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Understanding Hydrogen Reactivity
and Ethanol Oxidation on Metal Catalysts:
From Thermal Catalysis to Electrocatalysis

A dissertation submitted in partial satisfaction
of the requirements for the degree
Doctor of Philosophy in Chemical Engineering

by

Xihan Liu

2026

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2026

ABSTRACT OF THE DISSERTATION

Understanding Hydrogen Reactivity
and Ethanol Oxidation on Metal Catalysts:
From Thermal Catalysis to Electrocatalysis

by

Xihan Liu

Doctor of Philosophy in Chemical Engineering

University of California, Los Angeles, 2026

Professor Philippe Sautet, Chair

Supported Pd-Au bimetallic nanoparticles are a promising class of catalysts used for hydrogenation and oxidation reactions. Recently, the role of dynamic restructuring of Pd regions at and near the nanoparticle surface in response to modulating gas (H_2 and O_2) concentration was highlighted for controlling the surface Pd oxide stoichiometry. Here we investigate the mechanism of formation and decomposition of Pd hydride (PdH_x) at and near the bimetallic nanoparticle surfaces, a key species for controlling the activity, selectivity, and stability of Pd catalysts in many hydrogenation reactions. Density functional theory (DFT) calculations provide additional insights into the stability and energetics of PdH_x formation under varying H fractions and Pd sub-structures. Our results reveal a complex interplay between Pd ensemble size, surface structure, and hydrogen environment in determining the kinetics and thermodynamics of PdH_x formation. By elucidating the mechanisms underlying surface PdH_x formation and decomposition, the rational design of dynamic catalysts with controlled Pd hydride stoichiometries becomes possible.

Hydrogen dissociation is an essential step in hydrogenation catalysis and critical to catalyst performance. Recently, Au–Pd core-shell nanoparticle catalysts have emerged as a highly promising class of materials for hydrogenation catalysis. Yet, fundamental understanding of the origin of bimetallic synergy in these core-shell catalysts and their interaction with hydrogen remains largely unknown. Here, we investigate the kinetics of hydrogen dissociation and recombination over Au–Pd core-shell catalysts using the hydrogen-deuterium (HD) exchange reaction. Density functional theory calculations indicate that subsurface hydrogen plays a major role in accelerating the hydrogen-deuterium exchange reaction by providing a lower-energy pathway for recombinative desorption of hydrogen and deuterium, which is the rate-limiting step. Altogether, our combined experiment-theory approach revealed that lattice strain and hydride formation can significantly influence the hydrogenation behavior of Au–Pd core-shell nanoparticles and is relevant to further advance the design of core-shell materials for hydrogenation catalysis.

The ethanol oxidation reaction (EOR) has attracted considerable attention because of the high energy density of ethanol and its low-cost, renewable production from biomass. However, EOR suffers from sluggish kinetics and generally does not proceed to complete oxidation. In this study, we employed first-principles calculations to investigate the stability of Pt_n clusters on various graphite surfaces, determine the optimal hydroxyl coverages, and explore potential-dependent EOR pathways. Our results show that the formation of Pt_n clusters on defective graphite is highly favorable, particularly when the initial kinetic energy imparted to the clusters during hard-landing experiments is taken into account. The calculations further indicate that complete ethanol oxidation requires low-to-intermediate potentials and may involve changes in cluster configuration. At low potentials, the EOR exhibits low reactivity but high selectivity, whereas at high potentials, its reactivity increases at the expense of selectivity. In addition, our DFT calculations reveal CO poisoning of the cluster catalysts,

in agreement with experimental observations.

The dissertation of Xihan Liu is approved.

Dante A. Simonetti

Panagiotis D. Christofides

Anastassia N. Alexandrova

Philippe Sautet, Committee Chair

University of California, Los Angeles

2026

Dedicated to my family.

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* These authors contributed equally to this work.

CHAPTER 1

Research Background

1.1 Heterogeneous Catalysts

Catalysts are of great importance in chemical processes. The application of catalysts began in the very early stages of human civilization, back to the 16th century, when people utilized inorganic chemicals to catalyze the reaction from alcohol to ether [1]. Catalysts are reusable, and they can alter the reaction pathway to reduce the activation energy; therefore, the overall reaction can have a higher reaction rate and lower energy consumption [2]. People have been using some specific catalysts to control the selectivity of the reaction to maximize the production of desired products and minimize that of byproducts, including enzymes. A large part of enzymes are naturally derived, yet researchers have been actively engineering enzymes towards particularly severe environments recently, such as extreme pH [3]. Nowadays, catalysis has become a popular subject as it is a promising strategy for mitigating the environmental challenges associated with the combustion of fossil fuels and facilitating the generation of clean and renewable energy [4]

Catalysts, in general, can be classified into two categories based on their phases: homogeneous and heterogeneous catalysts. The former refers to catalysts that are in the same phase as the reactants, while the latter refers to those that remain in a different phase from the reactants. Heterogeneous catalysts have been extensively studied because their applications are widespread in many industries, including petrochemical refining, environmental protection, and polymer manufacturing [5, 6]. In addition, since heterogeneous catalysts

are in different phases, they are easy to separate and recover and are reliable under harsh operating conditions [5]. A well-known example of heterogeneous catalysis is carbon dioxide (CO_2) treatment. As a greenhouse gas, CO_2 can be hydrogenated over heterogeneous catalysts and converted into value-added chemicals [7, 8].

1.2 Electrocatalysis

Electrocatalysis is a branch of catalysis in which catalysts accelerate electrochemical reactions involving electron transfer. The rates and selectivity of these reactions can be controlled by the applied electrode potential [9]. In electrocatalysis, many processes can occur at electrochemical interfaces, such as adsorption and desorption, electron- and charge-transfer reactions, and solvation and desolvation [10]. Promising applications of electrocatalysis in energy storage include electrolyzers and fuel cells [11–13]. Several specific reactions have benefited from the development and advancements of electrocatalysts, for example, electrochemical reduction of CO_2 (CO_2RR). In CO_2RR , CO_2 is treated under electrochemical conditions and converted to high-value C_{2+} products, commonly known as ethanol and ethylene [14]. Copper-based catalysts have been widely studied for this CO_2 reduction reaction because of their high selectivity [14–16]. Another aspect of electrocatalysis is the reaction in the opposite direction of CO_2RR , where people convert C_2 products to CO_2 , with ethanol being most extensively studied. Ethanol oxidation reaction (EOR) attracts people’s attention for its potential application in direct alcohol fuel cells (DAFCs), where chemical energy stored in alcohol molecules can be converted into electrical energy for other purposes [17]. To better understand the mechanisms of electrochemical reactions and the roles of catalysts in electrochemical reactions, many computational tools have been developed and refined [18, 19]. In the electrochemical context, density functional theory calculations are difficult since the electrolyte-electrode interfaces are intrinsically complicated, and the calculations are performed at constant charge, but not at constant potential [20]. The computational hydrogen

electrode was developed to describe the ion-electron transfer reactions [21, 22]. To address the necessity of the treatment of the electrolyte at the interfaces, many approaches have been developed, including continuum approximations to fully ab initio methods [22–26].

1.3 Dissertation Objectives

This dissertation investigates, from a theoretical perspective, how catalyst structure influences reaction activity and selectivity. Although the systems examined range from extended metal surfaces to supported metal clusters, and the reaction conditions span thermal environments (e.g., temperature and pressure) and electrochemical environments (e.g., pH and electrode potential), they are unified by a common theme: understanding how catalyst structures evolve in response to changing reaction conditions and how these structural changes subsequently affect reaction activity and selectivity.

The dissertation begins by examining hydride formation and decomposition on Pd–Au catalysts. It evaluates the stability of hydride structures under different pretreatment and modulation conditions employed experimentally, elucidates hydrogen incorporation and desorption pathways under these conditions, and relates the calculated kinetic barriers to experimental observations. This work demonstrates how hydrogen coverage varies with experimental conditions and how the resulting hydride structures govern the rates of hydride formation and decomposition.

The dissertation then investigates hydrogen activity on Au–Pd core–shell catalysts. It evaluates the stability of structures with different hydrogen coverages and demonstrates the temperature dependence of hydrogen adsorption on these catalysts. In addition, it reveals how Pd shell thickness affects the experimentally observed HD exchange rates, which can be correlated with differences in hydrogen coverage, particularly the availability of subsurface

hydrogen. This work further demonstrates that lattice strain can influence the strength of hydrogen adsorption and thereby contribute to the hydrogen reactivity of the catalyst.

The dissertation then turns to the ethanol oxidation reaction. This part of the dissertation investigates the stability of Pt_n clusters ($n = 1-5$) supported on pristine and defective graphite surfaces, with vacancy sizes ranging from mono- to tetra-vacancies. It determines the preferred OH coverages under realistic electrochemical conditions and subsequently examines the EOR pathways at three applied potentials while considering three OH coverages and two cluster configurations. The calculated reaction pathways demonstrate that the catalyst structure evolves with both the reaction intermediate and the applied potential. These structural changes are manifested through variations in OH coverage and cluster configuration. The relative stability of these structures, in turn, influences the overall reaction pathway and determines whether partial or complete oxidation is favored.

Altogether, this dissertation provides a comprehensive theoretical investigation of two catalytic systems: hydrogen reactivity on Pd–Au catalysts and the ethanol oxidation reaction on Pt_n cluster catalysts. By combining first-principles calculations with experimental observations, the results emphasize the importance of identifying the relevant catalyst structures under realistic reaction conditions, whether thermal or electrochemical. More broadly, this dissertation demonstrates how condition-dependent catalyst restructuring can govern reaction activity and selectivity.

CHAPTER 2

Hydride Formation and Decomposition at Pd-Au Bimetallic Interfaces

2.1 Introduction

Supported palladium (Pd) and its alloy nanoparticles are widely used for catalysis, hydrogen separation, purification, and storage [27]. Recent studies have shown that the structure of the nearest environment of Pd atoms in different surface facets plays a key role in developing low-cost hydrogen carriers for practical fuel cell applications [28]. Pd ensemble sizes define the feasibility of H₂ activation and subsequent hydrogenation and dehydrogenation reactions. Hence, an optimal palladium structure ranging from atomically dispersed to sub-nm and larger Pd clusters is often needed for favorable adsorption and subsequent reactions [29]. In heterogeneous catalysis, Pd-based nanocatalysts catalyze selective hydrogenation of alkynes for large-scale industrial applications [30]. The addition of a second metal, thereby forming alloys, enables a strategy to leverage geometric and electronic effects between the host metal and active catalytic centers to further improve selectivity and activity [31, 32]. Recent efforts have also shown that the catalytic activity of bimetallic alloys can be tuned dynamically by pretreatment of Pd-Au catalysts, which results in changes in elemental distribution, ensemble size, and electronic structure at the surface and can possibly enable metastable configurations that deviate from the thermodynamically most favorable configurations [33–36].

Metallic Pd has a relatively high capacity to dissolve O, C, and H atoms and, depending on the gas environment, tends to form oxide, carbide, and hydride phases that may participate in the catalytic reactions. In particular, in hydrogenation reactions, the formation of Pd hydride (PdH_x) is hypothesized to play a role in determining the reaction activity and selectivity [37–40]. Palladium hydride (PdH_x) has been shown to exhibit a phase transition between a low-H content α -phase and a high-H content β -phase, and more recently, a metastable hexagonal close-packed (hcp) structure at high H content in nanoscale particles has also been evidenced [41]. Pd hydride is important for catalyzing hydrogenation reactions and separation science, with its application to membranes [42–45]. The H atoms in PdH_x can be located on the surface, subsurface, and interstitial sites after absorption and dissociation of H_2 on the surface of a Pd cluster or nanoparticle. Thermodynamic stability data and in-situ experimental observations of PdH_x in pure Pd nanoparticles (Pd NPs) have shown that H atoms introduce lattice distortions and that the stability of PdH_x is dependent on Pd nanoparticle size [46, 47]. The kinetics of formation of PdH_x in pure Pd and its bulk alloys are well established, but little is known about the kinetics of hydride formation in bimetallic Pd nanoalloys [48]. This is largely due to the difficulty of characterizing sub-nanometric Pd domains and possible inhomogeneous Pd distribution in the alloy within larger bimetallic NPs with standard structural characterization methods such as XRD, XPS, and XAS. Pd and Au are highly miscible, but the intra-particle compositional and structural configuration can range from Au-core-Pd-shell to Pd-core-Au-shell structures in addition to quasi-homogeneous mixing [49–53]. The surface distribution of Pd atoms in Pd-Au particles significantly influences the performance of the catalysts; e.g., isolated Pd sites are useful for CO oxidation and higher H_2O_2 selectivity in H_2O_2 synthesis, and Pd regions have been shown to have low energy barriers for the oxygen reduction reaction (ORR) [54–56].

