous catalysis more common, which has stimulated the use of ASM to rationalize activation barriers of reactions involving heterogeneous catalysts. Aleksandrov et al. investigated alkyl hydrogenation on Pd (111) surfaces and on Pd nanoparticles (Figure 12).⁷⁹

Figure 12. Scheme used to analyze ethyl hydrogenation promoted by Pd catalysts.⁷⁹ E_{Coads} accounts for the interaction energy between the ethyl group and the hydrogen, while E_{Int} accounts for the interaction between the Pd catalyst and the reacting fragments.

The activation energy barrier was decomposed as in Eq. 8:

$$\Delta E^\ddagger = \Delta E_{\text{Int}}^\ddagger + \Delta E_{\text{Def,Adsorbate}}^\ddagger + \Delta E_{\text{Def,Surf}}^\ddagger + \Delta E_{\text{Coads}}^\ddagger, \quad (\text{Eq. 8})$$

where $\Delta E_{\text{Def,Adsorbate}}^\ddagger$ and $\Delta E_{\text{Def,Surf}}^\ddagger$ are the deformation energies of the ethyl and Pd fragments from the reactants to the transition states, $\Delta E_{\text{Int}}^\ddagger$ accounts for the interaction between the Pd catalysts and the reacting fragments, and $\Delta E_{\text{Coads}}^\ddagger$ accounts for the interaction energy between the alkyl group and the hydrogen. Within this definition, $\Delta E_{\text{Int}}^\ddagger$ is positive (which is at odds with the convention in homogeneous catalysis), since the interaction between the reacting fragments and the Pd catalyst decreases as the forming alkane detaches from the Pd surface in the transition state. Consistency between Eq. 7 and standard usage in homogeneous catalysis is restored if the total interaction energy driving the reaction is considered as $\Delta E_{\text{Int}}^\ddagger + \Delta E_{\text{Coads}}^\ddagger$. Aleksandrov et al. preferred to keep the two contributions separate to isolate the metal-fragment

interaction in $\Delta E_{Int}^\ddagger$ and to derive chemical insights that could be correlated with the experimental behavior. This case demonstrates the natural difficulties in establishing unique conventions between heterogeneous and homogeneous catalysis.

In this case, the deformation (strain) terms turned out to be not significant and, interestingly, they were going in opposite directions for the surface and the reactant molecules. $\Delta E_{Def,Surf}^\ddagger$ stabilizes the transition state since the Pd nanoparticle is more relaxed in the transition state, where forming ethane is almost desorbed, than in the initial state, where the ethyl and hydrogen fragments are adsorbed. In turn, the deformation of ethyl is stronger in the transition state due to a five-coordinated C atom interacting both with the Pd catalyst and the H atom. The interaction energy between the surface and the adsorbates is of course stronger in the initial state than in the transition state, where the forming C_2H_6 molecule starts to detach from Pd. Aleksandrov et al. correlated this with the impact of hydrogen loading on the studied barrier. When the content of hydrogen increases and subsurface hydrogen begins to be present in the nanoparticle, the catalyst-adsorbate interaction becomes weaker in the starting material, leading to a reduction of approximately 20 kJ/mol in the overall barrier.

As stated above, ASM was initially developed to analyze equilibrium structures.^{21,22} To this extent, the thermodynamics of adsorbate-catalyst complex formation can be analyzed in terms of the interplay between stabilizing and destabilizing forces, as in the analysis of the activation energy of a reaction. This approach has broadened the applicability of ASM to heterogeneous catalysis, as equilibrium structures can be easily obtained with computational tools. For example, Sautet et al. analyzed the adsorption energy of benzene to different sites of the Pd (111) surface, E_{ads} , using Eq. 9:

