

**EXPLORING DESIGN OPPORTUNITIES OF BIFUNCTIONAL
CATALYSTS USING DENSITY FUNCTIONAL THEORY AND
MICROKINETIC MODELING**

A Thesis

Presented to

the Faculty of the Department of
Chemical and Biomolecular Engineering
University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Chemical Engineering

by

Hieu A. Doan

August 2012

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Abstract

Several examples of catalysts that perform multiple site-specific functionalities under steady-state reaction conditions have been reported in the literature. The most common systems are bifunctional catalysts where each of the two distinct sites catalyzes different reaction steps independently. Using density functional theory and microkinetic modeling as the main computational tools, we want to explore bifunctional catalyst design strategies for reactions where multiple functionalities can improve the overall reaction rate. Our results indicate that there are theoretical limits for the achievable activity improvement and bifunctional catalysts do not necessarily outperform single-site catalysts. More specifically, for CO oxidation on bimetallic systems we found that the overall activity is not significantly altered when bifunctional catalysts are considered, but equally active bifunctional catalysts may be tailored from less active and cheaper components.

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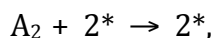
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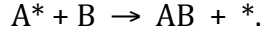
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Chapter I. Introduction

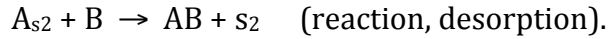
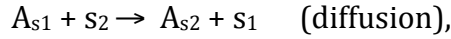
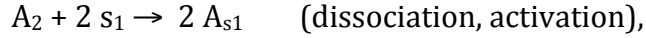
1. Background and Motivation

Advances in density functional theory (DFT) allow us to investigate catalytic reactions at solid surfaces in great detail and reasonable accuracy, while keeping the computational cost at a reasonable level [1]. While chemical accuracy is usually not achieved, DFT calculations have been proven to be extremely useful to study trends in activity and selectivity throughout the periodic table. In a large number of publications, Nørskov and his co-workers have pioneered the use of DFT and descriptor-based microkinetic modeling for computational catalyst design and materials screening (e.g., methanation catalysts) [2–4]. According to the Sabatier principle, interactions between the catalyst and the reactant must be “just right”. If the interaction is too weak, the reactant fails to bind to the catalyst and reaction will not occur. On the other hand, if the bond between the reactant and the catalyst is too strong, it will prevent products from leaving the surface. The importance of the Sabatier principle is best seen in the descriptor-based approach, which results in volcano curves that allows for prediction of the optimal catalyst [5]. The descriptor-based approach is fast, efficient and does not have to rely on expensive DFT calculations [6]. The volcano shape is determined by competing reactions steps and the simplest mechanism with only two competing steps can be schematically written as





In this mechanism, strong binding of A^* leads to a fast dissociative adsorption rate of A_2 , but on the contrary, the second step becomes very difficult if A^* is strongly adsorbed. Hence, a compromise in terms of the binding strength of A^* is necessary to optimize the reaction rates of both steps simultaneously. The schematic Sabatier volcano in Figure 1 suggests that it may possible to increase the reaction rate if we consider an additional diffusion process between the two catalytic sites s_1 and s_2 such as



This is conceptually similar to the frequently reported hydrogen spill-over effect from the metal particle to the catalyst support [7], or the recently published H_2 activation mechanism on a Cu(111) surface doped with isolated Pd atoms [8]. In reality, s_1 or s_2 can be a variety of sites with distinguishable properties. A transition metal nanoparticle has terrace, step and corner sites in close proximity and also interacts with the support material. If the metal particle is composed of an alloy of two or more metals, different catalytic sites exist even on the same crystalline surface facet. We define a bifunctional mechanism as the interplay of two different sites each of which catalyzes one or more elementary steps at steady state reaction conditions and call such system a bifunctional catalyst.

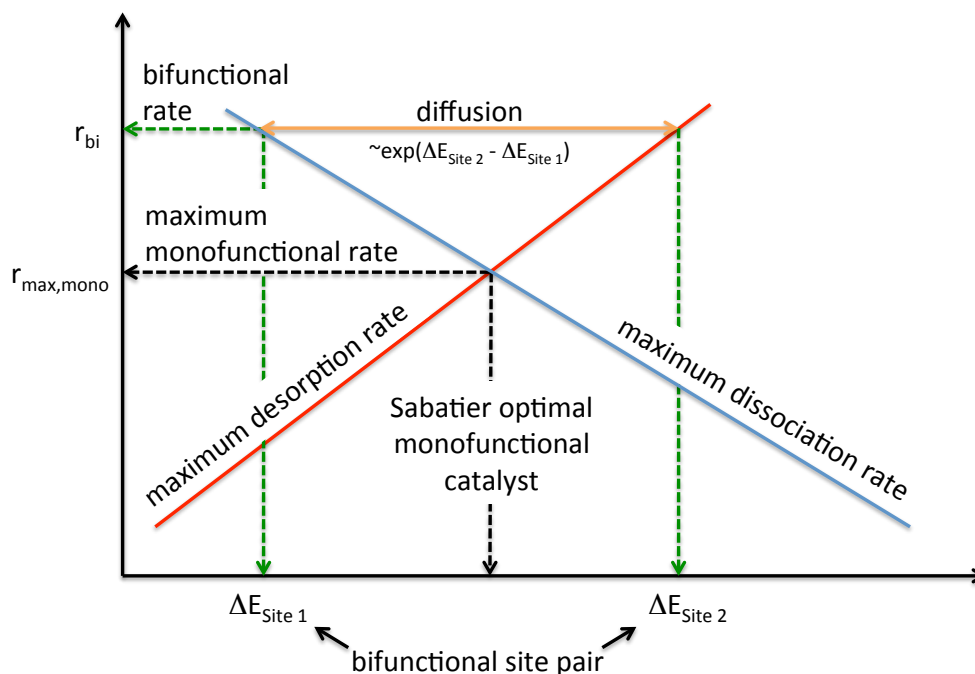


Figure 1 Sabatier volcano with improved bifunctional reactivity.

There have been several studies claiming that measured improvements in catalytic activity can be explained in terms of bifunctional catalyst surfaces for reactions such as preferential CO oxidation (PROX), water-gas-shift (WGS) and hydrogen production [9–11]. An illustration of a bifunctional mechanism is depicted in Figure 2, where CO preferentially adsorbs on the Pt/Mordenite (M) catalyst, O₂ completely poisons the Fe/M catalyst, and the Pt-Fe/M bimetallic system greatly enhances activity and selectivity of PROX by providing independent adsorption sites for both reactants. The goal of this thesis is to explore the feasibility of different bifunctional catalyst designs and suggest types of reactions where multiple functionalities can improve the overall reaction rate. Once this is achieved, we would be able to systematically create more active, selective and affordable

catalysts that could potentially revolutionize the way chemicals and energy are produced.

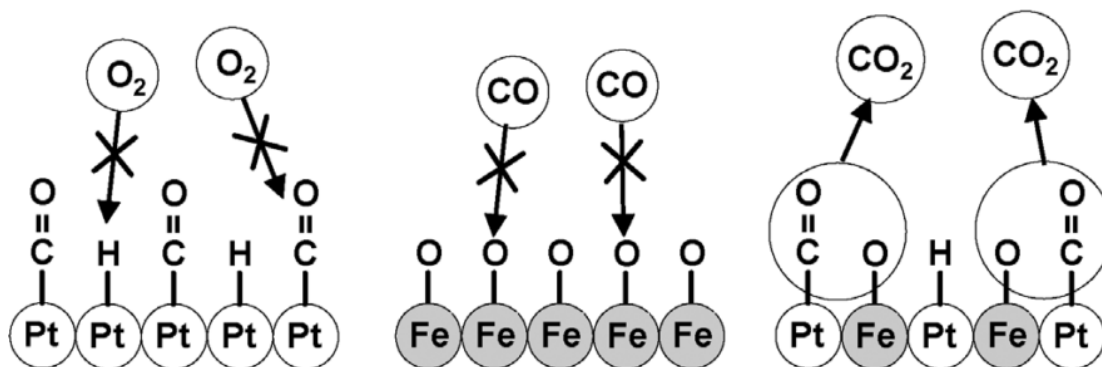


Figure 2 Bifunctional PROX mechanism on Pt/M, Fe/M and Pt-Fe/M (Adapted from Ref. [9]).

2. CO oxidation as a prototypical reaction

In recent years, our understanding of CO oxidation as a prototypical catalyst for heterogeneous processes has led to enormous progress in fundamental insight into catalysis. CO oxidation is one of the best-known heterogeneous reactions and can thus be considered the benchmark reaction for evaluations of heterogeneous catalysts [12]. Despite much effort that has been put into studies of this seemingly simple reaction, not all of its facets have been explored nor the complete picture of this process has been obtained; many interesting phenomena regarding CO oxidation have caused controversies that are still discussed today (e.g., kinetic oscillation in the critical run-way episode of reactors, active phase for RuO₂). A fundamental advantage of CO oxidation as the probe reaction is that it has a single rate determining step (O₂ activation) and a weakly bound product (CO₂), which makes the measurement and the interpretation of reaction data a simple task.

Furthermore, the fact that the reaction can occur over 13 orders of magnitude of pressures allows the study of catalyst to be performed over a wide range of reaction conditions. It is also possible to extend the use of CO oxidation to probe dynamics of other chemical reactions with the readily available experimental studies and fairly mature theoretical picture of the course of CO oxidation. Therefore, CO oxidation is chosen as the model reaction to evaluate performance of bifunctional catalysts.

3. Thesis outline

The theoretical background of DFT calculations is briefly summarized in Chapter II. In Chapter III, I will discuss the concept of scaling relations and descriptor-based catalyst design followed by their applications in microkinetic modeling in Chapter IV. Chapter V explains the role of the active site in nano-particle catalysts based on study of Au/TiO₂ poisoned by NaBr. Chapter VI covers theoretical investigations of bifunctional catalysts from model design to activity evaluation. Finally, Chapter VII summarizes this thesis and gives some thoughts on future research.

Chapter II. Density Functional Theory

1. Background

Density functional theory has been the electronic structure calculation method of choice to study a wide range of solid-state systems over the past five decades. Its successful applications in heterogeneous catalysis, rational catalyst design, metallurgy, and material science have been well established. This chapter will cover the most important aspects of DFT, and I refer the interested reader to a number of good textbooks [13] and reviews [14,15] on this method. All the calculations in this thesis are performed using the freely available Grid-based Projector Augmented Wave DFT code GPAW [16,17] and the Atomic Simulation Environment (ASE) [18].

1.1 The Schrödinger equation

In quantum mechanics, the solution to the Schrödinger equation contains all information regarding the total energy and other properties of a system. For a body of N interacting electrons, the time-independent Schrödinger equation is

$$\hat{H}\Psi = E\Psi, \quad (1)$$

where E is the total electronic energy of the system and $\Psi = \Psi(r_1, r_2, \dots, r_N)$ is the wavefunction which depends on spatial coordinates r_i of all N electrons. According to Born-Oppenheimer approximation, which is based on the large mass difference between electrons and nuclei, the motion of electrons can be decoupled from that of nuclei and electrons are assumed to be moving in a static external potential[19].