The direct observation of the dynamic surface structures at the sub-nanometer level is experimentally challenging, and intermediate catalyst states are often not detected during

steady-state experimental measurements. The heterogeneity of surface species remains a major research challenge [57]. Modulation excitation (ME) experiments, where the gas environment, temperature, or electric potential are periodically changed, have been shown to enhance the signal-to-noise ratio towards the detection of the surface species that actively participate in the (reversible) interaction. ME coupled with X-ray absorption spectroscopy (ME-XAS) also enables probing of intermediate states formed reversibly, present at low concentration. In a recent work, we applied the ME-XAS approach to probe the dynamic restructuring of surface PdO_x , Pd, and Pd-Au species in bimetallic (Pd-in-Au) nanoparticles under modulating (H_2 and O_2) gas conditions [58].

Herein, we examine the role of surface and sub-surface Pd clusters on the dynamics of Pd hydride formation and decomposition, using the previously studied system of ca. 30 atomic % Pd-Au bimetallic nanoparticles (7.0 nm in diameter, with the standard deviation of 1.7 nm) embedded on a SiO_2 support (using a raspberry colloid templated (RCT) synthesis method) [58]. The raspberry colloid synthesis approach is a multi-step colloidal synthesis procedure for obtaining well-defined catalysts consisting of a macroporous metal oxide support (in this case silica) with metallic nanoparticles (here: Pd-Au) residing at the pore walls [58–60]. A key feature of the system is that the nanoparticles are substantially embedded in the support, giving them high thermal stability and making the nanoparticles resistant to sintering at elevated temperatures and under catalytic conditions.

This Pd-Au system has been shown to possess a heterogeneous distribution of Pd atoms within the Au host, ranging from three-dimensional Pd-rich regions to surface Pd_nAu ($n=1, 2, \text{ or } 3$) ensembles [33]. To capture the surface dynamics of the Pd-Au bimetallic nanoparticles we designed an in-situ approach and used periodic modulation of the gas environment between H_2 and He and quantified the local structure of Pd atoms in $\text{Pd}_{30}\text{Au}_{70}/\text{SiO}_2$ and $\text{Pd}_{100}/\text{SiO}_2$ nanoparticles by XAS using a fast acquisition rate of 1 Hz. For gas modulation,

we used a total of 60 cycles, each cycle consisting of 60 s of He and 60 s of 20% H_2 balanced with He. We hypothesize that periodic switching of gas pulses of He and H_2 will cause the periodic switching of the compositions of Pd regions, from metallic Pd to Pd hydride and back (Figure 1). This method enabled the observation of near-surface Pd hydride formation and decomposition time scales and the estimation of the fraction of Pd atoms at and near the surface of Pd regions participating in hydrogenation and dehydrogenation dynamics. To gain insight into the mechanism of the observed structural and kinetic changes in the Pd environment, we performed a systematic investigation of the stability of various Pd and PdO_x structures in Au as a function of a wide range of Pd and H concentrations, by using density functional theory (DFT) calculations of Pd in model bimetallic surfaces. Using this approach, we accounted for the effects of hydrogen activation, diffusion, and absorption.

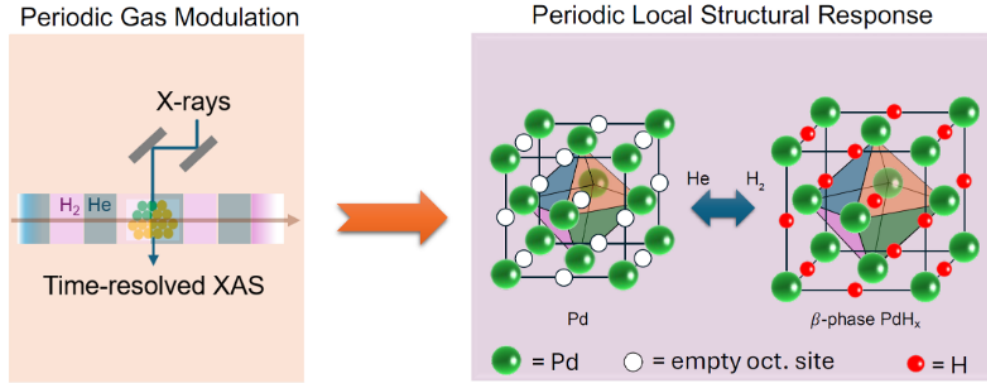


Figure 2.1: Schematic overview of time-resolved XAS experiments. ME-XAS experiments on Pd and 30% Pd-Au RCTs were conducted at 100 °C, while the pretreatment in He was carried out at 210 °C. Transformation between the Pd and PdH_x in the PdAu lattice is shown in the right panel.

2.2 Methods

2.2.1 Density Functional Theory (DFT) Calculations

We performed DFT calculations using plane-wave basis sets and the projector augmented-wave (PAW) method [citation] as implemented in the Vienna Ab initio Simulation Package (VASP) [61, 62]. The plane-wave kinetic energy cutoff was set at 450 eV. The Methfessel-Paxton smearing scheme was employed with a broadening value of 0.2 eV [63]. All structures were optimized via ionic relaxation, with total energy and forces converged to 10^{-5} eV and 0.02 eV/Å, respectively. Gas-phase H_2 was optimized in a $14 \times 15 \times 16$ Å³ cell at the Γ -point. Lattice constants of bulk face-centered cubic Au, Pd, and Pd_1Au_3 alloy were optimized according to the third-order Birch-Murnaghan equation of state, using a $19 \times 19 \times 19$ and $10 \times 10 \times 10$ Monkhorst-Pack k-point grid for the pure and alloy systems, respectively [64–66]. Unless stated otherwise, we employed the alloy lattice constant for all Pd/Au (111) slab models to reflect the global concentration of Pd in the synthesized bimetallic nanoparticles. All slab models with 4, 5, and 6 layers are spaced by 12, 14, and 16 Å of vacuum, respectively, along the direction normal to the surface to avoid spurious interactions between adjacent unit cells. We fixed the bottommost layer at bulk positions to mimic bulk properties. The Brillouin zone was sampled using a Γ -centered $5 \times 5 \times 1$, $4 \times 4 \times 1$, $3 \times 3 \times 1$, and $3 \times 3 \times 1$ k-point grid for a 3×3 , 4×4 , 5×5 , and 6×6 unit cell of the (111) facet, respectively.

We employed the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, along with the dDsC correction to account for van der Waals interactions [67–69]. PBE-dDsC provided Au and Pd lattice constants of 4.14 and 3.93 Å, within <0.1 Å of the experimental benchmark of 4.08 and 3.88 Å, respectively [70]. The optimized lattice constant of Pd_1Au_3 alloy was 4.09 Å, in good agreement with the experimental value of 4.03 Å from Vegard’s law [71].

2.3 Experimental Observations

Our collaborators performed steady-state XAS to determine the local structures of Pd and PdH_x in Pd-Au RCT. Prior work on PdH_x has shown that using the empirical relationship (Eq. (2-1)) between Pd-Pd bond length change (ΔR), determined by the steady-state EXAFS measurements, and y , the H/Pd ratio of palladium hydride, the latter can be obtained for Pd in Pd nanoparticles as well as Pd-Au bimetallic nanoparticles [38, 72–74]:

$$\frac{\Delta R}{R} = 0.066y - 0.0164y^2. \quad (2-1)$$

Table 2.1 lists the best fit parameters obtained by the EXAFS analysis of spectra measured at RT in steady state conditions in He environment (the pre-MES and post-MES were measured before and after H₂/He modulation at 100 °C, respectively) and PdAuH - in H₂ environment, indicating an increase in Pd-Pd interatomic spacing from 2.77 to 2.80 Å, yielding $\Delta R/R=0.011$. The changes in the local coordination environment of Pd seem negligible (within the experimental error) at room temperature. We note that the ratio of Pd-Pd and Pd-Au coordination numbers (Table 2.1) is greater than their relative fraction (1:3) in the alloy, consistent with segregation of Pd to Pd-rich regions, as expected. Using a crude estimate of the H/Pd ratio $y = 0.17$ (obtained after solving Eq. (2-1)), two scenarios may be proposed. The first one, a homogeneous model, corresponds to H occupying, on average, 17% of all octahedral sites in all Pd regions with the nanoparticles. The second, heterogeneous, model corresponds to a fraction of regions in which the H occupancy is 100%, coexisting with the metallic regions. Within the limitations of the ensemble-averaging nature of steady-state XAS, we cannot resolve between these possibilities. The tie between them will be broken when ME XAS is combined with theoretical modeling (vide infra).

Table 2.1: Ensemble-averaged EXAFS fitting results under steady-state conditions at room temperature: coordination numbers, distances, their mean-squared disorder values, and the photoelectron energy origin corrections. The amplitude factor was obtained by fitting to Pd foil EXAFS and fixed to 0.8. Uncertainties in the last significant digits are given in parentheses.

	Pre-MES (in He)	Post-MES (in He)	PdAuH (in H₂)
N_{PdPd}	3.0(1.1)	3.6(1.3)	3.2(5)
N_{PdAu}	7.7(1.2)	7.6(1.4)	7.4(6)
R_{PdPd} (Å)	2.77(2)	2.77(2)	2.80(1)
R_{PdAu} (Å)	2.80(2)	2.80(1)	2.80(1)
σ_{PdPd}^2 (Å ²)	0.008(3)	0.008(3)	0.004(1)
σ_{PdAu}^2 (Å ²)	0.006(1)	0.006(1)	0.005(1)
ΔE_0 (eV)	3.2(6)	3.3(6)	3.2(3)

In summary, XAS analysis of spectra collected under steady-state conditions shows that, from the ensemble-average perspective, the Pd-Au alloy does not undergo significant restructuring as a result of changing gas atmospheres. Furthermore, no significant change in Pd-Pd interatomic spacing is observed before and after the modulation experiment. A clear increase in Pd-Pd interatomic spacing is observed; however, when the system is exposed to H₂ at room temperature, corresponding to saturated PdH_x in the 30% Pd-Au RCT system. Therefore, modulation-excitation experiments with enhanced sensitivity to the effects of H incorporation into Pd regions may be more suitable for investigating these effects than the steady-state experiments.

Our collaborators carried out time-resolved XANES and EXAFS of Pd and Pd-Au RCTs afterwards. To characterize the Pd hydride formation kinetics, they utilized the multivariate

curve resolution – alternating least squares (MCR-ALS) method to decompose the time-resolved XAS spectra of the core-shell Pd/PdH_x nanoparticle system [75]. Prior to using this method, the variations between the spectra are first studied by principal component analysis that represents all the time-resolved spectra using a small number (N) of (abstract) principal components. Later, an iterative process is used to deconvolve the data matrix into the N spectra of unique pseudo-species and their concentration profiles. The MCR-ALS analysis identified two pseudo-species in each experiment, which captured most of the signal variance. These species can be assigned to metallic Pd and the hydride PdH_x, respectively, based on the comparison of MCR-generated spectral components with reference/literature spectra for Pd and PdH_x. Transient processes observed at the beginning of the H₂/He cycling were not included in the analyzed spectra by excluding the first 30 cycles for Pd and PdAu NPs. In agreement with previous reports, the formation of PdH_x from monometallic Pd in H₂ flow was noticeably faster than its decomposition in He flow, as evident from Fig. 2.2 [76]. We estimated the characteristic time scales of the PdH_x formation/decomposition as 6 and 12.2 s, respectively, by fitting a first-order exponential decay model to the corresponding signals.