$$E_{ads} = E_{ads,Int} + E_{ads,Def} \quad (\text{Eq. 9})$$

where $E_{ads,Int}$ and $E_{ads,Def}$ are the equivalent of $\Delta E_{Int}^{\#}$ and $(\Delta E_{Def,Adsorbate}^{\#} + \Delta E_{Def,Surf}^{\#})$ in the barrier terms.⁸⁰ This analysis indicated a strong interaction, $E_{ads,Int}$, between benzene and the Pd (111) surface (from -1 to -2.5 eV depending on the adsorption site), with deformation of the benzene geometry upon coordination resulting in a sizeable destabilizing term (from +0.5 to +1.5 eV depending on the adsorption site, see Figure 13). The deformation energy of the surface was shown to be negligible. This study allowed Sautet et al. to explain why the bridge adsorption site (see Figure 13a) with the molecule showing the largest distorted structure (see Figure 13b) corresponds to the strongest adsorption energy. Distortion of benzene enhances the interaction between the electronic states of benzene and the electronic states of the metal near the Fermi level. The carbon atoms of the distorted benzene acquire a partial sp^3 character thereby reducing the aromaticity. This distortion increases the HOMO energy and decreases the LUMO energy (see Figure 13b), allowing stronger interactions with the vacant and filled electronic states of the metal.

Figure 13. a) Geometries of benzene chemisorbed on Pt(111) on a bridge site and an hcp site. c) HOMO-LUMO benzene orbital energy gap and interaction energy between the molecule and the surface as a function of the molecular distortion energy. Adapted with permission from Ref. 80.

This scheme was also used to explain the stronger adsorption of benzene on Pt and Rh, compared with that on Pd. Larger deformation of benzene on Pt and Rh results in the lowering of the benzene HOMO-LUMO gap, resulting in a stronger interaction with the electronic states of Pt and Rh and thus in larger adsorption energies.⁸¹

This approach proved to be particularly useful in rationalizing the lower adsorption energy of alkenes on Pt-Sn alloys compared with pure Pt.^{82,83} Adsorption energies, E_{ads} , decrease on the alloy although the geometries and the hybridization of the alkenes are similar to those calculated

for the pure Pt system. Thus, the interaction of the alkene with Pt, E_{int} , is only slightly favored relative to that with the Pt-Sn alloy (see Table 1). The main difference between Pt and Pt-Sn is in the energy cost related to the modification of the surface, $E_{\text{Def,Surf}}$. Alkene coordination requires the formation of a Pt dimer that slightly protrudes from the surface. The energy cost for the optimal deformation of the surface was shown to be higher for the alloy, resulting in a decrease in the overall adsorption energy. The importance of the surface deformation energy in determining the adsorption energy, as highlighted by energy decomposition analysis, was further confirmed in a series of other alloys,^{84,85} suggesting that surface deformation energy is another important factor in determining the reactivity of alloys, besides the well-known shift of the d-band center upon alloying.^{18,86} In fact, the d-band center is a property of the catalyst alone, while the higher energy cost to deform the alloy is a consequence of the catalyst-adsorbate interaction. The magnitude of the surface deformation and its contribution to the binding energy therefore depends on the specific adsorbate considered, an observation in agreement with experimental behavior.

Table 1. Energy contributions for an adsorbed ethane and cyclopentene molecule in kcal/mol. Adapted with permission from Ref. 84.

C ₂ H ₄			C ₅ H ₈		
Pt	Pt ₃ Sn	Pt ₂ Sn	Pt	Pt ₃ Sn	Pt ₂ Sn
-24	-16	-14	-22	-10	-7
4	8	12	4	11	15
33	34	35	36	37	36
-61	-58	-60	-61	-58	-59

While the work cited above indicated that the energy required to deform the surface can play a relevant role when different catalysts are considered, other studies indicated that the

1
2
3 deformation energy of the adsorbate also plays a major role, as demonstrated in the binding
4 energy of C_2H_x ($x = 0-4$) species to (111) surface of Pd, Pt, Rh and Ni.⁸⁷ As reported in Figure
5
6
7 14a, the adsorption energy of acetylene does not follow the trend that a decrease in the amount of
8
9 H in the molecule corresponds to a stronger interaction. This could be easily explained via
10
11 energy decomposition analysis, which indicates a large and out-of-trend deformation energy for
12
13 acetylene adsorption (see Figure 14b) compared with a more regular trend in the interaction
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15 energy (see Figure 14c).
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Figure 14. a) Adsorption, b) interaction and c) deformation energies for adsorption of C₂H_x (x = 0-4) species on different (111) surfaces. Adapted with permission from Ref. 87.