The Hamiltonian $\hat{H}$ is then written as

$$\hat{H} = \sum_{i=1}^N \left(-\frac{1}{2} \Delta_i^2 \right) + \sum_{i=1}^N v(r_i) + \sum_{i < j}^N \frac{1}{|r_i - r_j|} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee}, \quad (2)$$

where the first summation is a kinetic operator, the second term is the external potential action on the electrons (if the external potential is absent, this term equals the attractive forces between nuclei and electrons), and the last term accounts for electron-electron interactions.

1.2 The Hohenberg-Kohn theorems

It is possible to obtain a precise solution for equation (2) using different wavefunction methods, given that a small number of electrons and nuclei are considered. However, the task becomes computationally very demanding for extended systems of heterogeneous catalysis. In 1964, a breakthrough achieved by Hohenberg and Kohn [20] provided the very basis of DFT, which reduces the problem of N interacting electrons with $3N$ degrees of freedom to only three degrees of freedom. They showed that there is a one-to-one correspondence between the ground state energy and the ground state electron density; therefore the total energy can be expressed as a function of the electron density, ρ , as follows

$$E[\rho] = \langle \Psi[\rho] | H | \Psi[\rho] \rangle. \quad (3)$$

However, equation (3) does not say anything about the form of the functional dependence of the energy on density; it only tells us that such a functional exists.

1.3 The Kohn-Sham equations

In 1965, Kohn and Sham [21] presented a scheme to map a many-body problem of a system of interacting particles located in an external potential, onto a system of non-interacting single electron states, $\phi_i(r)$, in an effective potential, with

the same ground state density. According to Kohn and Sham (KS), the exact ground-state electronic energy as a functional of electron density can be written as

$$E[\rho] = E_{kin}^{non}[\rho] + E_{pot}^{int}[\rho], \quad (4)$$

where $E_{kin}^{non}[\rho]$ is the kinetic energy of the non-interacting system and $E_{pot}^{int}[\rho]$ is the potential energy of the interacting system. This is shown in the following equation,

$$E_{pot}^{int}[\rho] = E_{ext}[\rho] + E_H[\rho] + E_{xc}[\rho], \quad (5)$$

where the first term is the external potential, the second term is the classical Hatree energy, and the last one is the exchange correlation that contains all quantum mechanical effects. The estimation of exchange-correlation energy is the main challenge of DFT and if it is precisely calculated, DFT is an exact method.

The kinetic energy of the non-interacting electron system is

$$E_{kin}^{non}[\rho] = \sum_i^N \int \varphi_i^*(r) \nabla^2 \varphi_i(r) dr, \quad (6)$$

where $\varphi_i(r)$ is the KS-orbital that can be obtained from solving the single-electron KS equations

$$\left\{ -\frac{1}{2} \nabla^2 + v_{eff}(r) \right\} \varphi_i = \varepsilon_i \varphi_i. \quad (7)$$

In equation (7), ε_i is the KS orbital energy corresponding to the KS orbital φ_i . The effective potential is given by

$$v_{eff}(r) = v_{ext}(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}(r). \quad (8)$$

The exchange-correlation potential $v_{xc}(r)$ is the functional derivative of the exchange-correlation energy $E_{xc}[\rho(r)]$ as follows

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)}. \quad (9)$$

In order to solve KS equations, we start out with an initial guess of electron density and estimate the effective potential by approximating a form for the functional dependence E_{xc} . The KS equations are then solved and we obtain the KS orbitals, which can be used to calculate the density as followed

$$\rho(r) = \sum_{i=1}^N |\varphi_i(r)|^2. \quad (10)$$

If the density is the same as initial guess within a given threshold, the calculation is converged and the total energy can be computed using equations (4), (5), and (6). Otherwise, a new density obtained by density mixing and is used in equation (8) to obtain the effective potential again and the procedure is reiterated until the density is converged. The overall DFT strategy for calculating electronic properties is illustrated in Figure 3.

1.4 The exchange-correlation functional, basis sets and k-point sampling

As mentioned earlier, the exchange-correlation functional poses the greatest challenge for DFT calculation. It is impossible to evaluate E_{xc} exactly and several empirical and semi-empirical functionals with different strength and weaknesses have been proposed. The most commonly used approximations in solid-state physics are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). In this thesis, I use GGA based on the revised Perdew-Burke-Ernzerhof (RPBE) functional [22], which has shown good description of the energetics for adsorbed species on surfaces.

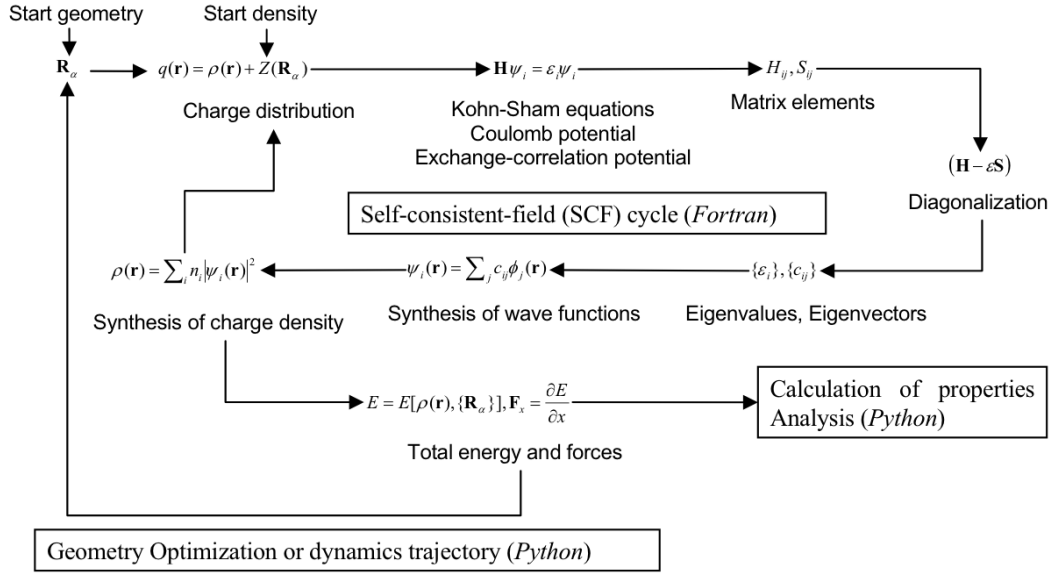


Figure 3 Schematic diagram of key steps during a density functional theory calculation.

Adsorption on extended metal surfaces is best described with 2-D periodic, semi-infinite surface slabs, but it is a very popular approach to expand wave-functions into plane wave basis set, which in turn requires periodicity in all 3 dimensions. Thus, when plane waves are used, surfaces are created by introducing a sufficiently large vacuum space between any successive surface slabs. The wavefunction for such periodic systems can be expanded using Bloch's theorem

$$\psi_i(r) = \sum_j c_{i,j} \phi_j(r) = \sum_G c_{i,k+G} e^{i(k+G)r}, \quad (11)$$

where $c_{i,k+G}$ is the expansion coefficients, k is a wave vector limited to the 1st Brillouin zone and the reciprocal lattice vector G . For large kinetic energies $|k+G|^2$, the coefficients $c_{i,k+G}$ approach zero and, therefore, a finite number of plane waves is sufficient to evaluate the wavefunction and the total energy.

In this thesis, we use an alternative approach where the wave function is represented numerically on a finite grid instead of being expanded into basis set

functions. One of the main advantages of this representation is the increased flexibility when choosing the periodic boundary conditions and it is possible to simulate a true 2-D periodic, semi-infinite slab. The accuracy of the grid based wave function representation is controlled by the number of grid points or grid point spacing, which was chosen to be 0.18 Å in this thesis. This spacing has been tested extensively and yields the best compromise between numerical accuracy and memory requirements during the calculation.

Once the eigenvalues (KS orbitals) $\varepsilon_n(k)$ are calculated from KS equations, the total energy can be obtained by integration of all occupied states over the 1st Brillouin zone. In practice, this integration is approximated by a summation over selected k-points with weight ω_i

$$E \approx \sum_i \sum_{n \in OCC} \omega_i \varepsilon_n(k_i). \quad (12)$$

The KS equations must be solved for each k-point independently, which allows for efficient parallelization of the code. Since dense k-point sets improve the accuracy while increasing the computational cost at the same time, an optimal k-point must find a balance between the two. Popular schemes for finding k-points have been proposed by Chadi-Cohen [23] and Monkhorst-Pack [24], which generate special k-point sets with good estimates for the total energy at reasonable computational cost. All calculations in this thesis have been performed with a (4x4x1) Monkhorst-Pack k-point scheme.

2. Lattice Constant Calculations

Lattice constants of all tested bifunctional catalysts in this thesis are calculated by the following procedure:

- Construct $L1_0$ bulk structure using ASE interface.
- Calculate the electronic energy for a range of lattice constants.
- Fit the energy into the expression below and identify the lattice constants where energy is at minimum.

$$p_0 + p_1a + p_2c + p_3a^2 + p_4ac + p_5c^2 \quad (13)$$

Here, p_n are the coefficients and a, c are the lattice constants in the $L1_0$ crystal structure. The GPAW set-ups are the same for all calculations, where I use a Monkhorst-Pack k-point set of $11 \times 11 \times 11$, RPBE for exchange-correlation functional, and the number of grid points in x, y , and z are 24, 24 and 24. These numbers of grid points are equivalent to a grid spacing of approximately 0.18 Angstroms in all directions; however, lattice constant variations can cause the number of grid points to change when grid spacing is held constant, with the consequence that artificial energy jumps can be encountered. Hence, we used a fixed number of grid points instead of constant grid spacing for consistent results.

3. Surface Adsorption Calculations

Adsorption geometries and energies are calculated by first creating a surface facet of interest in ASE. Gold surfaces that will be discussed later in chapter 3 are modeled as slabs with a (2×2) unit cell for the close-packed fcc(111), a (2×1) unit cell for the stepped fcc(211), and a (1×1) unit cell for the kinked fcc(532) surface. All bimetallic surfaces are cut along the (111) direction of the $L1_0$ crystal structure and are further simply referred to as fcc(111) because of the close similarity of both surfaces, and the fact that they coincide when monometallic systems are considered. We chose a (2×2) surface unit cell, corresponding to a nominal coverage of $\frac{1}{4}$ ML,

and a vacuum region of 12 Angstroms for Au and 7 Angstroms for the bimetallic L1₀ systems separates the surface from the simulation box boundary along the normal direction to the surface. The fcc(111) surfaces are constructed as four-layer slabs where the top two layers are allowed to relax, while the bottom two were fixed in the bulk position. The Au(211) and Au(532) surfaces are modeled with an equivalent thickness and constraints as the fcc(111) surface. Electron densities and wavefunctions are represented on real-space grids with grid spacing of 0.18 Angstroms in all directions of the unit cell. The RPBE functional is used to describe exchange and correlation, and the Brillouin zone is sampled using a 4x4x1 Monkhorst-Pack k-point set. The Kohn-Sham states are populated using a Fermi-Dirac distribution with $k_bT = 0.1$ eV [25], and total energies are then extrapolated to $k_bT = 0$ eV. The adsorption (binding) energy E_b is calculated using the following equation

$$E_b = E_{ads+slab} - E_{slab} - E_{gas}, \quad (14)$$

where E_{slab} is the total energy of the slab, $E_{ads+slab}$ is the total energy of the slab with adsorbate and E_{gas} is the gas phase reference energy of adsorbed species. With this definition, a negative E_b indicates exothermic adsorption.