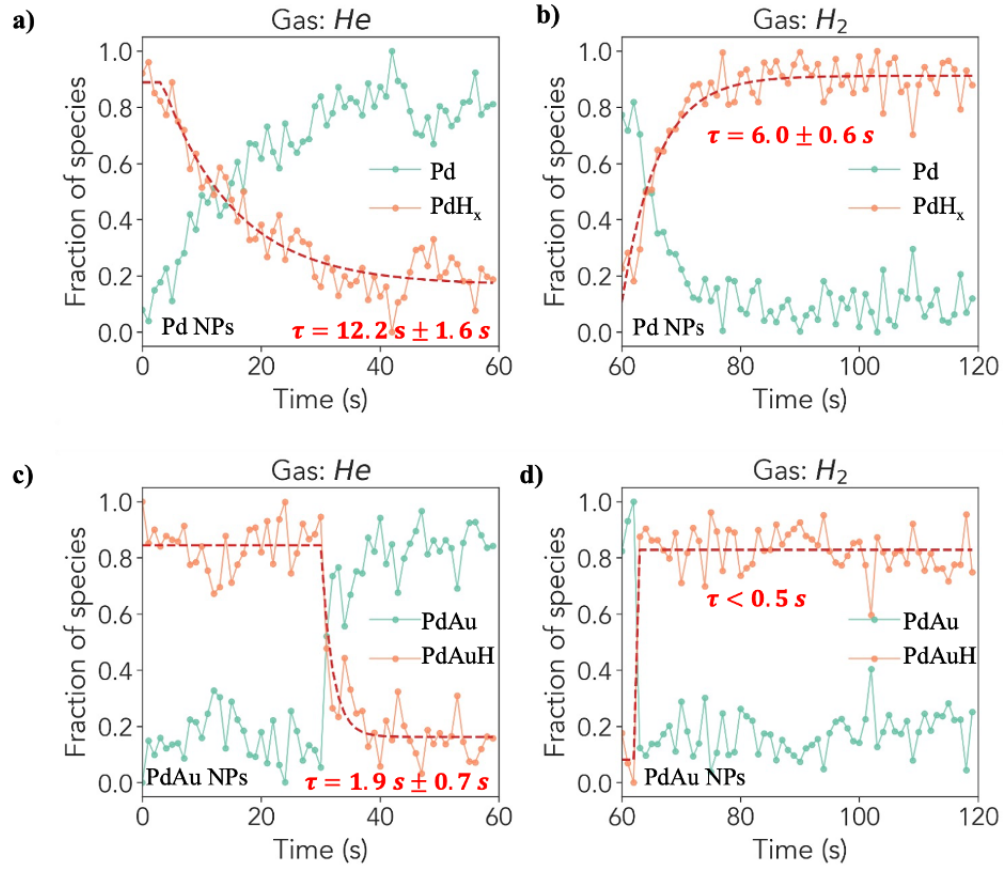


Figure 2.2: MCR-ALS analysis-based concentration profiles for 2 species using period-averaged spectra over 30 cycles for Pd nanoparticles pretreated in He atmosphere at 210 °C. MCR-ALS analysis-based concentration profiles for 2 species using period-averaged spectra over 30 cycles in PdAu NPs pretreated in He atmosphere at 1 atm. (a) and (c) correspond to the He half-period of 60 s, while (b) and (d) correspond to the H₂ half-period of 60 s. Dashed red lines show the exponential decay and rise profiles which were used to obtain time constants of Pd hydride decomposition (Pd: 12.2 s $\pm$ 1.6 s; PdAu: 1.9 s $\pm$ 0.7 s) and formation (Pd: 6.0 s $\pm$ 0.6 s; PdAu: <0.5 s).

As discussed above, steady-state XANES and EXAFS spectra of Pd-Au RCTs pretreated in H₂ at room temperature characterize the saturated hydrogenation state (PdAuH) of Pd-Au RCTs with an ensemble-average content of PdH_x formation corresponding to an H/Pd ratio

of 0.17. MCR-ALS-based time-resolved XANES spectra, when compared with these steady-state conditions, highlight that Pd-Au RCTs do not undergo complete hydrogenation and dehydrogenation between two half-cycles. Data in Figure 2.2 reveal important differences in the kinetics of PdH_x formation/decomposition between the samples. While for monometallic Pd the decomposition of PdH_x begins immediately after the flow switch from H₂ to He, a pronounced induction period of ca. 30 s is observed for bimetallic Pd-Au before PdH_x begins to decompose after the switch. Additionally, it can be observed that the rates of Pd-PdH_x interconversion are greater for Pd-Au than for Pd during both the formation of PdH_x (characteristic time of less than 0.5 s, likely mass-transfer-limited) and its decomposition after the induction period (characteristic time of 1.9 s).

They note that the interpretation of trends in the transient XAS data presented herein crucially relies on rigorous evaluation of the characteristic time scales relevant for the chemical transformations and transport phenomena within the sample. As demonstrated previously, under the operating conditions in the same setup as the one used in this work, the characteristic time scale of the convective gas transport through the entire sample bed is on the order of 0.001 s, i.e., much smaller than the time scale of the changes observed in Fig. 2.2 [58]. They also note that the XAS signal observed for monometallic Pd begins to change in response to the change of gas composition immediately after the switch in both the H₂-to-He and He-to-H₂ direction (Figs. 2.2a and 2.2b). Notably, the signal evolves at a rate that is much slower (on the order of tens of seconds) than the imposed perturbation (0.005 s) or the characteristic (plug flow reactor) convective transport through the bed (0.001 s, *vide supra*), with PdH_x formation in H₂ atmosphere being significantly faster than PdH_x decomposition in He.

The XAS signal observed for the bimetallic PdAu samples behaves drastically differently from the monometallic counterpart. First, the kinetics of PdH_x formation/decomposition

are much faster (on the order of a few seconds) for the bimetallic sample, which can be seen very clearly by comparing responses in Figs. 2b and 2d. The kinetics of PdH_x formation in PdAu (Fig. 2.2d) is the fastest signal observed in our dataset and, as such, delineates the lower boundary of the mass-transport rate at the reactor scale. In other words, even if this signal reflects the mass transport rather than chemistry, all other signals that are slower (Figs. 2.2a, 2.2b, and 2.2c) must definitely reflect the kinetics of chemical transformations. The second (qualitative) difference between Pd and PdAu samples is the approximately 30 s induction period observed in Figure 2.2c between the start of the He half-period (H_2 -to-He switch) and the start of the PdH_x decomposition. In view of the aforementioned assertions regarding the rate of mass transport in the reactor, this induction period can be confidently interpreted as a purely chemical phenomenon.

In summary, experimental data and analysis results pose the following questions that we hypothesize can be answered in terms of the local structure and composition of Pd-Au and PdH_x species: 1) Why were the changes observed during the H_2 -He modulation partial and reversible? 2) Why was there a delay in the hydrogen desorption portion of the modulation period (the hydrogen adsorption appeared to be virtually instantaneous)? 3) Why were the rates of formation and decomposition of PdH_x so different?

2.4 Theoretical Investigations

For an in-depth understanding of the stability of Pd hydride species and hydrogen diffusion pathways responsible for observed experimental barriers (for the reaction kinetics and for the presence of an induction period), we further conducted an ab initio study of various Pd hydride structures and activation mechanisms by DFT calculations. Previous work on surface and subsurface showed that surface H_2 activation is generally exothermic and subsurface hydride formation is typically endothermic, with Pd being the only exception [77]. Weaker

binding and lower diffusion barrier into the subsurface in near-surface alloys (NSA) compared to monometallic counterparts have been reported [77]. Hence, a stability assessment of various hydride structures under the modulated experimental conditions was carried out to identify potentially stable and metastable candidate structures. A detailed scheme to evaluate the formation energy of various structures was shown in Figure A.1. Previous DFT studies have also suggested that the surface hydrogen diffusion barriers were quite low for all 23 transition metals that were investigated, with barriers ranging from 0.04 to 0.28 eV [78]. A more detailed study of hydrogen diffusion pathways was conducted here to explain the observed hydride formation and decomposition time scales (see Section 2.4.2).

2.4.1 Stability Assessment

A diverse range of structures with various ensembles of Pd on Au was examined using DFT calculations, sampling these structures under different hydrogen coverages and calculating their normalized formation energies (see Figures A.2 and A.3). These calculations show that stable formation of hydride species under H_2 pressure reaction conditions requires extended Pd regions modeled as Pd layers on Au. Here we will explore these layer models of Pd-rich regions observed in the experiments in detail.

We will first examine the hydride structures in the bilayer structure that includes two layers of Pd on two layers of Au, therefore with a total of four layers in the (3×3) periodic slab. The surface presents a (111) termination. From the initial hydrogen population, where we introduced up to 9 hydrogen atoms to the 3×3 bilayer Pd slab on the surface or into the subsurface layer, we observed that the surface hydrogen atoms had better stabilization effects than the subsurface hydrogen atoms. The stabilization effect was maximized with 9 surface atoms, reaching a 1:1 H-to-Pd ratio for the surface atomic layer, with all H atoms at fcc sites. Also, we were not able to find any metastable structures for the subsurface population at low hydrogen coverages (0 to $2/3$ ML). Even at higher hydrogen coverage ($2/3$ ML to 1

ML), the subsurface-populated structures were higher in energy than the surface-populated counterparts (see Figure A.2). Therefore, the surface sites are clearly first populated, and subsurface occupation only starts when the surface coverage is 1 ML.

We kept the surface layer of our 3x3 unit cell fully covered by a total of 9 hydrogen atoms and began to introduce additional hydrogen atoms in the subsurface layer. For the surface hydrogen atoms, we considered both fcc hollow and hcp hollow sites. For the subsurface hydrogen atoms, we only took the octahedral sites (oct) into account since the octahedral hydrogen atoms were always more stable than the hydrogen atoms at the tetrahedral sites (tet) for both fcc and hcp positions of the H adlayer. Our results were in good agreement with previous work [citation]. Additionally, we found the vibrational entropy and zero-point energy correction pivotal in the cases where the hydrogen coverages were high. This finding was also confirmed in Nazarov et al.’s work [79]. Without those two factors, we inferred that it was barely possible to determine the most stable structures accurately from our calculations. Hence, the free energy calculations for structures with high hydrogen coverages included vibrational entropy and zero-point energy correction.

The normalized free energies were computed at the 4 different experimental conditions, shown in Figure 2.3. At room temperature and 0.2 bar of H_2 , the subsurface layer is almost fully occupied (8/9 ML coverage) and the most favorable configuration corresponds to surface H atoms in the hcp position, hence in a different position compared to the case where the subsurface is vacant. Note that populating the second subsurface layer is not favorable, since octahedral sites in this layer are formed by 3 Pd and 3 Au, and the binding energy of H is unstable. At high temperature (210 °C) and low H_2 pressure (taken as 0.001 bar), no subsurface site is occupied, and only the surface remains completely full (H atoms in fcc sites). This suggests that modulation of the H content could be achieved by desorption of the subsurface H atoms, keeping the surface occupied. However, for the two-Pd-layer model,

in the conditions of experimental modulation ($T=100$ °C), P varied from 0.2 bar to 0.001 bar, an estimate of the H_2 partial pressure under He flow, Figure 4b and Figure. 4c) no modulation of the H concentration is seen, and only the surface sites are occupied. We also developed a 2D stability diagram for the bilayer model to help visualize the most stable structures under different temperature and pressure conditions (see Fig. A.5).

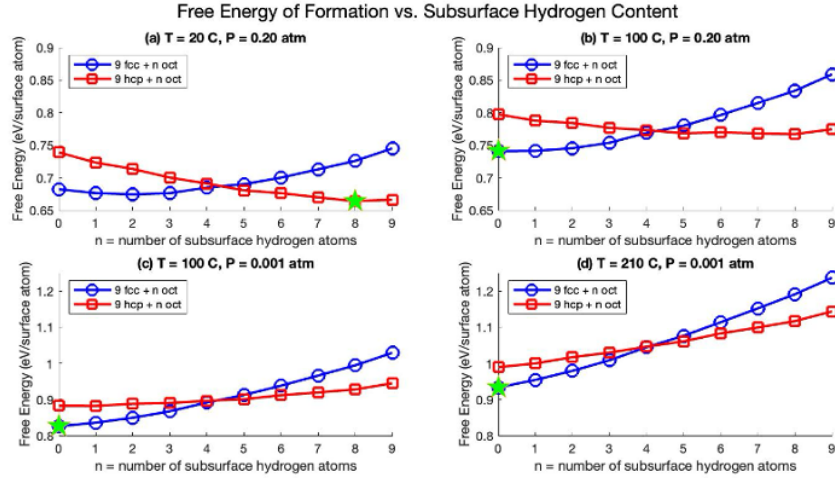


Figure 2.3: Free energies of formation as a function of subsurface hydrogen content for the bilayer structures under different experimental conditions from DFT calculations, a) $T = 20$ °C, $P(H_2) = 0.20$ atm; b) $T = 100$ °C, $P(H_2) = 0.20$ atm; c) $T = 100$ °C, $P(H_2) = 0.001$ atm; d) $T = 210$ °C, $P(H_2) = 0.001$ atm. All the points include the vibrational entropy and zero-point energy. In all selected conditions, the surface is completely populated with H adsorbates, which preferentially occupy the surface fcc (blue circles) or hcp sites (red circles) at resp. low or high subsurface H content. The most stable structure under each experimental condition is starred in green.

We performed a similar analysis for other Pd structures, namely the Pd trilayer structure, the Pd tetralayer structure, and the pure Pd(111) structure, and the side view of each structure and its stability diagram are shown in Figure 2.4. In this analysis, we did not

consider the partially H-covered case for each Pd layer. Only the fully vacant and the fully occupied H layers were included in the diagram. As we increased the number of Pd layers, the shaded region, representing the stability region of the hydride structures, also became broader. We also observed that all the structures would undergo modulation (as shown by the blue arrow in Fig. 2.4), except the bilayer structure, as discussed earlier. This could also robustly explain the experimental observations that the modulation was partial and reversible. In the modulation, the gas environment switched repeatedly between He and H_2 , and hydride species exhibited very different stabilities under the two conditions. Consequently, the hydride species during the modulation changed back and forth as the condition switched. Moreover, our DFT calculation showed that the change in the hydride species only took place in the subsurface, and the surface remained fully covered throughout the modulation. Finally, the modulation in the subsurface hydride species requires significant Pd domains, which represent only a fraction of the available Pd in the system.