4. VOLCANO RELATIONSHIP

Sabatier formulated the famous principle that an ideal catalyst for a given reaction should bind the involved reacting species not too strongly and not too weakly. This principle implies that catalytic activity has a volcano-like dependency on the growing binding strength of a catalyst: first it increases as the reactants become more easily activated, then reaches its peak and finally decreases as it becomes harder for products to detach from the catalyst (the so called “volcano relationship”). However, it took almost a century of research to reach this conclusion in the present form and to understand the fundamental chemistry underlying it.²⁵

One of the first reactions analyzed from this perspective was the electrochemical hydrogen evolution reaction (HER),

where “*” indicates the species adsorbed on the catalyst’s surface. Early experimental investigations in 1920s and 1930s attempted to construct relationships between HER activity and various properties of catalysts, such as the position in the periodic table, melting temperature and work function.^{88,89} Horiuti and Polanyi were among the first to realize that HER activity is governed by the binding strength of H* to the catalyst^{90,91} and that, for practical purposes, the binding of the other involved species (solvated protons or molecular hydrogen) can be safely neglected. The volcano relationship between the binding of H* and HER activity was understood only in 1950s through the analysis of the pertinent kinetic equations.⁹² Because the binding strength of H* to the catalytically active sites was impossible to measure until the mid-1970s, Trasatti⁹³ used hydride formation energies to construct the volcano relationship.

In the 1980s, Trasatti reported a similar volcano relationship (Figure 15) between “the enthalpy of lower→higher oxide transition” and the activity of a catalyst in the oxygen evolution reaction (OER), assuming a one-site mechanism⁹⁴:

The empirical volcano relationship for OER was discovered even though the reaction involves multiple intermediates strongly interacting with the catalyst, unlike in the simpler case of HER. In the 1990s, the volcano relationship for OER was also derived from kinetic equations after the realization that mechanisms of both HER and OER are governed by electron and proton transfer steps.⁹⁵ Soon, the application of volcano relationships to study OER was extended to alloys of Pt.^{96,97}

Figure 15. OER overpotential on various oxides in acid plotted as a function of the enthalpy of the transition from a lower to a higher oxidation state, ΔH , adapted from Ref. 94 with permission from Elsevier.

In this and many subsequent studies, the electrochemical activity of a catalyst is characterized by its overpotential, $\eta = V - V_{eq}$. Here, $V_{eq} = \Delta G/q$ is the equilibrium potential defined by the energy of the half-reaction, ΔG , and the amount of transferred charge, q , which captures the thermodynamic limitations of the half-reaction. In turn, V is the electrode potential required for a half-reaction to proceed on the given catalyst and it differs from V_{eq} due to the kinetics of the

catalyzed half-reaction. Experimentally, V is usually measured as the electrode potential when the current density reaches $j = 10 \text{ mA/cm}^2$. Computationally, V_{eq} is usually defined as the electrode potential that makes the reaction energy of *each elementary step* of the overall half-reaction non-positive, $\Delta G_i \leq 0$, which is usually in line with experimental values.^{26,98} With this definition, the overpotential is positive in oxidation half-reactions, negative in reduction half-reactions (sometimes positive values are reported for both cases) and zero for an ideal catalyst.