4. The Climbing Image Nudged Elastic Band (CI-NEB) Method

The Nudged Elastic Band (NEB) method is a state-of-the-art method for locating transition states on complex potential energy surfaces and is currently the most frequently used method for calculating activation energy barriers [26]. In order to locate the transition state, the NEB method searches for the minimum

energy path (MEP) that connects the initial state to the final state. The maximum on the MEP is a saddle point on the potential energy surface and corresponds to the transition state (TS) of the process. In a NEB calculation, the MEP is found by constructing a chain of images of the system between the initial and final state. Then, a spring interaction between adjacent images is added to ensure the continuity of the path. Finally, the band is optimized and brought to the MEP by minimizing the forces acting on the images after projecting out the force components acting out parallel to the reaction path. The CI-NEB is a small modification to the original NEB as the image with the highest energy is moved up along the potential energy surface to the top of the MEP (Figure 4). Once the calculation is converged, the climbing image corresponds to the TS image and its total energy can be used to find the activation energy barrier. In order to confirm that the TS image is a true saddle point, a frequency analysis based on the harmonic oscillator approximation is performed and only when a single imaginary vibrational mode along the reaction coordinate is found, the transition state search was completed successfully.

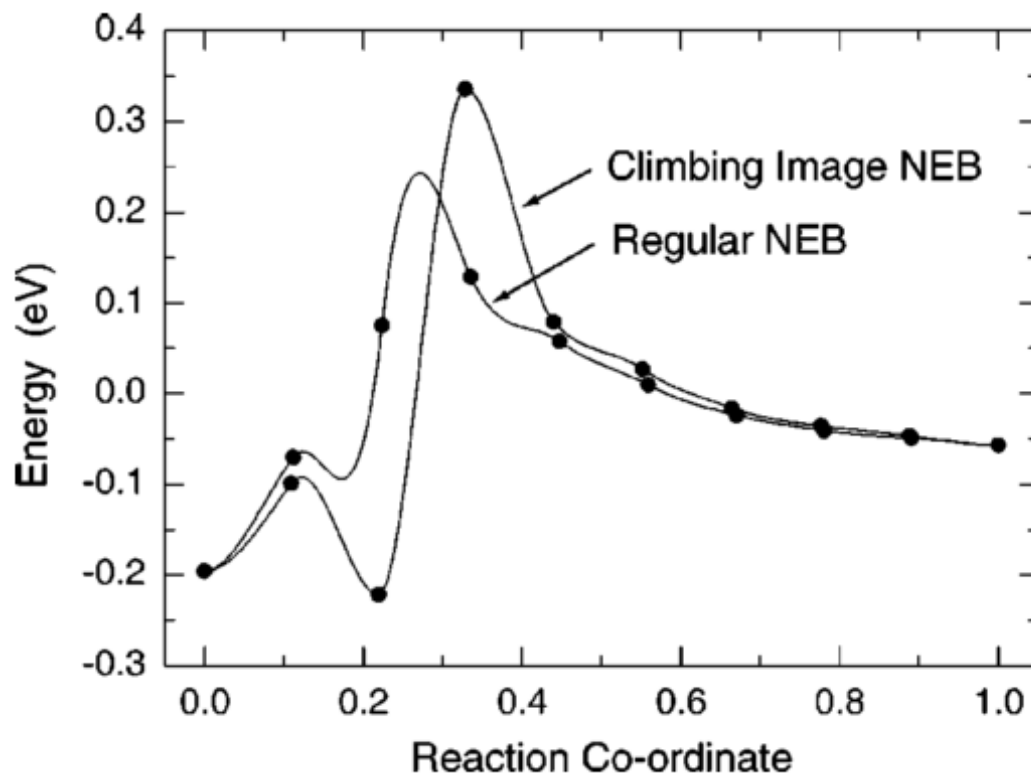


Figure 4 DFT calculations of the minimum energy path using NEB and CI-NEB for CH_4 dissociative adsorption on a Ir(111) surface (Adapted from Ref. [26]).

CHAPTER III. Scaling Relations and Volcano Curves

1. Scaling Relations for Surface Intermediates

The binding energy indicates how strongly a species is adsorbed to a surface; therefore, in the simplest sense it must depend on the strength of the bond formation between the adsorbate and the metal surface. If we assume that the bond strength is only function of the number and the type of bonds formed between the adsorbate and the surface, it is possible to extrapolate the binding energy of an atom or molecule from that of a chemically similar one (e.g., CH and CH₂, CH₃). Indeed, it has been shown that such a scaling relationship does exist and allows us to predict adsorption energies within a family of similar adsorbates [27–29]. This relationship is often expressed by the following linear equation

$$E_{ads2} = \alpha E_{ads1} + \beta, \quad (15)$$

where E_{ads} 's are the binding energy, α and β are the slope and y-intercept respectively. For hydrogen containing adsorbates AH_x, scaling slope β in equation (15) can be predicted by

$$\beta(x) = \frac{x_{max}-x}{x_{max}}, \quad (16)$$

where x_{max} is the maximum number atoms that can bind to the central atom A. For example, C can make a total of 4 bonds to the surface, or $x_{C,max}=4$, then the slope of CH₂ will be equal 0.5 with respect to C. In our microkinetic model, which will be mentioned in the next chapter, the binding energy of O₂ is scaled from that of atomic O using the relationship in Figure 5 [29].

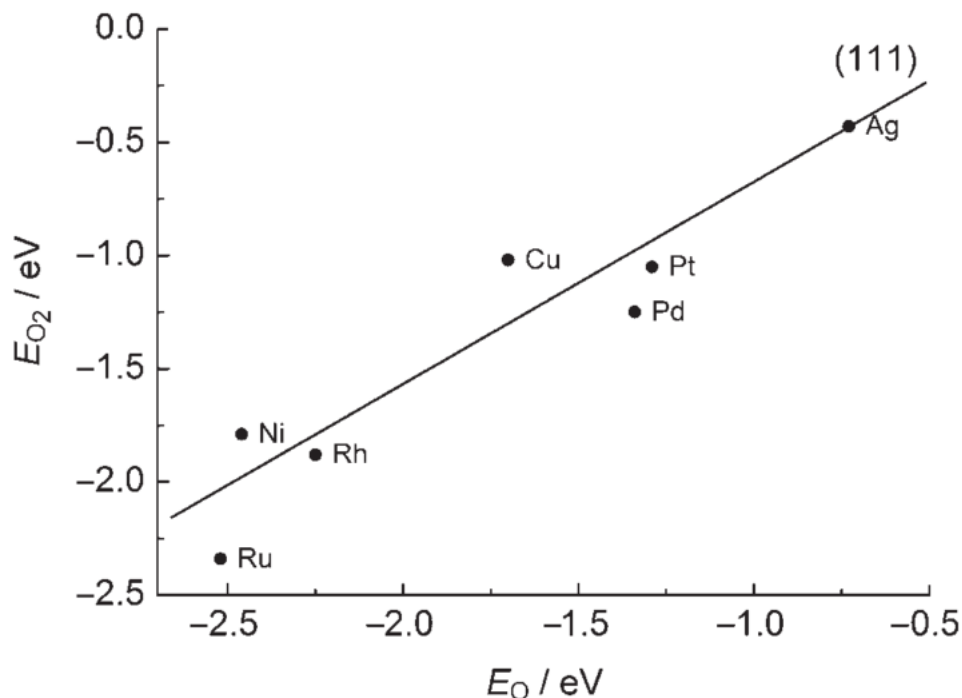


Figure 5 The scaling of adsorption energies between O and O₂ for different fcc(111) surfaces.
 $E_{O_2} = 0.89 \cdot E_O + 0.17$ eV (Adapted from Ref. [29]).

2. Scaling Relations for Transition States

Although a transition state is considered special along the reaction coordinate, it is not much more than an adsorbed molecule in certain geometry and a very short lifetime. Therefore, the stability of transition states also scales with adsorption energies of similar surface species. The two most popular types of linear relationships regarding this concept are transition state scaling (TSS) and Brønsted- Evans-Polanyi (BEP) relations. These relationships, in most case, have the same information content and are identical concepts with different names. In TSS, transition state energy is scaled from the initial state energy E_{IS} or final state energy E_{FS} as in equation (17), whereas in a BEP relation, the activation barrier is a linear

function of the energy difference between final and initial states (heat of reaction) as in equation (18):

$$E^{TSS} = \gamma^{TSS} E_{IS/FS} + \zeta^{TSS} \quad (17)$$

$$E^{BEP} = \gamma^{BEP} (E_{FS} - E_{IS}) + \zeta^{BEP}. \quad (18)$$

Both relationships are very useful because they allow us to calculate activation barriers for various catalytic processes by knowing only the adsorption energies of reactants and/or products. In this thesis, the BEP relationships for CO oxidation and O₂ dissociation in monofunctional case are derived from the TSS relationships in reference [29].

3. Theoretical Volcano Curves

The existence of scaling relationships for surface intermediates and transition states makes it possible to quickly evaluate catalyst performance across transition metals for various chemical processes without the need of a full set of DFT-derived energy parameters. In fact, the ability to predict catalytic activity based on the knowledge of only a few key energy descriptors is often termed descriptor-based catalyst design approach. Descriptors are energy parameters relevant to the chemical reactions under investigation (e.g., binding energy, dissociation energy) and can be quickly calculated for a large number of materials. In the optimal cases, only one or two descriptors should be required for catalyst screening, and the plot of reaction rate as a function of descriptor(s) is called a theoretical volcano curve. Figure 6 shows the relationship between the calculated rate of methanation and the adsorption energies in the form of a volcano curve [2]. From this figure, we could

easily identify the best catalyst as the one at the top of the volcano. This powerful catalyst evaluation approach will be applied to bifunctional cases throughout this thesis.

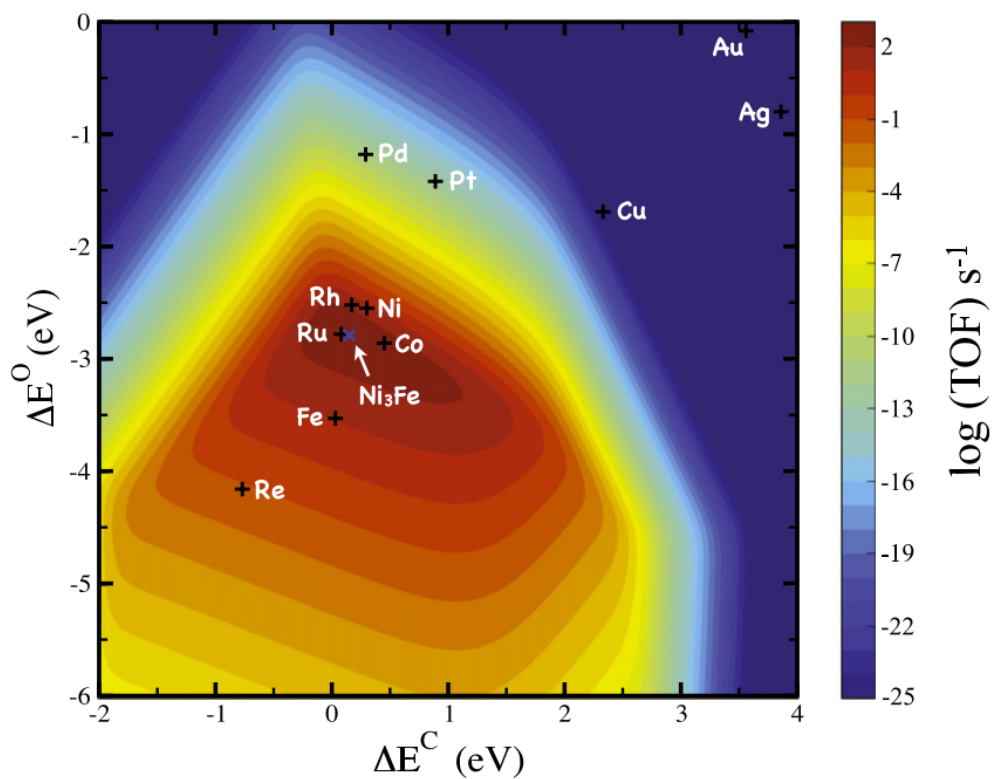


Figure 6 Volcano curve for the production of methane from CO and H₂ (Adapted from Ref. [2]).