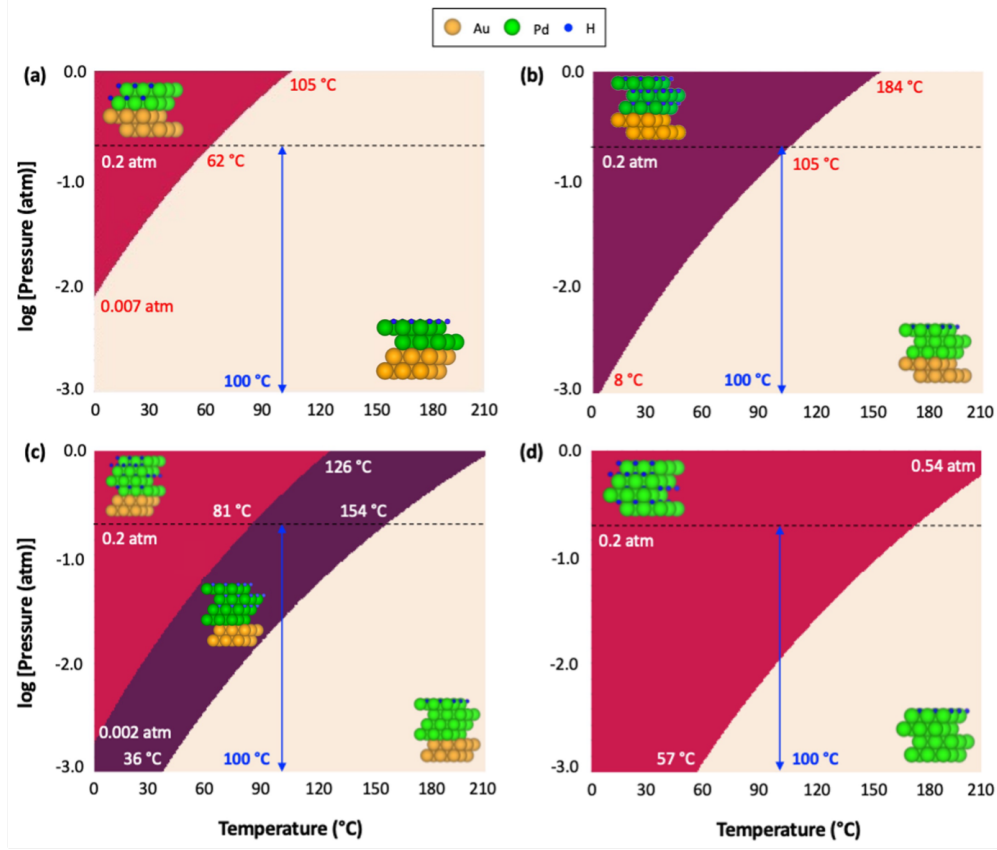


Figure 2.4: Stability diagram computed from ab initio thermodynamics for: a) Pd bilayer, b) Pd trilayer, c) Pd tetralayer, and d) pure Pd with varying surface/subsurface H concentrations. For simplicity, only the structures with the maximal number of H atoms in each layer are considered. Each layer can have a maximum of 9 H atoms in the 3×3 unit cell. The blue arrow indicates the experimental modulation conditions at 100 °C.

2.4.2 Hydride Formation and Decomposition

Removing or adding subsurface H atoms and keeping the surface site fully occupied is challenging from a mechanistic aspect since the desorption of subsurface H requires their migration via the surface, where desorption can occur. To better understand this aspect, we performed mechanistic modeling of the hydride formation and decomposition processes using DFT calculations. The modeling was performed on the bilayer model, and thicker models

were not considered due to the high computational cost. In the decomposition process, we started with the 3x3 surface fully covered (9 hydrogen atoms in fcc positions) plus 4 H atoms in subsurface octahedral sites. We continuously removed the hydrogen atoms in the subsurface layer until only the surface was occupied (9 H in fcc sites). Two different plausible mechanisms were proposed under the He modulation conditions ($T = 100\text{ }^{\circ}\text{C}$ and $P(\text{H}_2) = 0.001\text{ atm}$) as shown in Fig. 6. In the pathway shown with red lines, two surface hydrogen atoms (labeled in red) are first combined, forming a surface vacancy and one H_2 adsorbate. The hydrogen molecule is then desorbed, forming a second vacancy, and two subsurface hydrogen atoms migrate to the surface layer to fill up the two vacancies. The procedure was repeated to remove the two remaining subsurface H atoms. In contrast, in the pathway shown with black lines, one surface hydrogen atom (labeled in red) migrates to a nearby hcp site, opening a site for one subsurface H to migrate to the surface. This creates a metastable surface with one hydrogen atom beyond full coverage (a 9+1 H configuration). A hydrogen molecule is then formed and desorbed from the surface, and another hydrogen atom migrates to the surface to fill the new vacancy. Another two hydrogen atoms are removed in a similar fashion before reaching the structure with 9 H on the surface and no subsurface H. The black pathway has a lower overall free energy barrier (0.53 eV). The pathway of the reverse process under the H_2 modulation conditions ($T = 100\text{ }^{\circ}\text{C}$ and $P(\text{H}_2) = 0.2\text{ atm}$) is shown in SI Figure A.6. Furthermore, we developed pathways for hydrogen diffusion and computed the energy profile for pure Pd and PdAu alloy using different lattices (Figures A.8-A.10). We observed that the lattice parameter could impact the energy barrier for the diffusion and that the penetration of hydrogen from the Pd layer to the Au layer was thermodynamically unfavorable.

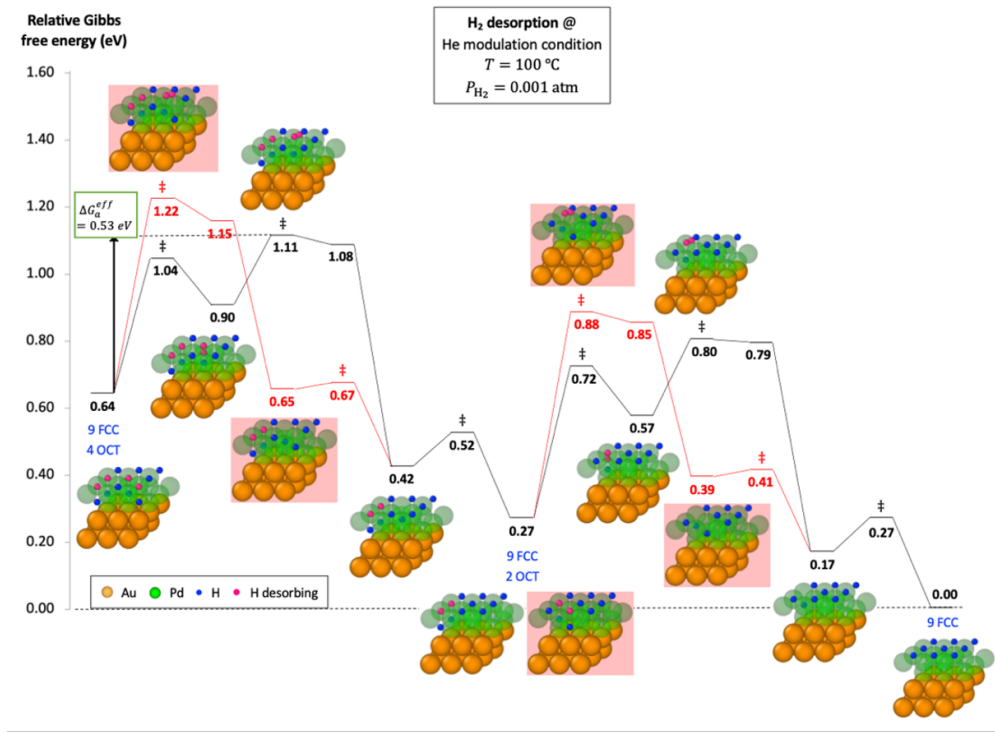


Figure 2.5: DFT-computed Gibbs free energy profile for the hydride decomposition process. The black and red lines represent two mechanisms under the He modulation condition, where $T = 100\text{ }^{\circ}\text{C}$ and $P(\text{H}_2) = 0.001\text{ atm}$.

We explain the delay in the desorption process by the necessity to remove some surface hydrogen to enable the subsurface hydrogen to migrate and desorb. As aforementioned, after the H_2 pulse in the modulation, the surface is fully covered, and there is no free channel for subsurface hydrogen content to desorb. While the thermodynamics in the He pulse allows subsurface H to desorb, this must be preceded by the desorption of more strongly bound surface H atoms, or by the formation of a metastable structure with one H atom displaced, to enable a subsurface H to desorb. This creates an extra barrier for the process. The Pd-Au alloy has a larger lattice constant, resulting in a larger Pd-Pd distance for the Pd-rich regions of interest here. This results in stronger H adsorption on the surface, resulting in a larger barrier to create the surface vacancy, and therefore a longer induction period. The delay for

H desorption observed in the experiment could, therefore, be explained by a “cork” effect created by the strongly bound surface H atoms, preventing the desorption of subsurface H atoms. For the creation of the hydride (adsorption process under H_2 conditions), H atoms at the fully occupied surface can readily penetrate into the subsurface, resulting in a lower barrier and a faster process.

2.5 Unifying Experimental and Theoretical Studies

The insights gained by correlating the steady-state and ME XAS measurements with theoretical modeling enabled us to obtain a much more detailed picture of Pd-in-Au catalysts compared to our previous studies [33, 72, 80]. Our electron microscopy analysis [7, 34] utilized high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging and elemental mapping to observe the segregation of Pd regions within the Au host [33, 58, 60, 72]. This observation confirms the conclusions from the steady-state EXAFS data. In the current work, by combining the insights from ME-XAS experiments and theoretical modeling, we resolve more details about the Pd segregation, separating them into three groups: Pd regions near the Au surface that change dynamically between metal and hydride (we call them “active”); metallic Pd regions in the Au core and Pd hydride regions in the Au shell between the core and the surface (both of these Pd regions are “spectators” because they do not restructure in response to the H_2 -He gas modulation. In order to describe the state of the hydride in the outer region, responding to the gas modulation, we employ the observation that the difference between the MXANES spectra at the two extremes can be compared to the difference between the two steady-state spectra and used to quantify the relative fraction of Pd atoms that undergo restructuring, which does not exceed approximately 0.3, similar to the analogous scaling procedure performed previously.³² Therefore, the changes in the average interatomic distance, which can be approximated as the weighted fraction of changes for “active” and “spectator” species, can be used to estimate the Pd-Pd

distance in the Pd hydride. Hence, the interatomic spacing changes in local Pd regions (active species) should be approximately 1/0.3 times greater than the increase of 0.015 Å for the PdH_x region. As a result,

$$\Delta R_{\text{active}} = \langle \Delta R \rangle / x,$$

where x is the fraction of “active” species. Therefore, the R_{PdH_x} can be estimated as 2.77 Å + 0.013/0.3 Å $\approx$ 2.81 Å, in very good agreement with literature for the Pd-Pd distance with stoichiometric Pd hydride, and, hence, characterizing the H occupancy in the outer region as nearly 100% [81].

Under the modulation excitation conditions, the changes occur between the two states of the particles (corresponding to the He and H₂ pulses) involving only outer Pd atoms with the fraction of f_1 . The remaining Pd atoms, partitioned into two regions (the hydride, in the interior shell, with the fraction of f_2 , and metallic, in the core, with the fraction of $f_M=1-f_1-f_2$), are unaffected by the modulating atmospheres. This conclusion is based on the evidence that the Pd-Pd distance under the He pulse during the ME experiment is greater than the corresponding distance under the steady-state experiment; hence, some hydride phase is present during the He pulse in the ME experiment, while under the steady state no such phase should be expected in the He regime. The average Pd-Pd distances measured by EXAFS in the He pulse and in the H₂ pulse are related to each other via Eqs. (2 and 3):

$$R_{\text{He}}^{\text{ME}} = (1 - f_1 - f_2)R_M + f_2R_{PdH_x} + f_1R_M \quad (2)$$

$$R_{\text{H}_2}^{\text{ME}} = (1 - f_1 - f_2)R_M + f_2R_{PdH_x} + f_1R_{PdH_x} \quad (3)$$

Therefore,

$$f_1 = \frac{R_{\text{H}_2}^{\text{ME}} - R_{\text{He}}^{\text{ME}}}{R_{PdH_x} - R_M} = \frac{\Delta R^{\text{ME}}}{R_{PdH_x} - R_M} \quad (4)$$

Under steady-state conditions, the average Pd-Pd distances under He and H₂ atmospheres are related to each other as follows:

$$R_{\text{He}}^{\text{SS}} = R_{\text{M}}$$

$$R_{\text{H}_2}^{\text{SS}} = (1 - f_1 - f_2)R_{\text{M}} + f_2 R_{\text{PdH}_x} + f_1 R_{\text{PdH}_x}$$

Therefore,

$$f_1 + f_2 = \frac{R_{\text{H}_2}^{\text{SS}} - R_{\text{He}}^{\text{SS}}}{R_{\text{PdH}_x} - R_{\text{M}}} = \frac{\Delta R^{\text{SS}}}{R_{\text{PdH}_x} - R_{\text{M}}} \quad (5)$$

Combining Eqs. (4) and (5) yields:

$$f_2 = \frac{\Delta R^{\text{SS}} - \Delta R^{\text{ME}}}{R_{\text{PdH}_x} - R_{\text{M}}} \quad (6)$$

Using the results for $\Delta R^{\text{SS}}=0.03$ Å, $\Delta R^{\text{ME}}= 0.005$ Å, $R_{\text{M}} = R_{\text{He}}^{\text{SS}}= 2.77$ Å, and, assuming the full H occupancy in the hydride regions, as demonstrated above, $R_{\text{PdH}_x}= 2.81$ Å, we estimate the values for f_1 , f_2 and f_{M} as 10%, 58% and 32%, respectively. Although this estimate is based on several approximations, the chief of them – the narrow size and compositional distributions of Pd-Au nanoparticles – have been validated in previous works [33, 58].