The development of volcano relationships in the twentieth century was sluggish because the binding energies of various species to catalysts, the key element in the relationships, were largely unavailable. Even now, binding energies remain very difficult to measure. Empirically constructed volcano relationships therefore continue to rely on other descriptors of catalytic activity. Such descriptors often reflect the electronic structure of the material, which is known to ultimately govern its chemical properties. For example, there are known empirical volcano relationships between the activity of Pt alloys in the oxygen reduction reaction (ORR):

and the positions of their d-band centers⁹⁹ as well as between the OER activity of perovskites and the occupancy of e_g electronic states.¹⁰⁰

In the beginning of the twenty-first century, electronic structure methods became powerful and reliable enough to provide sufficiently accurate binding energies of various species to catalysts. This development triggered a revolution in heterogeneous catalysis, providing the first versatile framework for the rational design of catalysts *in silico*.²⁶ Recently, this approach was combined with the degree of rate control concept (see Section 5),^{41,101} which could make computational catalyst screening even more efficient.¹⁰²

Volcano relationships were combined with electronic structure calculations for the first time in a study rationalizing the high activity of Co-Mo alloys in ammonia synthesis.¹⁰³ According to the volcano relationship, Co binds N too weakly to be a perfect catalyst, whereas Mo binds N too strongly. However, their alloy was calculated to have an N-binding strength that puts the catalyst at the top of the volcano. The concept that a better catalyst can be obtained by alloying two metals that are located on opposite sides of the volcano has led to the rational design and discovery of numerous catalysts. For example, Fe dissociatively adsorbs CO too strongly for CO methanation and Ni adsorbs CO too weakly, while Fe-Ni alloys feature an intermediate binding strength and are significantly better catalysts for this reaction.¹⁰⁴

Another example comes from HER in which highly active Pt catalysts can be improved by alloying Pt with a poorly performing HER catalyst, Bi.¹⁰⁵ The latter performs poorly in HER because the H* energy is 0.8 eV higher than that of 1/2H₂, whereas it should be exactly the same in an ideal catalyst. At the same time, Pt is one of the best HER catalysts because the H* energy is only ~0.1 eV lower than that of 1/2H₂.¹⁰⁶ As a result, the Pt-Bi alloy displays almost perfect H binding strength and is more active than pure Pt in HER. For HER, the volcano relationships between the experimental catalytic activity and the calculated H-binding energies have been presented for transition-metal¹⁰⁶ and phosphide catalysts.¹⁰⁷ Even the activities of nitrogenase and hydrogenase enzymes can be correlated to their suitable energy of H binding.¹⁰⁸ This observation has led to the discovery of HER activity of MoS₂ edges, whose structure resembles the active sites in these enzymes.¹⁰⁸ On the other hand, there are still some disagreements between calculated and experimental activation energies of HER.¹⁰⁹ Also, some catalysts on the right-hand side of the volcano may be covered by amorphous oxides in HER conditions, which complicates the interpretation of the experiments.¹¹⁰

Strictly speaking, the activity of a catalyst in a reaction with N intermediates has a multidimensional volcano-like dependency on N -binding energies, one for each involved species. For example, if the ORR mechanism is described by the simplified scheme,

then the catalytic activity forms a two-dimensional (2D) volcano relationship with the binding energies of adsorbed O^* and OH^* species (see Figure 16a;⁹⁸ note that spin unrestricted calculations may be necessary to describe the weakly binding side of the volcano in OER and ORR¹¹¹). At the same time, the binding energies of O^* and OH^* were calculated to linearly correlate with each other, forming a so-called scaling relationship.^{19,20,112} Such correlations can be used to reduce an N -dimensional volcano relationship into a straightforward one-dimensional (1D) volcano curve without significant loss of accuracy (Figure 16b). One-dimensional volcano curves are not only easy to visualize, they also simplify the rational design of new catalysts by decreasing the number of parameters to be optimized.

Figure 16. The volcano relationship between ORR activity and a) the binding energy of O and OH to the catalyst, ΔE_O and ΔE_{OH} , respectively, b) only the binding energy of O. The latter volcano relies on the strong correlation between binding energies of O and OH on various catalysts. Adapted from Ref. 98.