CHAPTER IV. Microkinetic Modeling

The primary purpose of microkinetic modeling in this thesis is to evaluate catalyst performance by calculating the turnover frequency (TOF) of reactions from energetic parameters derived from DFT or estimated from scaling relationships. Results from microkinetic modeling, such as the aforementioned theoretical volcano curve, are essential in catalyst design. This chapter will explain the most basic and important aspects of this method. Additional details of first-principle based microkinetic modeling can be found in papers by Gokhale *et al.* [30], Stoltze & Nørkov [31], and the standard reference “The Microkinetics of Heterogeneous Catalysis” by Dumesic *et al.* [32].

1. Background

A microkinetic model is based on a sequence of elementary steps in a catalytic cycle. Microkinetic models are typically based on the mean-field approximation and often neglect effects of surface coverage and lateral interactions. Therefore, microkinetic modeling does not work well in certain cases such as:

- Non-homogeneously covered surface or surface with island formations.
- Surface species don't diffuse quickly enough to maintain random mixing.
- Lateral interactions between adsorbates are dominant.

However, many catalytic processes, especially those performed at high temperatures, do not fall into the above cases, and microkinetic modeling becomes a useful tool for studying surface chemistry, trends in catalyst performance and chemical kinetics for reactor design. In addition, the descriptor-based catalyst

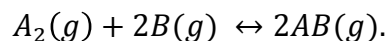
design process is not a quantitative method and only relies on the correct prediction of trends across transition metals. Therefore, the errors introduced by the mean-field approximation on similar catalytic surfaces are typically negligible. Building a microkinetic model requires the following steps:

- a. Propose a reaction mechanism.
- b. Estimate thermodynamics properties of all reactants, products and intermediates. These values could be obtained either from textbooks, database, experiments, or DFT calculations.
- c. Calculate equilibrium constants for each step and ensure that the model is thermodynamically consistent.
- d. Estimate the forward or reverse rate constant for each step using collision theory (adsorption/desorption) or transition state theory (surface reaction).
- e. Solve model for steady state coverages numerically using a mathematical package such as Matlab, Mathematica or in our case, python modules Scipy and Mpmath.
- f. Optionally, one can perform a sensitivity analysis to identify key features that control the performance of catalyst. This step can be the determination of reaction orders, apparent activation energy, degree of rate control, thermodynamic degree of rate control [33], or degree of catalyst control [34].

2. Sabatier Analysis

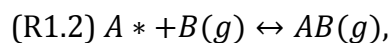
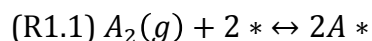
A full microkinetic model can sometimes be very hard to solve over the full range of reactivity descriptors because of the stiffness of the system of ordinary differential equations, which increases dramatically as one moves further away

from the volcano top. Hence, it is desirable to have yet another approximation that is qualitatively the same as the full microkinetic model, but easier to solve. Such method exists and been termed “Sabatier Analysis” [5]. Here, we explain the Sabatier analysis by examining the following simple catalytic process in both monofunctional and bifunctional cases



2.1 Monofunctional Sabatier Analysis

Assume that the reaction proceeds via two elementary steps:



where A_2 , B are gaseous molecules and asterisks represent active sites on the catalyst. The reaction rates for (R1.1) and (R1.2) can be written as:

$$r_1 = k_1 P_{A_2} \theta_*^2 - k_{-1} \theta_A^2 \quad (19)$$

$$r_2 = k_2 \theta_A P_B - k_{-2} P_{AB}. \quad (20)$$

Here, k_i and k_{-i} are the forward and reverse rates of reaction i . θ_s represents the coverage or the fraction of surface covered with species s . P_{A_2} , P_B , and P_{AB} are the partial pressures of A_2 , B and AB . According to equations (19) and (20), the unit of r_i would be in molecules/atoms of products per site per unit of time, or the TOF's of reactions (R1.1) and (R1.2). During the Sabatier analysis, the following assumptions are made:

- All activation barriers are estimated using TSS/BEP relationships.
- Only forward reaction rates are considered.

- Coverages of empty sites and surface species are “optimal” for each elementary step independently.

The second and third assumptions are unphysical but with this definition, the Sabatier analysis presents an exact upper bound to the achievable reaction rate, which has been shown by Bligaard *et al.* [5]. The optimal surface coverages that maximize the forward reactions of (R1.1) and (R1.2) are $\theta^* = 1$ and $\theta_A = 1$, respectively. Hence, equations (19) and (20) are reduced to

$$r_1^{Sab} = k_1 P_{A_2} \quad (21)$$

$$r_2^{Sab} = k_2 P_B. \quad (22)$$

The Sabatier rate is the slower one of the two, or

$$r^{Sab} = \min[r_1^{Sab}, r_2^{Sab}].$$

Since the partial pressures are usually given, the next step is to find the forward rate constants. According to transition state theory [35], the rate constant is given as

$$k = \frac{k_b T}{h} \exp\left(\frac{\Delta S^\ddagger}{k_b}\right) \exp\left(-\frac{E_a}{k_b T}\right), \quad (23)$$

where k_b is the Boltzmann constant, h is the Planck constant, T is the temperature, $\Delta S^\ddagger$ is the change in entropy between the initial and transition state, and E_a is the activation energy barrier. In order to calculate $\Delta S^\ddagger$, both initial and transition state entropy must be known. For reaction (R1.1), $S_i = S_{A_2}(g)$ and $S^\ddagger$ can be calculated by accounting for translation, rotation and all vibrational modes of the transition state. Since the goal of the Sabatier analysis is not finding quantitative reaction rates, but rather the trends, it can be assumed that the transition state has the geometry of an

adsorbed species, and the entropy of an adsorbate is so much smaller than the entropy of a gas molecule, such that

$$\Delta S_1^\ddagger = S_1^\ddagger - S_{A_2(g)} \approx -S_{A_2(g)}. \quad (23)$$

Similarly, the entropy change of transition state in reaction (R2) is

$$\Delta S_2^\ddagger = S_2^\ddagger - S_{B(g)} \approx -S_{B(g)}. \quad (24)$$

The activation energies are estimated using BEP relationships:

$$\Delta E_{a1} = \alpha_1 \Delta E_1 + \beta_1, \quad (25)$$

$$\Delta E_{a2} = \alpha_2 \Delta E_1 + \beta_2, \quad (26)$$

where ΔE_1 is the change in energy of the reaction (R1.1) or the dissociation energy of A_2 . This energy is chosen to be our descriptor with which both activation barriers scale. For dissociative adsorption of N_2 , NO , CO and O_2 on a number of transition metal surfaces, a BEP relationship has been established with $\alpha=0.87$ and $\beta=1.34$ [36]. Hence, we will use these values for α_1 and β_1 in equation 25. In equation 26, α_2 should be negative, such that the stronger A bonds to the surface, the higher the activation energy for the desorption process. We choose α_2 and β_2 to be -0.5 and 0.1, arbitrarily. For illustrative purposes, the following parameters are used to calculate the volcano plot in Figure 7: $P_{A_2}=25$ bars, $P_B=75$ bars, $T = 600$ °C, $S_{A_2(g)}=-200$ J/mol/K, $S_{B(g)}=-50$ J/mol/K. From Figure 7, we can clearly see that the Sabatier analysis clearly points to a descriptor value and in turn a material with optimal catalytic activity (where maximum desorption and dissociation rates intersect). We note that only qualitative information can be extracted from a Sabatier analysis, but it has been shown in several examples, that the maximum coincides within a few tenths of an eV with the maximum that is obtained from a full microkinetic model

[5,29]. Therefore it is adequate to use the simplified Sabatier analysis to study trends, but when surface coverages or quantitative information is desired, a full microkinetic model or even a kinetic Monte Carlo simulation may be necessary.

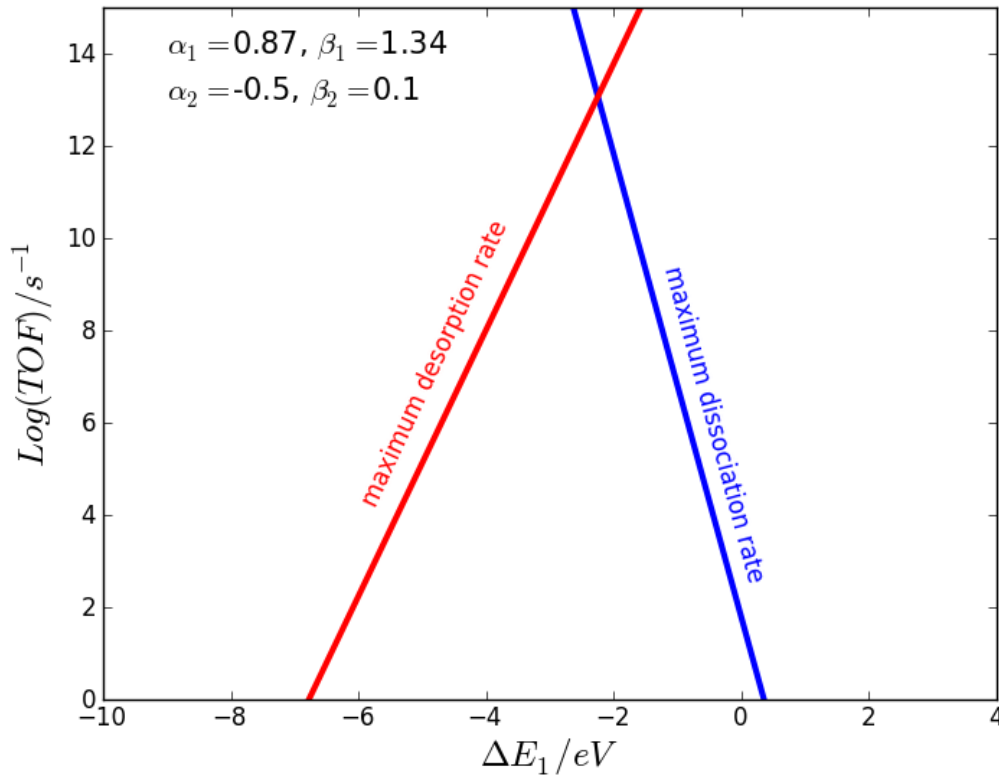
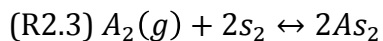
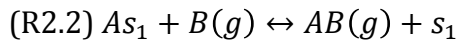
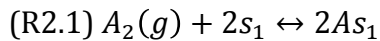
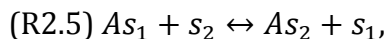
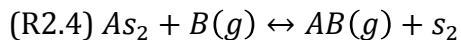


Figure 7 Volcano curve for the reaction $A_2(g) + 2B(g) \leftrightarrow 2AB(g)$ with $\alpha_1=0.87$, $\beta_1=1.34$, $\alpha_2=-0.5$, and $\beta_2=0.1$.