As a result, by combining the steady-state and ME experiments, we could resolve the heterogeneous distributions of Pd atoms in the Au nanoparticle, unavailable to either one of the experimental modes. Furthermore, theory played a critical role in arriving at this model (Fig. 2.6). Indeed, the presence of surface H adsorbates blocks the desorption paths of H from interior Pd regions, stabilizing them during the He pulses. Experimentally, this stabilization of H is evident via the elongation of the $R_{\text{He}}^{\text{ME}}$ vs $R_{\text{He}}^{\text{SS}}$ by ca. 0.01 Å (Fig. 2.2d).

2.6 Conclusion

In this work, we combined experimental techniques and theoretical tools to investigate the stability of hydride species and the kinetics of hydride formation in the AuPd alloy and pure Pd nanoparticles. Under modulation in He and H₂ gas conditions, we observed that the hydride formation process was partial and reversible. The DFT calculations indicated that the stability of hydride species under the two gas environments varied, and each time the gas environment changed, the hydride species changed from one to the other, making the process reversible. Moreover, only the subsurface hydrogen was modified during the modulation, and the surface remained fully covered, making the process partial.

In the experiments, we also found that for both catalysts, Pd and Pd-Au, the decomposition occurred more slowly than the formation process. Also, there was a noticeable delay in the decomposition process in the Pd-Au RCTs, but such delay was not observed in pure Pd. Our DFT results demonstrated an obvious cork effect in which the stable hydrogen surface layer impeded the desorption of the less stable subsurface hydrogen, explaining the slower decomposition of the hydride under He modulation periods. There was no free channel for the subsurface hydrogen to desorb as the surface was fully occupied, and the desorption of subsurface hydrogen always required the removal of some surface hydrogen, which was not thermodynamically favorable. On the other hand, in the adsorption process, the surface hydrogen could easily migrate downward to the subsurface as the subsurface was completely or partially available. Also, in the alloy, the lattice was stretched by the substantial Au constituent, and the hydrogen adsorption energy was larger, making the opposite process, namely desorption, more difficult. Therefore, such delay only appeared in the alloy, not in pure Pd. Intriguingly, we noticed the rate of hydride formation in the PdAu alloy was faster than that in pure Pd. We inferred that the hydrogen adsorption was controlled by hydrogen diffusion. The diffusion in pure Pd was 3-dimensional, whereas it was considered 2-dimensional in the alloy, as the hydrogen atoms were only enclosed within the Pd region

where hydrogen adsorption was much stronger.

In summary, our integrated experimental and theoretical investigation reveals the complex interplay of stability, kinetics, and structural factors governing hydride formation and decomposition in Pd and PdAu nanoparticles, advancing our understanding of hydrogen dynamics in catalytic systems.

CHAPTER 3

Strain Effects on Hydrogen Reactivity in Au-Pd Core-Shell Nanocatalysts

3.1 Introduction

Pd-based alloys are widely studied for hydrogenation catalysis [82, 83]. The addition of coinage metals like Au, Ag, and Cu can substantially improve the selectivity of Pd-based catalysts toward the desired, semi-hydrogenated products while usually drastically decreasing the activity [33, 83–85]. This well-studied activity–selectivity compromise can be surpassed through careful design of the metal distribution in the nanoparticle, specifically by departing from the conventionally used alloyed structures and tailoring the metal distribution toward a core-shell configuration [36, 86]. Au–Pd core-shell nanoparticles (NPs) can be up to 50 times more active in the selective hydrogenation of butadiene than alloyed analogues while maintaining high selectivity [36]. In core-shell systems, the catalytic activity largely depends on shell thickness. For example, Au–Pd core-shell nanorods (NRs) showed an optimal performance at a shell thickness of 6 atomic Pd layers for the selective hydrogenation of butadiene [36]. However, the optimal Pd-shell thickness depends on the reaction [87–90]. For example, in the selective oxidation of benzyl alcohol, the optimum was at ~ 3 Pd-shell layers for < 10 nm Au–Pd core-shell NPs [87, 89]. Thus, the Pd-shell thickness is an important parameter in regulating the catalytic performance of core-shell nanoparticle systems.

The enhanced performance of core-shell NPs arises from ligand and geometric effects that

modify the binding energies of the reactants, reaction intermediates, and products [91, 92]. The ligand effect refers to the interaction of the d-bands of the core metal with those of the shell metal. This ligand effect decays quickly and lasts only up to 2 monolayers from the Au–Pd interface [87, 91]. Strain arises from a lattice mismatch between the core and shell metal, leading to an upshift of the d-band center for the tensile strain present in Pd overlayers epitaxially grown on Au, giving rise to stronger reactant binding on the Pd surface [36, 93–95]. Strain in the Pd-shell is considerably influenced by the shell thickness and, in contrast to the ligand effect, also persists in thicker shells. Rapid lattice relaxation occurs within the first few layers of Pd deposited on an Au surface, followed by a progressively slower strain release until full relaxation is achieved after 30 monolayers [96, 97]. The strain can be retained by controlling the nanoparticle morphology, and Pd shells can adapt to the Au lattice up to a thickness of 10.5 nm when grown on flat Au surfaces [98].

Incorporation of hydrogen into the Pd lattice can occur in hydrogen-rich environments, leading to the formation of Pd hydrides (PdH_x), which alters the catalytic properties of Pd-based hydrogenation catalysts [40, 99, 100]. Palladium hydride exhibits a phase transition upon increasing hydrogen concentration from the low-hydrogen-content α -phase to the hydrogen-rich β -phase [101, 102]. The α - PdO_x is stable at room temperature for bulk Pd, and its stability decreases upon increasing temperatures and decreasing nanoparticle size [47, 103–106]. The formation of a subsurface hydride decreases the stability of surface-adsorbed hydrogen, thereby affecting the hydrogenation rates [99, 107]. Recent modeling work revealed that the Pd-shell of Au–Pd core-shell nanoparticles can also accommodate subsurface hydrogen in the form of PdH_x [108]. As a result, hydrogen binding on Au–Pd core-shell catalysts is not only impacted by ligand and geometric effects but also by the incorporation of hydrogen into the Pd lattice.

The hydrogen-deuterium exchange reaction ($\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$) is a powerful experimen-

tal tool to measure the interaction of hydrogen with a catalyst [99, 109]. Through this isotope-exchange reaction, one can assess the hydrogen dissociation and recombination steps on a catalyst surface. These elementary steps are critical in hydrogenation reactions and largely influence the catalytic performance both in terms of activity and selectivity [110]. This reaction has been used to study dilute Pd-in-Au alloys, showing that both the isotope exchange rate and rate-limiting step are strongly influenced by the Pd ensemble size [33, 109]. However, the interaction of hydrogen with core-shell structured Au-Pd systems has not yet been studied, and the kinetics of hydrogen dissociation and recombination over Au-Pd core-shell NPs are still unknown.

Here, we investigate Au-Pd core-shell nanoparticle catalysts in the hydrogen-deuterium exchange reaction for the first time and assess hydrogen dissociation and recombination as a function of Pd-shell thickness. For a set of well-defined Au-core Pd-shell NRs with different shell thicknesses, we characterized the degree and directionality of strain with sub-nm resolution using 4D scanning transmission electron microscopy. We assessed the temperature-dependent reaction kinetics of HD exchange over these core-shell catalysts and compared them to their alloyed counterparts. Complementing this with density functional theory (DFT) calculations allowed evaluation of hydrogen binding at the surface and in the subsurface of the Pd-shell and linked the experimental results to strain and hydride formation.

3.2 Methods

3.2.1 Density Functional Theory (DFT) Calculations

We carried out DFT calculations using the projector augmented-wave (PAW) method and plane-wave basis sets in the Vienna Ab initio Simulation Package (VASP) [61, 62]. We set the plane-wave kinetic energy cutoff at 450 eV. We employed the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with

the dDsC dispersion correction to take van der Waals interactions into account [67–69]. The Methfessel-Paxton smearing scheme was employed with a broadening value of 0.2 eV [63]. Structure optimizations were done via ionic relaxation, with the total energy and forces converged to 10^{-6} eV and 0.05 eV/Å, respectively. Two types of Pd/Au(111) slabs were created, one with 5 Pd layers and the other with 1 Pd layer. Both slabs were separated by 12 Å of vacuum along the direction normal to the surface (z-direction) to avoid spurious interactions between any two adjacent unit cells. The Brillouin zone was sampled using a Γ -centered 5x5x1 k-point grid for a 3x3 unit cell of the (111) facet. The bottom two Au layers were fixed, and all other layers were allowed to relax during the optimization. The free energy calculations included the vibration of hydrogen in both adsorbate states and the gas phase. In this work, we chose to use a model with a (111) facet for DFT calculations, different from the experimental observations. Previous studies showed that the surface and subsurface hydrogen adsorptions on Pd(111), Pd(100), and Pd(110) were similar in terms of adsorption energies [111, 112]. Besides, the (111) surface is known to have a minor lattice relaxation and to be more resistant to hydrogen-induced restructuring [113].

3.3 Experimental Measurements

Our collaborators prepared several samples of Au-Pd core-shell nanorods (NRs) with varying Pd-shell thickness. They determined the sizes of each sample using TEM, and the measurements for each sample are shown in Table 3.1, and the STEM images are shown in Figure 3.1.

Table 3.1: Properties of the Au-Pd core-shell catalysts. ICP was used to obtain the composition, and TEM was used to determine the sizes of the nanorods.

Sample	Pd content X_{Pd}	Length (nm)	Diameter (nm)	Metal loading on SiO_2 (wt%)
1L Pd	0.04	71 ± 8	22 ± 2	0.20
2L Pd	0.08	69 ± 7	21 ± 3	0.20
5L Pd	0.21	66 ± 6	18 ± 4	0.20
6L Pd	0.32	72 ± 8	24 ± 3	0.20
Au reference	0	68 ± 11	21 ± 2	1.00
Pd reference	1	20 ± 2	20 ± 2	0.15

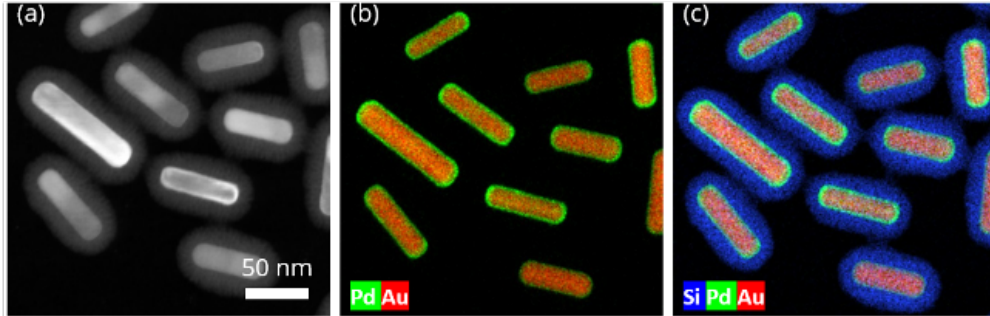


Figure 3.1: Au-Pd core-shell nanorods protected by a mesoporous silica shell. (a) Annular dark field scanning transmission electron microscopy (ADF-STEM) image of the NRs with 5L Pd, showing the mesopores of the silica shell, (b) energy-dispersive X-ray STEM (EDX-STEM) maps showing the Au-core Pd-shell structure, and (c) mesoporous silica shell. Prior to TEM analysis, the nanoparticles deposited on the TEM grid were heated at 200 °C for 1 hr in H_2 .

Additionally, they employed 4D-STEM to characterize the amount and directionality of strain in the Au-Pd core-shell NRs, and the 4D dataset was generated where each pixel in

the 2D ADF contains a 2D NBED pattern [114]. A section of the Au-core (blue rectangle overlaid in Figure 3.2a), whose lattice parameter, measured with high-resolution STEM (HR-STEM), corresponded to the bulk Au lattice (407 pm), was used as reference for strain mapping. Strain was computed in the direction perpendicular and parallel to the NR long edge surface, yielding the ε_{xx} and ε_{yy} strain maps, respectively (Figure 3.2b, c). This was achieved by following the 200 and 020 diffraction disks across the NR. The bottom part of the NR was slightly off the zone axis, and the diffraction disks in the y-direction were less bright and defined, resulting in noise in the ε_{yy} strain map. The resulting strain maps in Figure 2b and c show that while the Au is mostly unstrained and exhibits little lattice parameter variation across the particle, some parts of the Pd-shell show compressive strain, meaning that the lattice parameter in the Pd-shell is smaller than in the Au-core and approaching that of bulk Pd.