On the other hand, the linear correlation between binding energies of various species to the catalyst surface may prevent engineering a catalyst that is located at the top of the volcano. Consequently, better ORR catalysts could be found among materials that do not follow the calculated scaling relationship between the binding energies of O and OH.⁹⁸ Finding such materials is a difficult task, as it requires completely changing the nature of the catalytic material. For example, although alloys of transition metals, such as Pt-Y discovered through volcano relationships in Ref. 113 may be more active than pure Pt in ORR, ultimately they follow the same scaling relationships between adsorption energies of O* and OH*. Hence, alloys follow the same volcano relationship as pure transition metals and have the same theoretical limit

of maximum activity. However, a broad set of oxides follows a different set of scaling relationships (Figure 17)^{114,115} that result in volcanos with higher peak activities. The OER activities of RuO_2 ,¹¹⁶ SrCoO_3 ,¹¹⁷ and Ni-doped $\alpha\text{-Fe}_2\text{O}_3$ ¹¹⁵ are calculated to exceed the suggested maximal activity of transition metals and alloys. Only oxyhydroxide OER catalysts may exhibit relatively weak correlation between O^* and OH^* binding energies.¹¹⁸ Doping CoOOH or NiOOH materials allowed to move from the line dictated by the scaling relationships and approach the peak of 2D volcano relationship for OER.¹¹⁸

Figure 17. The volcano relationship between OER activity of various oxides and their O-binding energies. The horizontal dashed line at -1.23 V indicates the maximum possible catalytic activity dictated by thermodynamic constraints. Adapted from Ref. 116 with permission from Elsevier.

Doped RuO_2 is one of the few materials that has been identified to be able to entirely escape the scaling relationships between binding energies of OH^* and OOH^* , which bind to rutile $\text{RuO}_2(110)$ surfaces in a different way.¹¹⁹ As a result, the OER activity of RuO_2 doped by Ni and Co exceeds the maximum activity predicted by the simplified 1D volcano relationship and is closer to the peak of the multidimensional OER volcano. The increase in RuO_2 activity in

OER upon Ni and Co doping has also been confirmed experimentally.¹¹⁹ Identifying materials that break the scaling relationships between binding energies of key intermediates in a given reaction was proposed as a new paradigm for rational design of heterogeneous catalysts.¹²⁰ For example, one could tune the pore size in a catalyst to alter the binding energies of larger intermediates, while maintaining the binding energies of smaller intermediates.¹²¹ However, the pore size that could change the relative binding strength of OH* and OOH* is calculated to be only ~0.7 nm in RuO₂, so a catalyst exploiting this effect may be difficult to engineer.¹²²

The limitations imposed by the scaling relationships between binding energies of various intermediates are particularly severe for electrochemical reduction of CO₂ (CO₂RR). This reaction is of pivotal importance to addressing environmental challenges and can also produce valuable methanol and C₂ chemicals, as well as less valuable CO and CH₄.¹²³ Despite many efforts, the best CO₂RR catalysts often have overpotentials of 0.5-1.0 V for production of valuable hydrocarbons.¹²⁴ According to the scaling relationships, the challenge in using CO₂RR comes mostly from the following step,

whose significant endothermicity is roughly the same for all transition metals.¹²³ Because of many possible elementary steps, the volcano relationship between CO₂RR activity and CO adsorption energy has an unusual convex feature in the region of strong CO binding (Figure 18).

Figure 18. Volcano relationship between the onset electrode potential for CO₂ reduction and the CO binding energy adapted from Ref. 125 with permission of the PCCP Owner Societies. Under certain conditions, the reaction rate is controlled by the fastest of two competing elementary steps, CO*→CHO* and CO*→COH*, which leads to the convex feature in the strong CO binding region.

Typically the activity of a catalyst is determined by the slowest reaction step, which results in the regular concave shape of the volcano. However, at strong CO binding energies, the activity is determined by the faster of the two competing elementary steps,

and

leading to the convex shape. Such strong CO binding energies are difficult to achieve experimentally; the observed volcano relationship based on experimental data does not exhibit a convex feature.¹²⁶

One of the pathways of methanol formation from CO₂ proceeds only through intermediates that bind to the catalyst through O atoms. A volcano relationship was therefore found between the catalytic activity and O-binding energy, which led to the discovery of highly selective Ni-Ga

catalysts for this reaction.¹²⁷ New catalysts for CO₂ conversion may emerge among transition metal carbides that may activate CO₂¹²⁸ and whose scaling relationships between the binding energies and the key intermediates differ from those of pure metals.¹²⁹