2.2 Bifunctional Sabatier Analysis

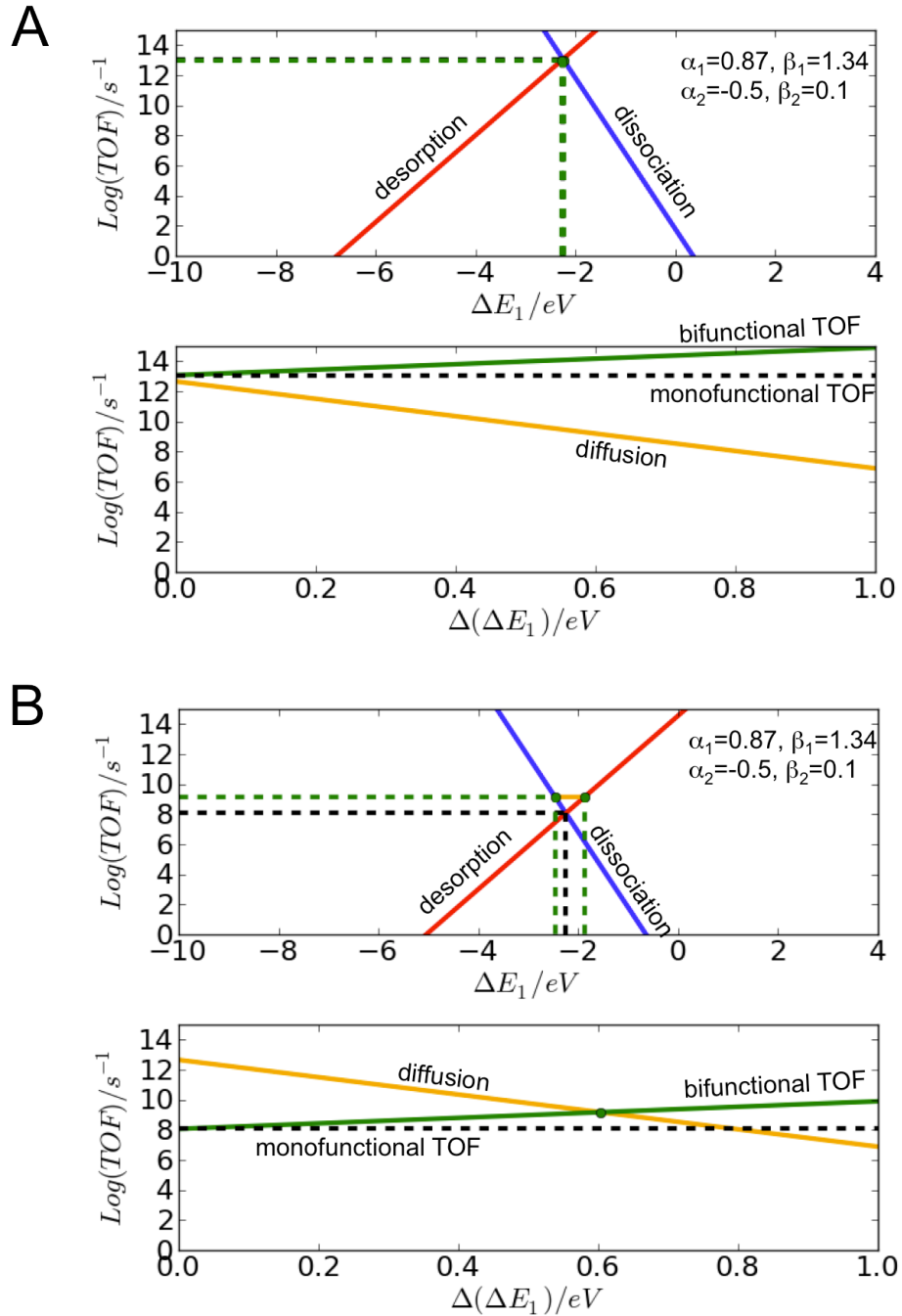
The bifunctional Sabatier analysis is an extension of the monofunctional case where a second type of catalytic site is added and diffusion is allowed. The bifunctional elementary steps are written as:



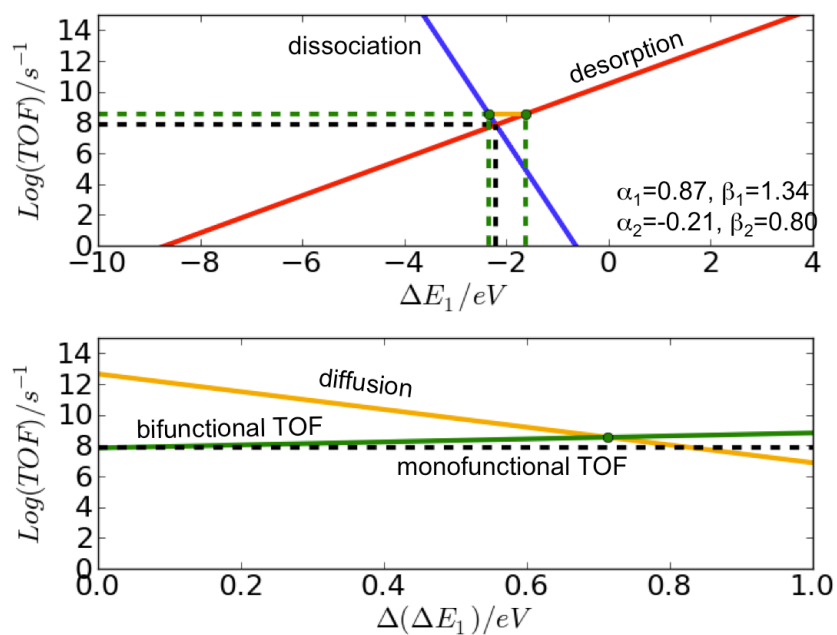


where s_1 and s_2 are two different types of active sites that corresponds two different values of ΔE_1 on the x-axis of the volcano in Figure 7. The kinetic nature of reactions (R2.1) - (R2.4) are essential the same as the monofunctional case and therefore investigated in a similar manner (i.e., using the same assumptions, energetic parameters and BEP relationships). For reaction (R2.5) that represents the diffusion of A between site 1 and site 2, we assume no activation energy barrier in the exothermic direction and activation energy barrier equals heat of reaction when diffusion is endothermic. The optimal coverages for As_1 and s_2 are both equal to 0.5. By investigating different slopes and intercepts in the BEP relationship for desorption (red line), we have identified two scenarios where bifunctionality does not yield any significant improvement (Figure 8, A and C) and two cases where two catalyst sites within a 0.5 eV range result in small improvements (Figure 8, B and D). In case (A), optimal monofunctional rate is equal to the maximum achievable value ($\sim 10^{13}$), hence no improvement is possible by bifunctional catalysts. We change the intercept in case (B) by artificially decreasing pre-exponential factor for adsorption/desorption and observed little improvement over the optimal monofunctional activity. In case (C), we broaden the volcano by decreasing the slope of the red line, and this leads to quickly increasing diffusion barriers. The slope of the red line is increased in case (D). The result is a narrow volcano that allows for more improvement in bifunctional activity. From these results, we conclude that by combining two catalysts on opposite sides of the top of the volcano and allowing

diffusions to occur, it is theoretically possible to create a bifunctional catalyst with higher activity than the optimal monofunctional one. However, as we move further away from the top of the volcano in opposite directions, diffusion becomes the rate-determining factor and limits the bifunctional performance.



C



D

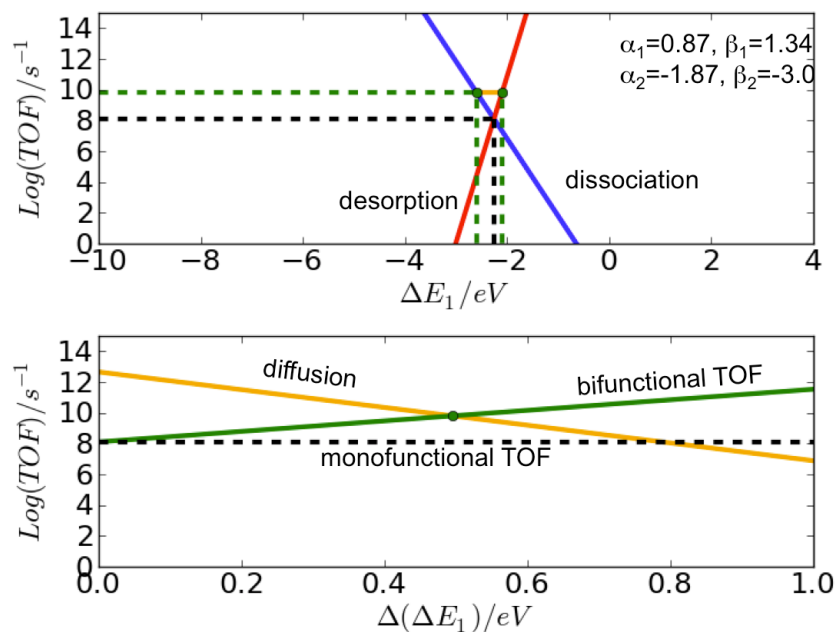


Figure 8 Theoretical limits of bifunctional activity for reaction $A_2(g) + B(g) \rightleftharpoons AB(g)$.

Chapter V. CO oxidation on Au/TiO₂ catalysts: NaBr poisoning and the nature of the active site

1. Introduction

Since it was discovered that supported gold nanoparticles are highly active in catalyzing CO oxidation at ambient temperature [37,38], substantial efforts have been carried out in order to understand the origin of Au catalysts' performance. Although many studies and computation models have shed light into this topic, they generally fail to reach a consensus on key issues such as the nature of active sites on Au nanoparticles [39]. For CO oxidation, it is generally accepted that the most important elementary step is oxygen activation on the catalyst surface. In addition, studies from the literature have shown that O₂ activation occurs only a fraction of the interface, probably at the corner or edge sites [40], or the metal-support interface. There are several methods for studying activity and number of sites on a catalyst such as transmission electron microscopy and chemisorption experiment; however, such methods may or may not directly provide the number of active sites on a catalyst surface.

In the experimental part of our collaborative study, we used an intentional poisoning technique to evaluate the number of active sites. The poisoning experiments are carried out by adding a controlled amount of poison, NaBr, to the Au catalyst while monitoring its activity at the same time. We expect that the reduction of catalytic activity as a function of added poison will determine not only the number, but also the distribution of the active sites. Density functional theory

calculations are employed to verify experimental results and provide insights to the poisoning mechanism. The most important findings are reported in the next section. For more detailed information about experimental set-up and procedure, as well as complete discussion on experimental and theoretical results, please refer to our publication [41] on this particular subject.