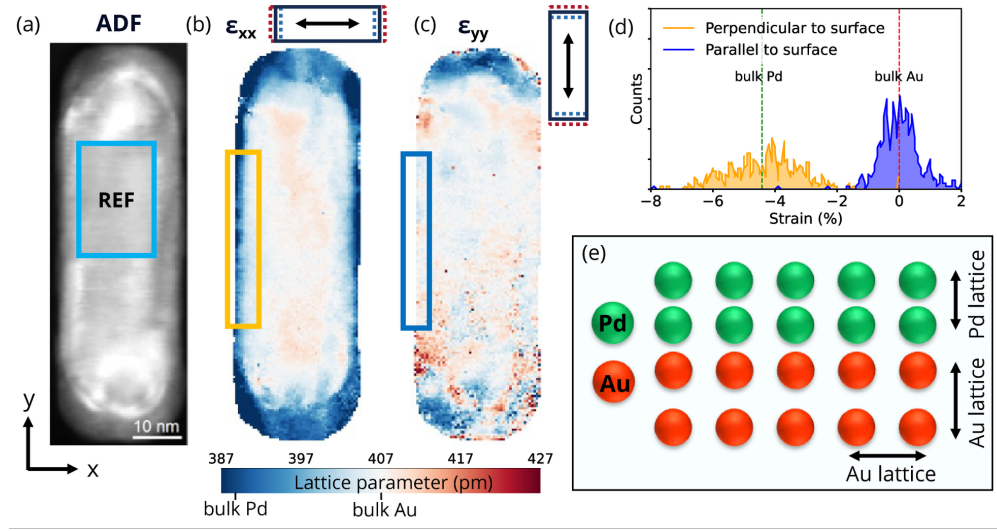


Figure 3.2: 4D-STEM strain mapping of an Au-Pd core-shell nanorod. (a) Annular dark field (ADF) image of the Au-Pd core-shell nanorod. On the long edges, the Pd-shell thickness was 1.6 nm, therefore 5 Pd layers, while at the tips it was 2.4 nm. The area marked as REF was used as a reference for the strain mapping. Each pixel contains a nanobeam electron diffraction (NBED) pattern. (b) Strain map in the x- and y-directions. The color scale is shown at the bottom, with red and blue corresponding to tensile and compressive strain, respectively. The corresponding lattice parameters in pm are written underneath: white is close to the Au lattice and blue close to the Pd lattice. Note that the noisy pixels at the bottom of the nanoparticle correspond to noisy NBED patterns, where the diffraction spots are not well-defined, and therefore strain quantification is inaccurate. (d) Histogram of the strain values of the Pd-shell in the regions marked in orange and blue in (b) and (c), with the vertical lines indicating the expected values for bulk Au and bulk Pd. (e) Schematic representation of the change of interatomic distances in the core-shell interface. In the direction parallel to the surface, the Pd (green) adapts to the Au (red) lattice parameter and does not relax, while in the direction perpendicular to the surface, the Pd relaxes to be close to the bulk Pd lattice.

Hydrogen-deuterium exchange experiments were performed on the Au-Pd core-shell NR cat-

alysts by our collaborators. During this reaction, isotope exchange rates were monitored by quantitative mass spectrometry (MS) [109]. The degree of HD exchange depended on the reaction temperature: an increase in temperature led to a decrease in H_2 and D_2 signals and an increase in the HD signal in a 1:1:2 ratio, as shown in Figure 3.3a for the Au-Pd core-shell catalysts with a 2L Pd shell. The conversion of the 2L Pd catalyst, calculated from the isothermal steps, is shown in Figure 3.3b. The catalyst loading was varied to reach similar conversion levels (15%) at 225 °C for all catalysts and to avoid approaching equilibrium conversion, which is 50% for this reaction and corresponds to a $1\text{H}_2/1\text{D}_2/2\text{HD}$ mixture. The catalysts showed no signs of deactivation, as the heating and cooling conversion profiles were nearly identical (Figure 3.3b), indicating the absence of irreversible structural changes. The 6L NR catalyst showed a reaction order of 1 both in H_2 and D_2 . In contrast to the Au-Pd core-shell catalysts, monometallic Pd and Au references showed no conversion at low temperatures, and isotope scrambling only started to occur well above 150 °C. The turnover frequencies (TOFs) increased with the Pd-shell thickness (Figure 3.3c). The catalysts are compared by TOFs to exclude nanoparticle size differences and the various catalyst loadings in the reactor. At 50 °C, the catalysts with 1L and 2L Pd show negligible conversion, while the catalysts with 5L and 6L Pd readily convert H_2 at this temperature. The TOFs increase with temperature for all the catalysts. Over the entire conversion range, NRs with 5L Pd show more than double the activity of the 2L catalyst. One reason for the lower activity of the 1L and 2L Pd samples is likely the partial intermixing of Au in these thin Pd-shells.

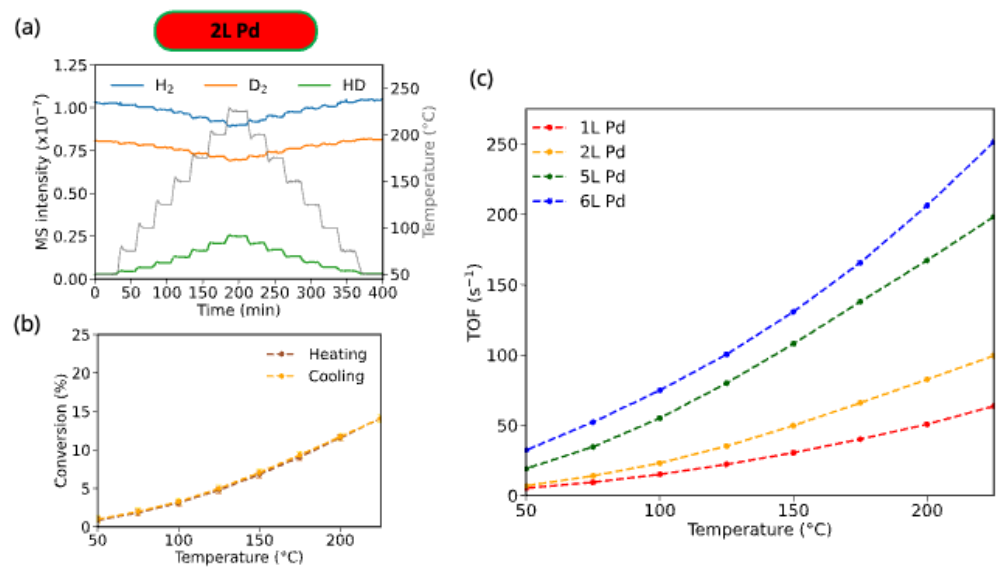


Figure 3.3: HD exchange activities of the Au-core Pd-shell catalysts. (a) Mass spectrometry data as a function of time for the catalyst with 2L Pd ($X_{Pd} = 0.08$), showing H₂ ($m/z = 2$) in blue, HD ($m/z = 3$) in green, and D₂ ($m/z = 4$) in orange. The stepwise temperature profile is shown on the right axis and plotted in grey. (b) H₂ conversion versus temperature on heating (brown) and cooling (orange) of the 2L Pd catalyst. (c) Turnover frequencies (TOF) of the nanorod catalysts with different layer thicknesses. TOF is expressed in molecules of HD converted per metal surface atom per second and was measured on cooling. Reaction conditions: total flow of 40 mL/min, of 10% H₂ and 10% D₂ diluted in Ar; ~ 5 -20 mg of catalyst (0.2 wt %, sieve fraction 90-212 μm) diluted with 100 mg of SiC ($> 212 \mu\text{m}$).

The metal distribution within the nanorod largely affected the activity of the nanorod catalysts. Upon alloying at 450 °C for 12 hours in H₂, the activity of the 5L NRs with $X_{Pd} = 0.21$ was significantly lower than that of the pristine 5L core-shell NRs that had only been reduced at 225 °C, as evident from the TOFs displayed in Figure 3.4a. The alloyed NRs showed negligible conversion at 50 °C. The conversion increased at higher temperatures, but only reached half of the activity of the core-shell catalyst at 225 °C, the highest temperature in the tests performed by our collaborators. Alloying resulted in an increase in apparent

activation energies and pre-exponential factors (Figure 3.4b and 3.4c). These parameters were calculated by constructing Arrhenius plots using the isothermal steps between 1 and 20% conversion. Data below 1% conversion were excluded because of the measurement error, which arises from the baseline correction, and at low conversions small errors in the baseline result in large errors in activity. Data above 20% conversion were excluded to stay away from equilibrium conditions (50% conversion), where the reverse reaction $2\text{HD} \rightarrow \text{H}_2 + \text{D}_2$ would take place, which would result in lower activation energies. Upon alloying, the apparent activation energy increased from 0.14 ± 0.03 eV to 0.34 ± 0.06 eV, with the pre-exponential factor showing an even more pronounced increase, rising by approximately two orders of magnitude from 9.71×10^5 to 1.28×10^8 for the core-shell and alloyed catalysts, respectively.

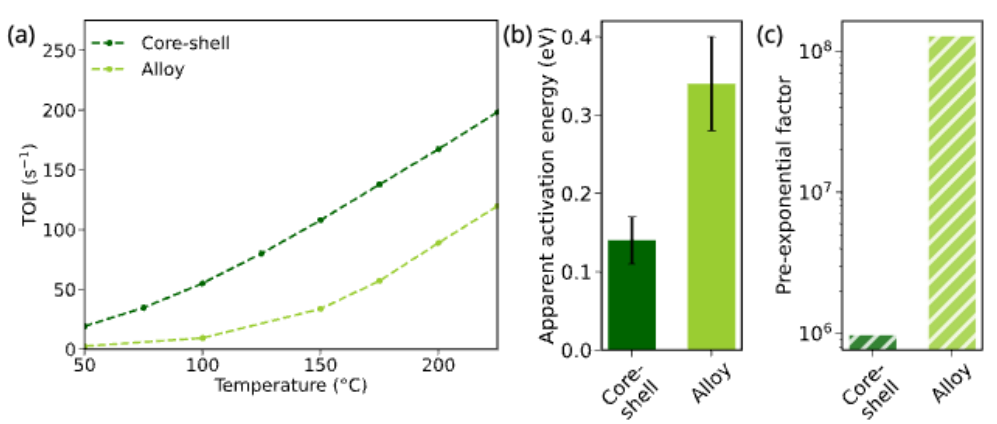


Figure 3.4: HD exchange activity of core-shell versus alloyed AuPd NRs. (a) Turnover frequencies expressed in HD molecules converted per metal surface atom per second for 5L core-shell nanorods (dark green) and alloyed nanorods (light green) with $X_{\text{Pd}} = 0.21$. (b) Apparent activation energies and (c) pre-exponential factors ($\mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$) of the core-shell and alloyed nanorods (5L Pd, $X_{\text{Pd}} = 0.21$). Apparent activation energies and pre-exponential factors were calculated at similar conversion levels (10-15%).

The apparent activation energy and pre-exponential factor of the Au-Pd core-shell catalysts were dependent on temperature, as indicated by the non-linear Arrhenius plots (Figure

3.5a). To assess this behavior, we selected different temperature windows, each including three data points, and calculated the apparent activation energies and pre-exponential factors. The results are summarized in Table 3.2 and visualized in Figure 3.5b and 3.5c for a lower (75-125 °C) and higher (175-225 °C) temperature range. Both the apparent activation energies and pre-exponential factors decreased with increasing temperature, suggesting a temperature-dependent reaction mechanism. The apparent activation energy at higher temperature was ~ 0.06 eV lower for both catalysts, and the catalysts with 2L Pd showed slightly higher apparent activation energies in both temperature regimes (~ 0.02 eV). The differences in pre-exponential factor were notably larger, decreasing by a factor of ~ 5 x from the lower to higher temperatures. The 5L Pd catalyst exhibited a larger pre-exponential factor at all temperatures, with the difference being more pronounced in the 75-125 °C range. This behavior is not observed for the catalyst with 1L Pd, which shows a linear Arrhenius plot over the entire temperature range.