Unusual volcano relationships may also arise when the scaling relationships between various binding energies are not exactly linear. For example, the geometry of N₂H is different on surfaces of early and late transition metals, which results in their non-linear correlation with the binding energies of N on the respective surfaces.¹³⁰ However, this complication does not seem to be critical for the volcano relationships for electrochemical N₂ reduction to NH₃.¹³⁰

In more complicated reactions, such as steam reforming of methane,

scaling relationships do not fully simplify the N-dimensional volcano relationships. Since some intermediates bind to the catalyst surface through C atoms while others bind through O atoms, both C- and O-binding energies are important to the catalytic activity. The N-dimensional volcano relationship for methane steam reforming can therefore be reduced to a 2D volcano plot, instead of the more common 1D volcano curve (Figure 19).¹³¹ A similar volcano was constructed for new alloys that could be active in formaldehyde synthesis from methanol.¹³²

Figure 19. The volcano relationship between the TOF of a catalyst in methane steam reforming and binding energies of atomic O and C to the catalyst. Adapted from Ref. ¹³¹ with permission from Elsevier.

The modern derivation of volcano relationships¹³³ comes from the analysis of microkinetic models based on Brønsted-Evans-Polanyi relationships, i.e., on the handy¹³⁴ assumption that activation energies of various elementary steps linearly correlate with their respective reaction energies. This analysis also revealed that the position of the peak of the volcano depends not only on the reaction temperature and pressure, but also on how close the reaction atmosphere is to the equilibrium between reactants and products. In principle, similar conclusions can be reached within the framework of ESM discussed earlier.^{24,44} In multistep reactions, the Brønsted-Evans-Polanyi relationships can be combined with scaling relationships to devise a microkinetic model. This way of constructing volcano relationships was later validated through comparisons of calculated and experimental data for ORR activity of various transition metals and their alloys.¹³⁵ Moreover, these volcano relationships were found to be similar to the much simpler “thermodynamic” volcanos based solely on the reaction energies of various elementary steps without taking kinetic barriers into account.

Occasionally, thermodynamic volcanos are also sufficient to analyze catalytic selectivity. Indeed, competing reaction pathways often exhibit different volcano relationships. Catalysts that fall closer to the peak of a particular volcano will be more selective towards the respective reaction. This approach was used to discover Pt-Hg¹³⁶ and later Ag-Hg and Pd-Hg catalysts¹³⁷ for selective electrochemical O₂ reduction to H₂O₂. Nevertheless, precise microkinetic models are indispensable in the reliable evaluations of catalytic selectivity in this reaction, since the selectivity may be extremely sensitive to the energy profile of the reaction.¹³⁵ For example, in the study of volcano relationships and the selectivity of CO reduction on transition metals, a BEP

microkinetic model containing ~100 elementary steps was employed¹³⁸. In addition, a microkinetic model with more than 50 steps was used in a joint computational and experimental study aiming to optimize the composition of Cu-Co alloys for higher selectivity of CO reduction to alcohols.¹³⁹ Such studies are not only time consuming, they also critically depend on the accuracy of the chosen exchange-correlation functional. To avoid such complications, the volcano relationship of the catalytic activity and selectivity on the binding energies of various species could be inferred from chemical intuition. For instance, this approach was used to discover Ni-Zn catalysts for selective hydrogenation of acetylene to ethylene without further hydrogenation to ethane.¹⁴⁰ Later Au-Ni catalysts were proposed for this reaction, since they are located close to the peak of the volcano for acetylene hydrogenation.¹⁴¹ At the same time, Au-Ni alloys were found to exhibit low ethylene binding energy, which prevents further hydrogenation.