2. Results and Discussion

Figure 9 shows the decrease in CO oxidation activity as a linear function of added amount of NaBr. The x-axis is the mole percent of NaBr relative to the total amount of Au in the catalyst. According to the x-intercept, the catalyst surface is completely deactivated when the amount of added NaBr reaches 11.2%. In other words, only about 11% of total amount of Au catalyst is available for catalysis. We also note that the apparent activation energy and O_2 order remain approximately constant while the linear decrease occurs, which indicates a pure site-blocking effect of NaBr. Furthermore, according to TEM results on the same catalyst obtained by Kungs' group [42], there is an average of 37% of Au atoms on the surface of a nanoparticle with a diameter of 3.2 nm. Therefore, 11% of total Au atoms for this particular catalyst can be approximated to 30% of the surface atoms ($37\% \times 30\% \approx 11\%$). Interestingly, corner and edge atoms accounts for 30% of the catalyst surface, thus, this result shows very good agreement with the current literature, where low-coordinated Au sites dominate CO oxidation by actively catalyzing the dissociation of O_2 .

Adsorption energies for O, CO, Br, and NaBr interacting with Au(111), Au(211), and Au(532) are reported in Table 1. We can see from comparing values in

Table 1 that Br and NaBr adsorb much stronger to all three Au surfaces than CO and O. This indicates that the presence of NaBr can poison the catalyst surface and block the adsorption of both CO and O, thereby reducing the catalytic activity. In addition,

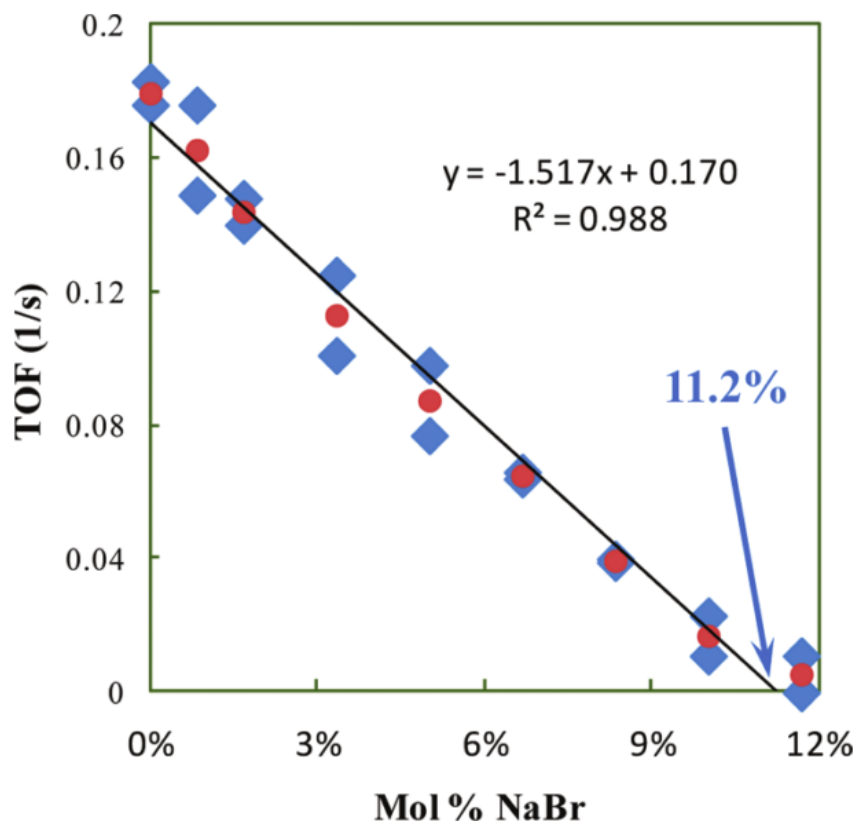


Figure 9 CO oxidation activity as a function of added NaBr at 0°C. Blue diamonds show two separate runs and red dots are the averages.

all adsorbates bind more strongly to the stepped (211) and kinked (532) sites than to the close-packed (111) facet. In particular, binding to the (532) surface as shown in Figure 10 is the strongest for all adsorbates. This trend has been previously observed for CO and O, and the binding energy change could be directly correlated to the coordination number of the most exposed Au surface atom [43,44]. More recently, it was shown that the CO and O binding energies are inversely proportional to the coordination number not only for Au, but also for a wide range of other

transition metals [45]. Our results extend these previous findings and show that the same trend can also be applied to Br and NaBr. Considering the fact that the active sites for CO oxidation on Au nanoparticles are under-coordinated corner and edge sites [46], the presence of NaBr causes an even more profound poisoning effect due to its much higher affinity to such low coordinated sites. In summary, we have shown that only the under-coordinated step and kink sites of Au/TiO₂ are active for low CO oxidation and the reaction is highly structure sensitive. These under-coordinated sites can be selectively blocked by NaBr, which allows for a good quantification method of the total number of active sites.

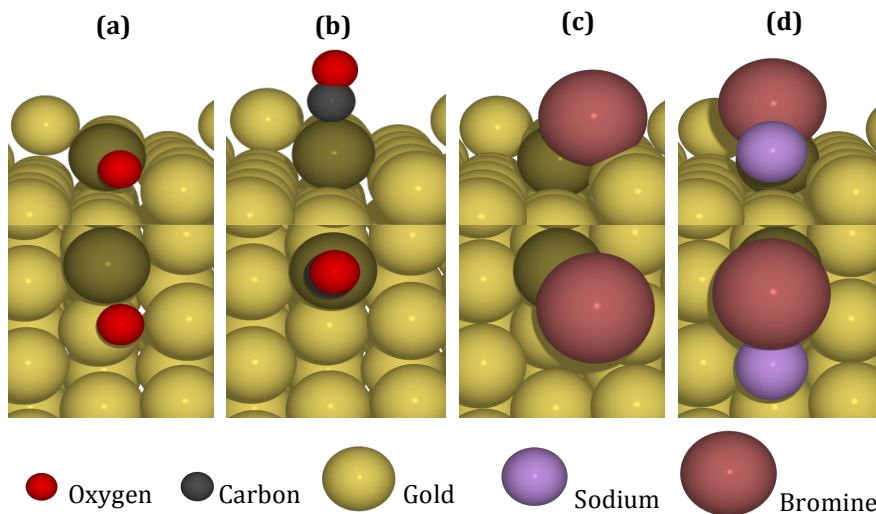


Figure 10 Binding geometries of a)O, b)CO, c)Br, and d)NaBr on Au(532) surface (split side and top view shown). The kink atom is darkened for clarity (Adapted for Ref. [35]).

Table 1 Calculated binding energies (in eV) of O, CO, Br, and NaBr on different surfaces.

		O		CO		Br		NaBr
Au(111)	fcc	0.29	top	-0.01	fcc	-0.65	fcc	-0.26
Au(211)	bridge	0.20	top	-0.30	bridge	-1.08	bridge	-1.29
Au(532)	kink	0.18	kink	-0.51	kink	-1.08	kink	-1.49
TiO ₂ (110)						0.95		-1.31

Chapter VI. Evaluation of bifunctional catalysts: Model design and Microkinetic modeling

1. Bifunctional catalyst models

Bifunctional catalysts can be engineered in many ways, but they can be reduced to the three principles given in Figure 11: i) metal/metal (ii) terrace/step/kink and (iii) metal/support interface.

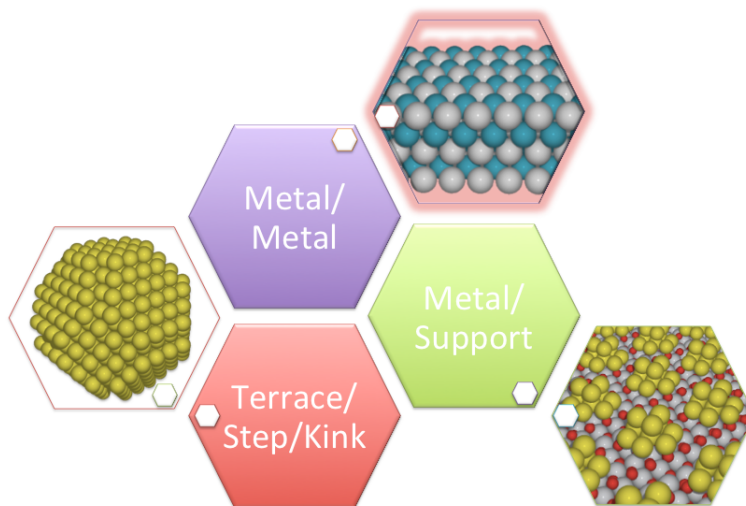


Figure 11 Different design strategies for a bifunctional catalyst.

For this thesis, we considered only the first category, namely metal/metal site pairs and modeled them as well-ordered, bimetallic surfaces ($L1_0$ alloys) as seen in Table 2. Lattice constants are obtained by following the procedure described in chapter II. For all models, the primary surface of interest is the flat (111) terrace, as it is the thermodynamically most stable facet and therefore most abundantly

present on a catalyst. The most characteristic feature of the (111) surface of an L1₀ alloy is the presence of alternating rows metals A and B, which maximizes the number of A/B site pairs. The close proximity of the two different sites minimizes the diffusion length between the sites, which can only be beneficial for the design of a bifunctional alloy surface.

Table 2 Modeled surfaces and calculated lattice constants.

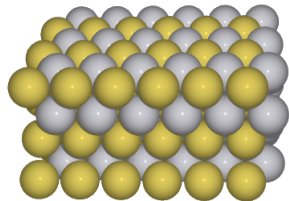
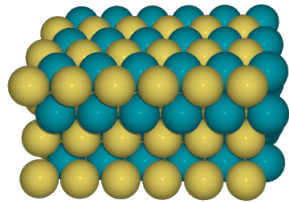
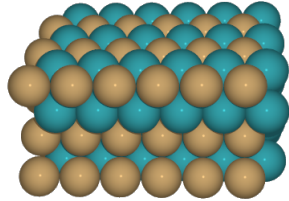
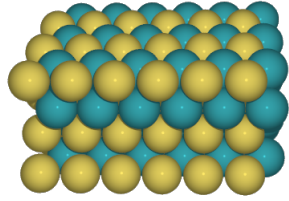
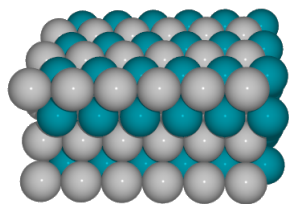
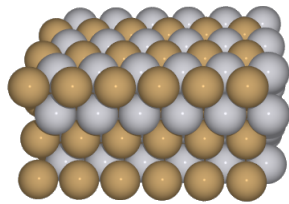
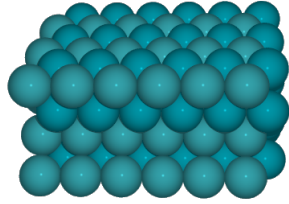
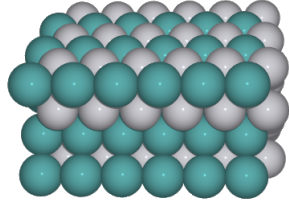
Surfaces	Lattice Constants	Models
AuPt(111)	$a = 4.098 \text{ \AA}$ $c = 4.124 \text{ \AA}$	
AuPd(111)	$a = 4.108 \text{ \AA}$ $c = 4.080 \text{ \AA}$	
CuRh(111)	$a = 3.821 \text{ \AA}$ $c = 3.784 \text{ \AA}$	
AuRh(111)	$a = 4.029 \text{ \AA}$ $c = 4.069 \text{ \AA}$	

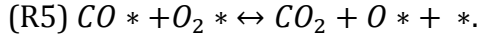
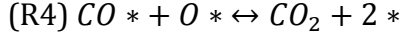
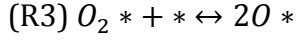
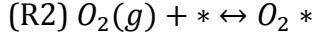
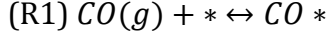
Table 2 Modeled surfaces and calculated lattice constants (continued).