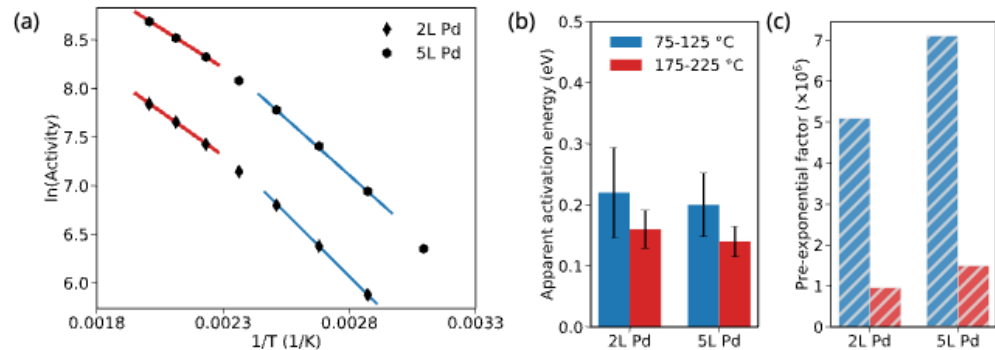


Figure 3.5: Temperature-dependent apparent activation energy and pre-exponential factor. (a) Arrhenius plots for the Au-Pd core-shell catalysts with 2 (diamond shape) and 5 (hexagon) Pd-shell layers. (b) Temperature-dependent apparent activation energy in eV and (c) apparent pre-exponential factors ($\mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$) of the Au-Pd core-shell nanorods with 2L Pd (left) and 5L Pd (right) measured from the cooling data. The Arrhenius parameters were calculated in two temperature ranges: 75-125 °C (blue) and 175-225 °C (red).

Table 3.2: Temperature-dependent apparent activation energies and pre-exponential factors for the Au-Pd core-shell nanorods with 2 and 5L Pd, based on the conversion data during cooling. The highlighted rows correspond to the data used to make Figure 3.5.

Temperature range (°C)	2L Pd		5L Pd	
	Activation energy (eV)	Pre-exponential factor ($\mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$)	Activation energy (eV)	Pre-exponential factor ($\mu\text{mol}_{\text{HD}} \text{g}^{-1} \text{s}^{-1}$)
50–100	No sufficient conversion at 50 °C		0.21 ± 0.08	1.2×10^7
75–125	0.22 ± 0.07	5.1×10^6	0.20 ± 0.05	7.3×10^6
100–150	0.21 ± 0.05	3.5×10^6	0.18 ± 0.04	4.4×10^6
125–175	0.19 ± 0.04	2.3×10^6	0.17 ± 0.03	2.9×10^6
150–200	0.18 ± 0.04	1.4×10^6	0.15 ± 0.03	1.9×10^6
175–225	0.16 ± 0.03	9.7×10^5	0.14 ± 0.03	1.5×10^6

3.4 Theoretical Investigation

For an in-depth understanding of the stability and effects of subsurface hydrogen in the HD exchange reaction, we performed DFT calculations. Our model consisted of a 3x3 periodic slab with 5 Pd layers on top of 3 Au layers with a (111) surface termination. The lattice parameter used is that of Au, and the in-plane lattice parameters of the slab are kept fixed. The relaxed epitaxial structure shows a release of the Pd-shell strain perpendicular to the surface, with Pd–Pd distances quickly converging to the bulk values when moving away from the interface, in agreement with experimental observations for the dominant surface of the

NR shown in Figure 3.2.

3.4.1 Temperature-dependent Adsorption Energy

We examined the stability of the subsurface hydrogen in a temperature range of 50-250 °C with 0.2 atm hydrogen pressure to allow a direct comparison to the experimental results. Under reaction conditions, the fcc hollow (fcc) surface sites are always fully covered with hydrogen. Only when the surface is fully occupied with hydrogen does the occupation of the subsurface octahedral (oct) sites start to become favorable. In our calculations, we initially assumed that each interlayer of oct positions between two Pd-shell layers is either fully occupied with hydrogen or empty. The stability of subsurface hydrogen decreases with temperature. The stability of fully occupied hydrogen interlayers is shown in Figure 3.6a, and the corresponding structures are shown in the schematic. Four distinct temperature regimes can be distinguished. In the low-temperature regime from 50 to 60 °C, the structure with 4 monolayers (MLs) of hydrogen is most favorable. This structure consists of a hydrogen surface layer and three subsurface hydride interlayers. The lowest energy configuration of interlayer occupation is shown in Table B.2 and Figure B.3 and consists of the surface occupied; the first Pd-Pd interlayer vacant; and the second, third, and fourth interlayers occupied. In the second regime, from 60 °C to approximately 175 °C, the 3 ML structure is the most energetically favorable. Increasing the temperature above 175 °C leads to destabilization of the subsurface hydrides, and the 2 ML structure becomes the most stable conformation until 195 °C, with hydrogen occupying the surface layer and 3rd interlayer. Note that replacing the fully occupied interlayer with two partially occupied interlayers (2nd and 3rd interlayers) results in a negligible energy difference (Table B.2). The fourth regime lies at temperatures above 195 °C. In this regime, the 1 ML structure is most stable, having a surface that is occupied with hydrogen but no full subsurface layer of hydrogen. Partial subsurface occupation is still possible in this regime. Thus, the calculations indicate that the amount of subsurface hydrogen decreases with increasing temperature, with substantial

subsurface hydrogen being present up to 195 °C. Consequently, we expect that under our experimental conditions, the surface of the catalyst is always occupied with hydrogen and the hydrogen occupancy in the subsurface is variable, decreasing with temperature.

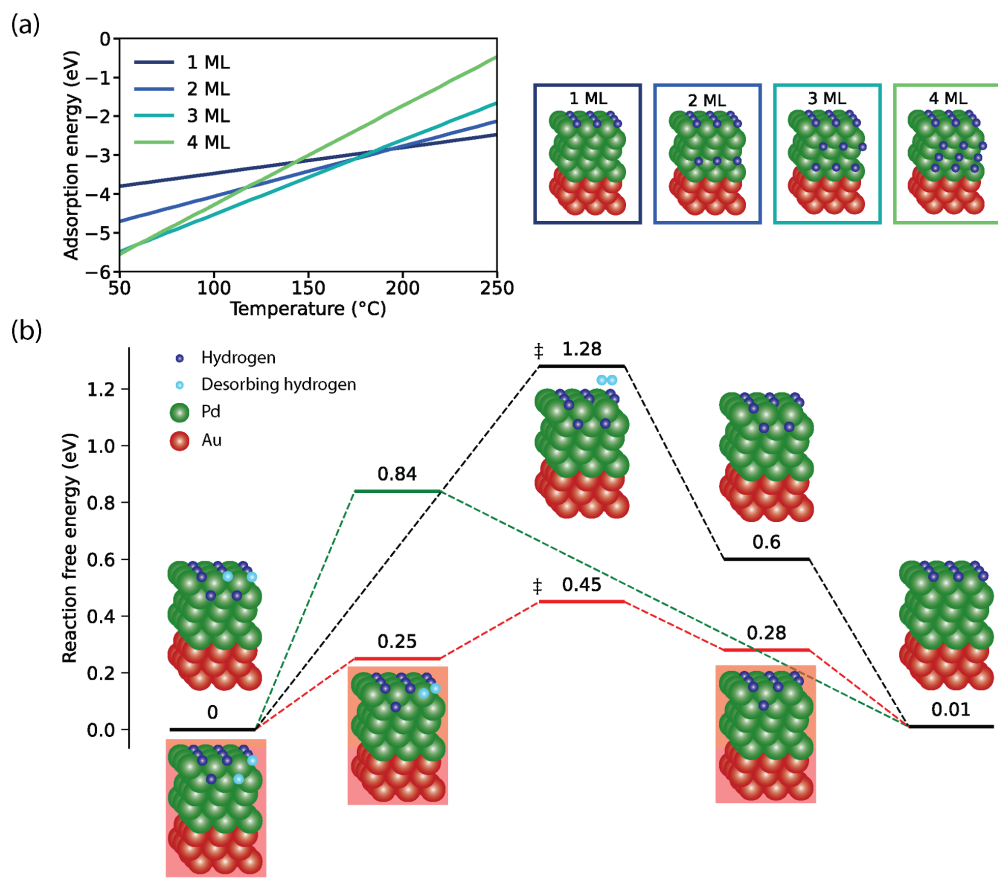


Figure 3.6: DFT calculations evaluating the stability of subsurface hydrogen in a 5L Pd-shell on Au-core model, and the mechanism of hydrogen desorption. (a) The stability of the subsurface hydrogen changes with temperature. Adsorption free energy diagram of different hydrogen monolayers at different temperatures. The schematics on the right depict the most favorable conformation. (b) DFT-computed Gibbs free energy profile for the hydrogen desorption process in the presence of subsurface hydrogen. Three possible pathways are shown. In black: recombination of two surface hydrogen atoms; in red: migration of a subsurface hydrogen to the surface upon which recombination and desorption occur; in green: migration of two subsurface hydrogens to the surface and subsequent desorption of those. The structures corresponding to the red and black pathways are shown in the schematics. Transition states are indicated by ‡. The reaction pathways shown were calculated at 200 °C and 0.2 atm of hydrogen pressure.

3.4.2 Hydrogen Desorption Process

To understand the impact of subsurface hydrogen on the experimentally measured HD exchange rates, we investigated how subsurface hydrogen can participate in the hydrogen desorption mechanism via transition-state modeling using DFT calculations. The reaction free energies of the intermediates and transition states of three plausible mechanisms were evaluated at 200 °C and 0.2 atm of hydrogen pressure for the 5L epitaxial Pd-shell model and are shown in Figure 6b. The starting point for all mechanisms was a fully covered surface of a 3x3 slab (9 surface hydrogens at the fcc sites) and two subsurface hydrogen atoms at the oct sites. The calculated reaction barriers show that the involvement of subsurface hydrogen substantially lowers the desorption barrier compared to the case where only surface hydrogens are considered, which is important since this desorption step is known to be the rate-limiting step in the HD exchange reaction over Au–Pd core-shell systems [33]. The overall thermodynamics of the desorption step in the presence of subsurface hydrogen is approximately zero, meaning that hydrogen desorption in the presence of subsurface hydrogen is not thermodynamically limited. This is different in a 1L Pd system, where subsurface hydrogen cannot be present, resulting in a final structure after desorption which is 0.61 eV higher in energy under the same conditions (Figure B.1). DFT calculations showed that hydrogen penetration into the Pd–Au interlayer drastically destabilized the system by approximately 2 eV for the complete occupation of the surface and subsurface of the 3x3 unit cell (0.22 eV per surface atom), compared to surface adsorption only, signaling that the subsurface occupation in the 1L Pd model is not accessible.

The three distinct pathways in Figure 3.6b show significant differences in energy barriers. The mechanism in black involves direct recombination and desorption of surface hydrogen atoms followed by the migration of the two subsurface hydrogen atoms to the surface. This mechanism has an overall energy barrier of 1.28 eV, and the reaction intermediate with two vacancies at the surface is 0.6 eV higher than the initial state. The mechanism in green first

allows the two subsurface hydrogens to migrate to the hcp hollow (hcp) sites at the surface, increasing the surface hydrogen coverage above 1 ML, followed by recombination and desorption of H_2 . The migration of two hydrogen atoms from the subsurface to the already fully covered surface comes with a large energy penalty of 0.84 eV. In the mechanism in red, one subsurface hydrogen migrates to an hcp surface site (with an energy cost of 0.25 eV); subsequently, it combines with a surface fcc hydrogen and H_2 desorbs. The single empty surface fcc site is then filled by migration of the other subsurface hydrogen. This combined (migration, recombinative desorption, and migration) pathway involving subsurface hydrogen provides a highly efficient path for H_2 desorption with an overall free energy barrier of 0.45 eV. The H-H recombination step occurs with a barrier of only 0.2 eV. The pathway can also be taken backward, leading to an easy adsorption of H_2 , producing two subsurface hydrogens. The subsurface hydrogen atoms therefore play a major role in accelerating the hydrogen-deuterium exchange and provide pathways compatible with the high rate measured (160 s^{-1} under these conditions). In addition, our DFT calculations demonstrated that additional subsurface hydrogen atoms can potentially act as spectators and further reduce the desorption barrier. The transition state may benefit from the stabilization effects of the spectator subsurface H. With 9 oct subsurface hydrogen atoms, the fcc- and hcp-covered structures have a desorption barrier of 0.28 and 0.39 eV, respectively, both lower than that of the 9fcc + 2oct structure, at 200 °C (Figure B.2).