Another recognized limitation of volcano relationships comes from the often neglected dependency of binding energies on the surface coverage of the considered or co-adsorbed species.^{133,135} Even in the simplest case of HER, the effect of H coverage on H binding energies and, hence, on the reaction kinetics may be significant.¹⁰⁶ However, the importance of such interactions depends on the reaction. For example, these interactions do not seem to be crucial in formaldehyde synthesis from methanol.¹³² However, in the case of CO methanation, coadsorption interactions between key intermediates may change the reaction rate by several orders of magnitude but only when the catalysts become densely covered during the reaction.¹⁴² In addition, such interactions may cause the volcano relationship to be less steep, although they did not change the position of the volcano peak. In contrast, the presence of co-adsorbed CO during CO₂ reduction affects the binding energies of H as well as other intermediates, thereby changing the optimal catalyst for HER and CO₂RR.¹²⁵

Moreover, most electrochemical reactions occur in water, which may affect the binding energies of various species to the catalyst. For example, the energies of various intermediates in electrochemical N_2 reduction were deliberately shifted by up to 0.2 eV to account for the formation of H-bonds with surrounding water.¹³⁰ Even larger corrections were suggested for the energies of OH^* and OOH^* intermediates in OER or ORR.⁹⁸

As reported above, volcano plots are able to depict the full thermodynamic scenario involved in a catalytic cycle only the reactants, intermediates and products of the reaction are considered. On the other hand, in homogeneous catalysis, it is customary to describe catalytic activity based on an analysis of transition states. For this reason, although linear scaling relationships are well established in homogeneous catalysis,^{143–145} volcano plots for homogeneous catalysts were not reported until a few years ago. However, using cross-coupling as a model reaction (see Figure 20), Corminboeuf et al. showed that volcano plots can be useful in helping to identify thermodynamically good catalysts in homogenous reactions.^{146,147}

Figure 20. The reaction mechanism for the Suzuki cross-coupling of olefins. Reproduced with permission from Ref. 147.

They screened thirty-six potential systems consisting of various metals, including Ni, Pd, Pt, Cu, Ag, Au, and various ligands, including CO, NH₃, PMe₃, acetone, and a N-heterocyclic carbene. From the linear scaling relationships between the different species involved in the reaction, the energy of each intermediate was correlated with the energy of intermediate **3** (see Figure 20), chosen as the descriptor intermediate. A volcano relationship between the free energy of the “potential determining step”, ΔG_{pds} , as determined by Eq. 10, and the free energy of the descriptor intermediate relative to the reactants, ΔG (**3**), was then constructed.

$$\Delta G_{pds} = \max[\Delta G(A), \Delta G(B), \Delta G(C), \Delta G(D), \Delta G(E), \Delta G(F)]$$

(Eq. 10)

where $\Delta G(X)$ is the free energy of the X reaction step along the catalytic cycle. The obtained plot (Figure 21) allowed them to identify the potential determining steps in the catalytic cycle, namely reactions A, E and F.

Figure 21. Volcano plot illustrating the thermodynamic scenario of the cross-coupling reaction. Adapted with permission from Ref. 147.

Catalysts leading to a very stable intermediate **3** in zone **I** of Figure 21 (strong binding in heterogeneous catalysis) undergo difficult reductive elimination (F); catalysts destabilizing intermediate **3** in zone **III** of Figure 21 (weak binding in heterogeneous catalysis) make the oxidative addition (A) potentially problematic. Finally, catalysts falling between in zone **II** of Figure 21 have the most appealing thermodynamic profile. Ni, Pd and Pt were found to be better

catalysts in this reaction than Ag and Au, which performed poorly during the OA step, in agreement with experimental observations. Moreover, the ligand effect is easily recognized and the results of ligand mixing or exchange can be predicted. For instance, it is clear that substitution of one NH_3 with one CO in Ni catalysts (Figure 21, green points) can shift the catalyst to the central region, which improves the thermodynamic scenario.

This kind of volcano plot can easily help to screen potentially promising catalysts. For instance, it would be enough to calculate the energy of intermediate **3** relative to the reactants to predict the potential step that governs the activity of the newly screened catalysts. Once the energy of the species involved in the determining steps is calculated, the catalyst can be classified as promising or not.