AgPd(111)	$a = 4.084 \text{ \AA}$ $c = 4.130 \text{ \AA}$	
CuPt(111)	$a = 3.933 \text{ \AA}$ $c = 3.731 \text{ \AA}$	
RhPd(111)	$a = 3.945 \text{ \AA}$ $c = 3.921 \text{ \AA}$	
RuPt(111)	$a = 3.919 \text{ \AA}$ $c = 3.930 \text{ \AA}$	

2. Microkinetic model of CO oxidation

2.1 Monofunctional Catalysts

Before studying CO oxidation on bifunctional catalysts, we attempt to reproduce the monofunctional (i.e., single site) volcano for this reaction. The reaction mechanism of CO oxidation is assumed to obey Langmuir-Hinshelwood kinetics [29]:



Reactions R1 to R5 represent adsorption of CO, dissociative adsorption of O₂ followed by recombination of adsorbed CO and adsorbed O or O₂. Reaction rates (TOF's) are calculated by the following equations:

$$r_1 = k_1 P_{\text{CO}} \theta_* - k_{-1} \theta_{\text{CO}} \quad (27)$$

$$r_2 = k_2 P_{\text{O}_2} \theta_* - k_{-2} \theta_{\text{O}_2} \quad (28)$$

$$r_3 = k_3 \theta_{\text{O}_2} \theta_* - k_{-3} \theta_{\text{O}}^2 \quad (29)$$

$$r_4 = k_4 \theta_{\text{CO}} \theta_{\text{O}} - k_{-4} P_{\text{CO}_2} \theta_*^2 \quad (30)$$

$$r_5 = k_5 \theta_{\text{CO}} \theta_{\text{O}_2} - k_{-5} P_{\text{CO}_2} \theta_{\text{O}} \theta_*. \quad (31)$$

The rates of change of coverage for adsorbed CO, O, and O₂ are expressed by the following a system of ordinary differential equations (ODEs):

$$\frac{d\theta_{\text{CO}}}{dt} = r_1 - r_4 - r_5 \quad (32)$$

$$\frac{d\theta_{\text{O}}}{dt} = 2r_3 - r_4 + r_5 \quad (33)$$

$$\frac{d\theta_{\text{O}_2}}{dt} = r_2 - r_3 - r_5 \quad (34)$$

Assume the temperature and pressure are given and all energetic parameters are known, it is possible to solve for all coverages numerically by combining the above system of ODEs with the overall site balance:

$$\theta_{\text{CO}} + \theta_{\text{O}} + \theta_{\text{O}_2} + \theta_* = 1. \quad (35)$$

Once the values for coverages are found, we can use equation 27-31 to calculate the TOF. We choose the set of reaction conditions: $T=600\text{K}$, $P_{\text{CO}}=0.67\text{ bar}$, $P_{\text{O}_2}=0.33\text{ bar}$, and $P_{\text{CO}_2}=1\text{ bar}$, which is similar to the one employed by Falsig *et al.* [29]. The BEP relationships shown in Table 3 are also derived from TSS relationships used in reference [29]. Reactions R1 and R2 are associative adsorption processes and can thus be assumed to have to activation barrier or $E_{a1,2} = \Delta E$. The entropies of gas molecules are taken from textbook values and the entropies of adsorbed species are assumed to be zero. The resulted volcano in Figure 12 shows that the ideal catalyst has the binding energy pair $(E_{\text{O}}, E_{\text{CO}}) \approx (-1.0, -1.25)\text{ eV}$ and the closest pure metals Pt and Pd are the best monofunctional catalysts for CO oxidation.

Table 3 Scaling relationships for CO oxidation on single-site catalysts [29]. E_{O} , E_{O_2} , E_{CO} , and $E_{\text{CO}_2\text{g}}$ are binding energy of O, O₂, CO and gas phase energy of CO₂ respectively. Units are in eV.

Reactions	Scaling Relationships
(R3) $\text{O}_2^* + ^* \rightleftharpoons 2\text{O}^*$	$E_a = 0.445^*(2E_{\text{O}} - E_{\text{O}_2}) + 1.461$
(R4) $\text{CO}^* + \text{O}^* \rightleftharpoons \text{CO}_2 + 2^*$	$E_a = 0.6997^*(E_{\text{O}} + E_{\text{CO}}) + 0.0417 - (E_{\text{O}} + E_{\text{CO}})$
(R5) $\text{CO}^* + \text{O}_2^* \rightleftharpoons \text{CO}_2 + \text{O}^* + ^*$	$E_a = 0.810^*(E_{\text{O}} + E_{\text{CO}}) - 0.059 - (E_{\text{CO}} + E_{\text{O}_2})$

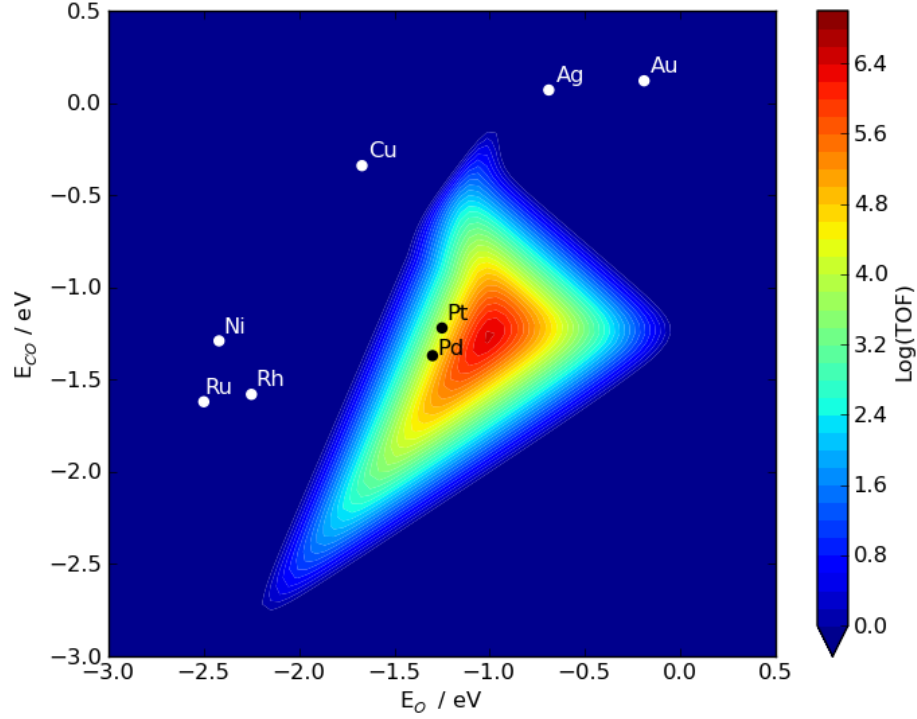


Figure 12 CO oxidation activity as a function of E_0 and E_{Co} . Coordinates of transitions metals are taken from reference [29].

2.2 Bifunctional Catalysts

2.2.1 Mechanism

The bifunctional mechanism for CO oxidation is a straightforward extension the monofunctional case and assumed to have the following elementary steps:

Table 4 CO oxidation mechanism on dual-site catalysts. $s=s_1$ or s_2 . s_1 and s_2 are two different catalytic sites.

Single site reactions	Mixed site reactions
(R1) $CO(g) + *s \rightleftharpoons CO*s$	(R6) $O_2*s_1 + *s_2 \rightleftharpoons O*s_1 + O*s_2$
(R2) $O_2(g) + *s \rightleftharpoons O_2*s$	(R7) $O_2*s_2 + *s_1 \rightleftharpoons O*s_1 + O*s_2$
(R3) $O_2*s + *s \rightleftharpoons 2 O*s$	(R8) $O_2*s_1 + CO*s_2 \rightleftharpoons CO_2(g) + O*s_1 + *s_2$
(R4) $O_2*s + CO*s \rightleftharpoons CO_2(g) + O*s + *s$	(R9) $O_2*s_2 + CO*s_1 \rightleftharpoons CO_2(g) + O*s_2 + *s_1$
(R5) $CO*s + O*s \rightleftharpoons CO_2(g) + 2*s$	(R10) $CO*s_1 + O*s_2 \rightleftharpoons CO_2(g) + *s_1 + *s_2$
	(R11) $CO*s_2 + O*s_1 \rightleftharpoons CO_2(g) + *s_1 + *s_2$

Table 4 CO oxidation mechanism on dual-site catalysts. $s=s_1$ or s_2 . s_1 and s_2 are two different catalytic sites (continued).

Diffusions	
(R12)	$O_2^*s_1 + ^*s_2 \rightleftharpoons O_2^*s_2 + ^*s_1$
R(13)	$O^*s_1 + ^*s_2 \rightleftharpoons O^*s_2 + ^*s_1$
R(14)	$CO^*s_1 + ^*s_2 \rightleftharpoons CO^*s_2 + ^*s_1$

Although there are many similarities between monofunctional and bifunctional microkinetic models, some features only exist in the later case. First, a new parameter P_1 or P_2 that specifies the fraction of site 1 or site 2 must be included

$$P_1 = \frac{s_1}{s_1+s_2} = \frac{s_1}{s} = 1 - P_2, \quad (36)$$

where s_1 , s_2 and s are the number of site 1, site 2 and the total number of sites on the surface. In the simplest sense, the overall TOF can be calculated by combining TOF of site 1 and site 2 with the corresponding site fractions. According to the definition of TOF, we have

$$P_1 \times TOF_1 + P_2 \times TOF_2 = P_1 \times \frac{n_1}{s_1 \times t} + P_2 \times \frac{n_2}{s_2 \times t}, \quad (37)$$

where n_1 and n_2 are the number of molecules produced from reactions on site 1 and site 2 ,and t represents the total reaction time in seconds. Substitute equation (36) into (37) we get

$$P_1 \times \frac{n_1}{s_1 \times t} + P_2 \times \frac{n_2}{s_2 \times t} = \frac{s_1}{s} \times \frac{n_1}{s_1 \times t} + \frac{s_2}{s} \times \frac{n_2}{s_2 \times t} = \frac{n}{s \times t} \quad (38)$$

or

$$P_1 \times TOF_1 + P_2 \times TOF_2 = TOF. \quad (39)$$

Second, as each site of type 1 may or may not be next to one or more sites of type 2, an interfacial interaction parameter called δ must be introduced to the model. This

parameter allows us control how much catalytic activity occurs at the interface of two different sites. We define δ such that $\delta = 0$ means total islands formation (i.e., no interfacial interactions) and $\delta = 1$ represents the case when all sites are perfectly mixed (i.e., maximum interfacial activity). Third, in order to avoid miscounting when incorporating both site fraction and interfacial interaction into our microkinetic model, we define an “correction” parameter f of which derivation will be shown next. Since the rate expressions are proportional to the possibilities of finding reacting sites, we assume the rates of reactions (R1)-(R14) can be reduced to:

$$r_1 \sim P_1^2 \times f_1 \quad (40)$$

$$r_2 \sim P_2^2 \times f_1 \quad (41)$$

$$r_3 \sim P_1 \times P_2 \times f_2 \quad (42)$$

$$r_4 \sim P_1 \times P_2 \times f_2, \quad (43)$$

where r_1, r_2 account for same-site reactions on site 1, site 2, r_3, r_4 generalize interfacial reactions and diffusions respectively, f_1 is the correction parameter for same-site reactions and f_2 is the correction parameter for the interactions between different (types of) sites. We can further assume that $f_2 \approx \delta$ and combine equations 40-43 with the site balance to solve for f_1 :

$$(P_1^2 + P_2^2)f_1 = 1 - 2\delta P_1 P_2 \quad (44)$$

then

$$f = f_1 = \frac{1 - 2\delta P_1 P_2}{P_1^2 + P_2^2}. \quad (45)$$

Lastly, for the reactions that involve reactants and/or products on site 1 and site 2 simultaneously, BEP relationships must be found in order to construct an activity

volcano plot. This last step presents the most computationally challenging aspect in my thesis and will be discussed in the next section.