Wodrich et al.¹⁴⁸ extended this approach to predicting the kinetic profiles of homogeneous catalysts using kinetic volcano plots. They investigated the hydroformylation of ethylene and explored 32 catalysts with different metal (Fe, Ru, Os, Co, Rh, Ir, Ni, Pt) or ligand (PH_3 , PMe_3 , PPh_3 , PCy_3) combinations.¹⁴⁸

Figure 22. Mechanism for the hydroformylation of ethylene. Reproduced with permission from Ref.149.

Scaling relationships describing the relative free energy of each catalytic cycle relative to the stability of a chosen intermediate as the descriptor, in this case intermediate **5** in Figure 22, were used to build a thermodynamic volcano plot ($-\Delta G_{pds}$ vs ΔG (**5**) as described above). In addition, the linear correlation between the energy of intermediate **5** and all transition states occurring in the catalytic cycle allowed them to build a kinetic volcano plot as well, where the y-axis is defined as the free energy of the kinetic determining step, $\Delta G_{kds}^\ddagger$ (see Eq. 11):

$$\Delta G_{kds}^{\ddagger} = \max[\Delta G^{\ddagger}(3 \rightarrow TS_{3,4}), \Delta G^{\ddagger}(5 \rightarrow TS_{5,6}), \Delta G^{\ddagger}(6 \rightarrow TS_{6,7}), \Delta G^{\ddagger}(7 \rightarrow TS_{7,2})]$$

(Eq. 11)

Analysis of the two plots in Figure 23 quickly allowed to identify the catalysts that will perform poorly. From a thermodynamic point of view, systems forming too stable intermediates (very negative ΔG (5) in Figure 23a) can have difficulty releasing the aldehyde product (step 7 to 2) or inserting the olefin into the M-H bond to form an alkyl group (step 3 to 4). Similarly, the catalysts that destabilize the intermediates (very positive ΔG (5) in Figure 23a) will perform poorly due to difficulties in CO coordination (step 4 to 5). From a kinetic perspective, the plot in Figure 23b highlights olefin hydrogenation (step 3 to 4) and oxidative addition of H₂ (step 6 to 7) as important to the reaction kinetics (very negative $-\Delta G_{pds}$ in Figure 23b). The systems closer to the top of both volcano plots, i.e., those with good thermodynamic and kinetic profiles, clearly involve metals from group 9, while metals from groups 8 and 10 appear to perform worse.

Figure 23. Volcano plots illustrating a) the thermodynamic scenario and b) the kinetic scenario for the hydroformylation reaction. Adapted with permission from Ref. 149.

Linear scaling relationships derived separately for each ligand showed that the steric hindrance of the ligand affects the last two transition states of the catalytic cycle. The height of the volcano increases with the steric hindrance of the phosphine ligand (see Figure 24),

indicating that the kinetic determining energy barrier decreases when bulkier ligands are involved. This observation allowed the authors to correlate the kinetic determining energy barrier with a steric descriptor, such as the Tolman cone angle, and to estimate the activation barriers of various bulky catalysts without computationally expensive calculations to locate the transition state controlling the kinetics.

Figure 24. Kinetic volcano plots for the hydroformylation reaction separated by ligand type. Adapted with permission from Ref. 149.

5. SUMMARY AND OUTLOOK

Catalysis is a broad discipline historically divided into scarcely communicating subfields. Nevertheless, the fundamental principles of catalysis remain the same, whatever the nature of the specific catalyst under investigation. In this perspective we highlighted particular concepts (the energy span model, the energy decomposition analysis together with the activation strain model, and the volcano relationships) developed mostly within one specific subfield of catalysis, either heterogeneous or homogeneous, and that we think could help to frame and to analyze catalytic

processes in the other subfield. We also highlighted niche applications of these concepts out of the original subfield.

Besides their potential as bridges connecting homogeneous and heterogeneous catalysis, we believe these tools may also serve as useful guides in the engineering of emerging classes of catalysts, such as metal-organic frameworks¹⁴⁹ and size-selected clusters, which can be considered new subfields between homogeneous and heterogeneous catalysis. We believe that the wider application of such tools will push computational catalysis into a leading role in the discovery of new catalysts that address pressing environmental and sustainability concerns.

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