2.2.2 Bifunctional BEP relationships

Since our bimetallic models are created from transition metals, they are expected to follow the same BEP lines as pure metals and other transition metal alloys. In order to verify such prediction, we compare the known monofunctional NEB relationships to new scaling relationships established from CI-NEB calculations for O₂ dissociation on mixed-site catalysts. To this end, we have calculated the O₂ dissociation barrier for a number of binary alloys and under the constraint that O₂ is adsorbed on the most stable site, but the two resulting O* atoms are bound to two distinct sites s_1 and s_2 . During these calculations it occurred frequently, that the O* atom that was supposed to bind to the weaker adsorption site, first, moved towards the stronger adsorption site, followed by a diffusion to the weaker site. In order to avoid this convoluted pathway, it was attempted to block this pathway by introducing a spectator O* atom that could simply block adsorption to the second available strong binding site. With this modification, it was always possible to find the desired reaction pathway in the CI-NEB calculations for O₂ dissociation. Our results, plotted in Figure 13, confirm that O₂ dissociation on all tested L1₀ alloys follows the same BEP line that was derived for pure metals even in the presence of spectator oxygen atoms. In other words, for O₂ dissociation the same BEP relationship used for pure catalysts can be used to approximate activation barriers for bifunctional ones. Without further proof, we assume this conclusion is also valid for the CO oxidation reaction on transition metal alloys. With this generalization we

can extrapolate our bifunctional microkinetic models to various combinations of transition metals.

2.2.3 Bifunctional volcano plots

The complete microkinetic model for bifunctional catalysts has 14 rate expressions and six ODEs corresponding to time evolution of O_{s1} , O_{s2} , CO_{s1} , CO_{s2} , O_{2s1} , and O_{2s2} . These ODEs are solved numerically in the same manner as monofunctional case for coverages O , CO , and O_2 on either site 1 or site 2. Figure 14 shows volcano plots for selected bifunctional systems, where fraction of site 1 and interfacial interaction parameter are set to 0.5 and 1.0 respectively.

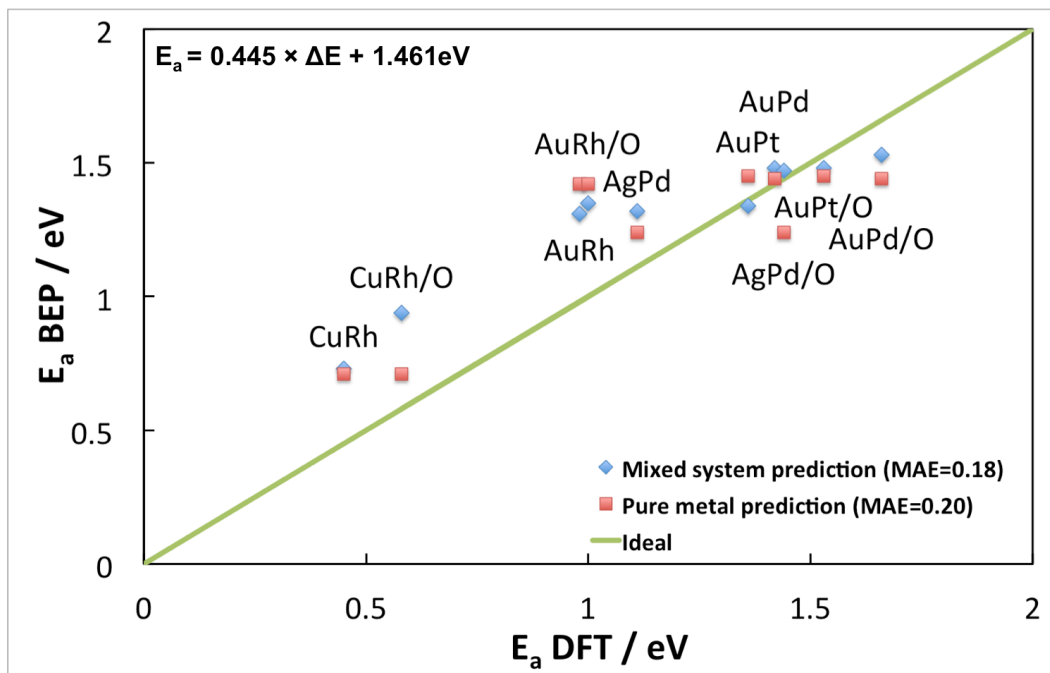


Figure 13 Activation barriers for O_2 dissociation on selected bifunctional catalysts are approximated with BEP relationship (ordinate) and DFT calculations (abscissa). Mix system prediction uses energetic parameters calculated on mixed-site surfaces. Pure metal prediction uses energetic parameters calculated on pure metal surfaces.

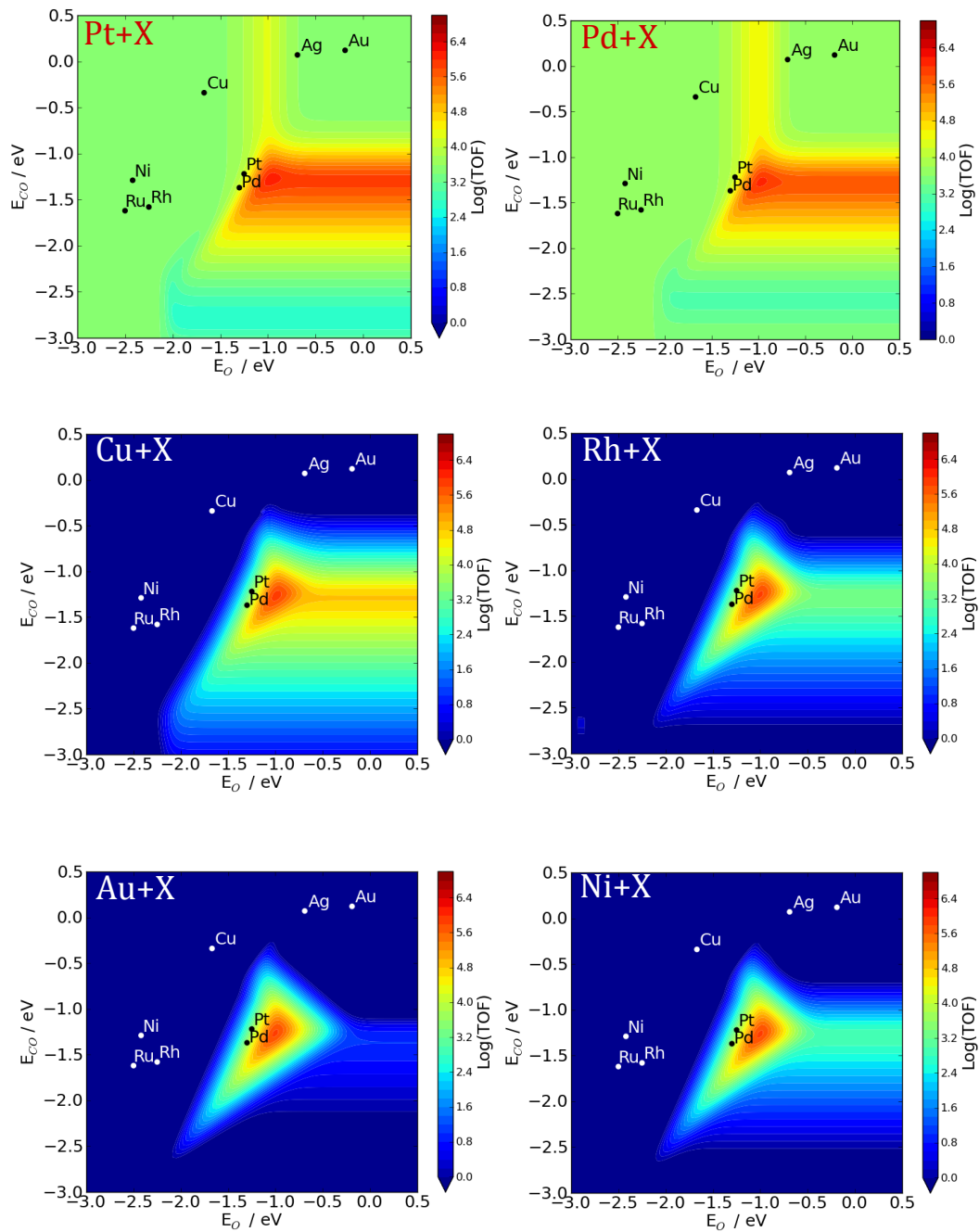


Figure 14 Bifunctional volcanoes for mixed Pt, Pd, Cu, Rh, Au, and Ni catalysts at $T = 600$ K, $P = 2$ bars and maximum interfacial interaction.

According to the set of volcanoes in Figure 14, no bifunctional combination is identified to have higher activity than that of the optimal monofunctional catalyst. However, we see large increase in catalytic activity when combining sites that are

horizontally across the top of the volcano. In the case of mixed Pt and mixed Pd, any combination with a pure site that has the same CO binding energy but lower oxygen binding energy, will result in an alloy that is much more active than either Pt or Pd and almost as active as the optimal elementary metal. Furthermore, metals that are mono-functionally inactive such as Au, Cu, Rh, and Ni, noticeable improvements can only be seen when they are combined with a much more active site such as Pt or Pd. In those cases, bifunctional catalysts will assume the performance of the more active site.

Chapter VII. Summary and Outlook

In this thesis we have used descriptor-based analysis of CO oxidation on various modeled alloys to gain further insights into the bifunctionality of heterogeneous catalysis. Density functional theory is used to calculate energetic parameters that serve as descriptors and derive BEP relationships for interfacial reactions between different types of site. Microkinetic modeling is used to calculate catalytic activity, which allows us to evaluate the performance of various modeled bifunctional catalysts. We find that, by combining sites across the top of the volcano, it is theoretically possible to create bimetallic catalysts that are more active than the optimal monofunctional one. However, the shape of the volcano limits the choice of site pairs and only small bifunctional improvement over monofunctional optimum has been observed for CO oxidation. We also see that in cases of mixed-Pt and mixed-Pd, exceptional catalytic improvements are achieved with a second site located to the left of the top of the monofunctional volcano. Given a broad range of suitable descriptor values, a large pool of candidates can be considered.

Although microkinetic modeling provides us reasonable trends in catalytic activity, several assumptions employed by this method may not be optimal for detailed studies that require much higher chemical accuracy. In those cases, interactions between adsorbates must be taken into account and kinetic Monte Carlo simulations may be considered as it can spatially resolve the distribution of adsorbates on the surface. Since only bimetallic surfaces are considered in this thesis, a continuation of this research should focus on other systems with promising

potential in multiple functionalities such as nanoparticles with steps/kinks and terraces or metal/support interfaces.

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