To compare with experimental Arrhenius analysis, we now focus on enthalpy barriers for H_2 desorption, instead of free energy barriers. At 200 °C, a full coverage of subsurface hydrogen atoms is unstable, and the desorption process will occur from structures that present a small number of subsurface hydrogen atoms, for example, from 9fcc + 2oct to 9fcc, which presents an enthalpy barrier of 0.42 eV (Table B.3). When lowering the temperature to 100 °C, two effects with opposite effect on the enthalpy barrier can occur. The first effect is related to the temperature dependence of the enthalpy. If the number of subsurface hydro-

gen is kept constant, the enthalpy barrier increases from 0.42 eV at 200 °C to 0.45 eV at 100 °C. The second effect is related to the temperature-dependent number of subsurface hydrogen atoms in the Pd-shell. At 100 °C, the subsurface hydrogen atoms become stable, so they increase in number. This results in a decrease of the enthalpy barrier at 100 °C, but this effect is small, much smaller than the previously discussed change of the free energy barrier. If we consider full coverage of subsurface hydrogen atoms and include the fact that surface hydrogens prefer an hcp site in this case, calculations show a decrease of the enthalpy barrier at 100 °C to a value of 0.43 eV (Table B.3). Determining which effect dominates for the barrier, temperature-dependent enthalpy or subsurface H coverage, is not safely possible from calculations due to limited accuracy. In the experiment, we observed a small increase in apparent activation energy at low temperatures, suggesting that the temperature-dependent enthalpy effect may dominate. Yet, in both the experiment and theory, the variations with temperature are small.

3.5 Unifying Experimental and Theoretical Studies

Our findings demonstrate that the hydrogen dissociation capability of the core-shell Au-Pd NRs is strongly related to the Pd-shell thickness, as an increased Pd-shell thickness resulted in increased TOFs in the HD exchange reaction (Figure 3.3). This layer thickness effect can in part be ascribed to Au intermixing in the thin Pd-shells, while the thicker Pd-shells are more pure core-shell systems. Although STEM-EDX reveals a core-shell structure also for the 1L and 2L Pd catalysts after pretreatment at 200 °C, some Au intermixing in the thin 1L and 2L Pd-shells cannot be excluded [36]. By testing the 1L Pd catalysts after different pretreatment temperatures, we indeed confirmed partial alloying upon pretreatment at 225 and 250 °C. The catalyst shows higher activities and more core-shell-like HD exchange behavior when using a pretreatment temperature of 100 °C. Thus, while the 1L Pd-shell is highly strained, partial intermixing causes lower catalytic activities than expected, which is

in line with previous work on selective hydrogenation [36]. The same catalysts showed higher activity with thicker Pd-shells in the selective hydrogenation of butadiene [36]. It is generally accepted that the rate-limiting step in hydrogenation reactions over Au-Pd or Pd catalysts is hydrogen dissociation or the addition of hydrogen to the unsaturated hydrocarbon [52, 110, 115]. The similar behavior of the Au-Pd core-shell NRs in the hydrogen-deuterium exchange reaction and selective hydrogenation of butadiene highlights the important role of hydrogen dissociation activity in the hydrogenation mechanism.

Alloying of the core-shell structure resulted in a large drop in isotope exchange rate, which is in line with previous research showing significant loss of activity after alloying of core-shell structures in hydrogenation reactions [36, 106]. The decrease in activity upon alloying is associated with a doubling in the apparent activation energy and a 100-fold increase in the pre-exponential factor. The resulting values ($E_{\text{act}} = 0.34 \text{ eV}$ and $A = 1.28 \times 10^8 \mu\text{mol}_{\text{HD}} \text{ g}^{-1} \text{ s}^{-1}$) are comparable to those obtained for dilute Pd-in-Au alloys with Pd monomers in the Au surface reported in the literature [33, 109]. While larger Pd ensemble sizes might be expected from the higher Pd content in our alloy ($X_{\text{Pd}} = 0.21$), it is likely that the alloying treatment in hydrogen at 450 °C drove most of the Pd into the subsurface, leaving only a small percentage of isolated Pd atoms on the surface [116]. Indeed, only Pd monomers were observed in CO-DRIFTS after alloying core-shell nanoparticles ($X_{\text{Pd}} = 0.35$) in hydrogen [117]. While for a Pd-on-Au monolayer hydrogen desorption is known to be the rate-limiting step in the HD exchange reaction, hydrogen dissociation is rate-limiting for Pd monomers in an Au surface [33]. This change of rate-limiting step can explain the large increase in pre-exponential factor upon alloying of the core-shell structure, which is probably not linked to the number of active sites but to a change in apparent activation entropy [109].

Strain mapping with 4D-STEM on the Au-Pd core-shell nanorods confirmed that the lattice parameter in the Pd-shell is larger than bulk Pd, and thus that strain is present in our

system. From surface science studies, we expected a strained surface up to 30 monolayers of Pd on Au, with some degree of strain release [97]. The HR-STEM data reveals that the average lattice parameter in the Pd-shell follows this expected strain relaxation trend. Our 4D-STEM mapping showed that in the flat long surface of the nanorods, the Pd adapts to the lattice parameter of the Au in the direction parallel to the surface, but is relaxed in the perpendicular direction (Figure 3.2). This is in line with recent literature that showed epitaxial growth in the direction parallel to the surface but strain release in the perpendicular direction [87, 89]. However, in the curved tips of the nanorod, strain release in both directions was observed. Similarly, 4D-STEM mapping of Au-Pd core-shell nanocubes showed that strain can be preserved up to a 10.5 nm Pd-shell thickness, as long as no rounded edges were present, as strain release was only observed in curved surfaces [98]. 4D-STEM can therefore give direct insight into the variation of lattice parameter in a nanoparticle, not possible to obtain from bulk or surface techniques where only average strain is observed.

Our DFT calculations demonstrate that the presence of subsurface hydrogen facilitates the rate-limiting desorption of hydrogen from the surface by participating in the desorption mechanism. This is in line with studies that showed how subsurface hydrogen can participate in the HD exchange reaction on Pd nanoparticles and with the higher catalytic activity usually associated with the formation of a Pd hydride phase in hydrogenation reactions [40, 100, 118–120]. The inaccessibility of subsurface hydrogen in the 1L Pd core-shell catalyst is contributing to the low reactivity observed in the experiments compared to its counterparts with thicker Pd layers. In our 5L Pd core-shell system, the presence of subsurface hydrogen makes hydrogen desorption thermodynamically neutral, and the participation of subsurface hydrogen in the hydrogen desorption mechanism lowers the hydrogen desorption barrier by 0.83 eV (Figure 3.6b). The results of our calculations explain the low experimental apparent activation energies for the core-shell NRs. We find only a small difference in apparent activation energies between the 2L and 5L Pd catalysts, as both systems can have subsurface

hydrogen present [108]. The slightly higher apparent activation energy of the 2L Pd NRs may be caused by the higher energy cost for subsurface hydrogen occupying the first layer compared to occupation of the 2nd and 3rd interlayer in the 5L Pd-shell system (Table B.2). Besides, recent calculations on a 2L Pd system show that the energy barrier for hydrogen desorption (0.53 eV) is slightly higher for 2L Pd in the presence of subsurface hydrogen than in our case of 5L Pd [108]. Finally, we observe that additional subsurface hydrogen content that does not directly participate in the desorption mechanism can help lower the free energy barrier of hydrogen desorption (Figure B.2). Recent work of Chu et al. shows that the near-surface hydrogen species can alter the preferred pathway of H_2 dissociation and enhance the selectivity of the COOH pathway in CO_2 hydrogenation on $\beta\text{-Ga}_2\text{O}_3(100)$ catalyst [121]. However, further investigation of the electronic structures is required to fully understand the influence of spectator hydrogen in the reaction.

The Au-Pd core-shell catalysts exhibited temperature-dependent apparent activation energies and pre-exponential factors (Figure 3.5), which may in part be linked to hydride stability (Figure 3.6a). It is well-known that Pd can intercalate hydrogen in the subsurface, forming Pd hydride at room temperature, which gradually desorbs at higher temperatures [103–106]. While it is difficult to provide experimental proof for the different amounts of hydrogen present at different temperatures in the Pd-shell of our catalysts, the DFT calculations in Figure 6a show that the stability of the subsurface hydrogen in the Pd-shell decreases upon increasing the temperature from 50 to 250 °C. Recent modelling work has shown that subsurface hydride stability is Pd-shell thickness dependent: while the 2L Pd-shells only form a hydride phase up to 62 °C, subsurface hydrogen is stabilized in thicker 4L Pd-shells up to 154 °C [108]. Our work extends the calculations to a 5L Pd system and shows that fully occupied subsurface hydrogen interlayers are expected up to 190 °C, and that the stability of the subsurface hydrogen decreases upon increasing the temperature from 50 to 250 °C (Figure 3.6a). Figure 3.6c shows that at 200 °C, the 5L model with the surface fully

occupied by adsorbed H and with 2 subsurface hydrogen atoms is 0.01 eV more stable than the surface-only adlayer, which has no subsurface hydrogen, indicating that it is possible to have partial occupancy for the 5L model up to 200 °C. Although the 2L and 5L models both present Pd₆ subsurface octahedral sites for hydrogen, the subsurface hydride exhibits very different stabilities. In the range of considered temperatures, subsurface H is not stable for the 2L model, while it is stable for the 5L model. Subsurface H atoms enable a low barrier for desorption and adsorption of hydrogen and a high rate for H₂/D₂ exchange. This explains the observed reactivity difference, with the 5L core-shell catalysts showing a much higher TOF than that of the 2L catalyst (Figure 3.3c). While our experimental work does not show major differences in the temperature-dependent behavior of the catalysts with 2L and 5L Pd, the high pre-factor at low temperatures indicates an increased number of active sites at low temperatures compared to high temperatures, which can be linked to the amount of subsurface hydrogen present in the Pd-shell. This is further substantiated by the absence of this temperature-dependent behavior in the 1L catalysts where no hydrides can be present. Together, theory and experiment show that subsurface hydrogens impact the reaction mechanism and thus affect the HD exchange performance of Pd-shell Au-core catalysts.

The Pd-shell thickness-dependent HD exchange activity of the Au-Pd core-shell nanorods observed in experiments is likely related to both lattice strain in the Pd-shell, as tensile-strained Pd has a stronger interaction with hydrogen, and intermixing effects [36]. The high activity of the 5L and 6L Au-Pd core-shell nanorods in the HD exchange reaction can be ascribed to lattice strain, as our 4D STEM data clearly shows that strain is retained even in these thick Pd-shells. Our DFT calculations also showed that the strain in the Pd layers made the subsurface hydrogen adsorption more favorable, and the alloying effect of the Au substrate was very minimal (Table B.3). The presence of the strain on Pd is critical to stabilize subsurface hydrogen configurations at the considered reaction temperature. In the absence of strain, subsurface hydrogen only occurs at low temperature, and no subsurface

hydrogen is present under reaction conditions (Figure B.4). Additionally, our previous work shows that the hydrogen penetration into the subsurface layers is more exergonic and has a smaller effective barrier when strain is applied [108]. Therefore, the subsurface hydrogen is both more thermodynamically favorable and kinetically accessible when Pd layers are strained in the surface plane to the Au lattice. If instead the ligand effect were dominant, a volcano plot would be expected with an activity optimum around 2-3 Pd layers, which has previously been observed in the literature for oxidation reactions [87, 89]. Due to the low weight loading of our catalyst samples, we could not assess the possible charge transfer between Au and Pd, but based on previous studies, ligand effects are not expected in shells thicker than 2-3 Pd layers [87, 91, 121]. While a larger presence of subsurface hydrogen might be expected in the thicker Pd-shells, it is unlikely that hydrides alone can explain the Pd-shell thickness-dependent catalytic activity, as also in low amounts, subsurface hydrogen facilitates the mechanism of hydrogen desorption. The thinner 1L and 2L Pd-shell systems are highly strained, but less active as they are more prone to intermixing of Au in the thin Pd-shell upon pretreatment.

3.6 Conclusions

Our study shows that the activity in HD exchange over Au-Pd core-shell catalysts strongly depends on the Pd-shell thickness, and that thick shells still maintain significant strain parallel to the surface as evidenced by our 4D-STEM measurements. Increasing the Pd shell thickness results in higher TOFs, in line with selective hydrogenation butadiene studies of the same nanoparticles, indicating the relevance of hydrogen reactivity in hydrogenation reactions. Alloying leads to a pronounced decrease in TOFs accompanied by an increase in apparent activation energy and pre-exponential factor, which can be attributed to a change in the rate-limiting step from desorption-limited on the core-shell system to dissociation-limited on the alloy. Moreover, the core-shell systems exhibited a temperature-dependent activation

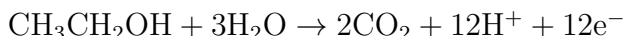
energy and pre-exponential factor, likely caused by the higher stability of subsurface hydrogen in the Pd-shell at the lower temperatures of our test. With DFT calculations, we showed that the subsurface hydrogen plays a crucial role in reducing the energy barrier for hydrogen desorption, which is the limiting step in the HD exchange reaction in core-shell systems. Altogether, our work shows that strain in Pd-based catalysts can be used to modulate the interaction with hydrogen at the surface and in the subsurface, which can be exploited to control the catalytic performance of core-shell systems in selective hydrogenation reactions.

CHAPTER 4

Ethanol Electrooxidation on Pt Cluster Catalysts Supported on HOPG

4.1 Background

Ethanol, as a clean fuel, has attracted significant attention for electrochemical energy conversion due to its high energy density and easy and cheap production from renewable biomass [122, 123]. It is also easier to store and transport than hydrogen, which makes direct ethanol fuel cells attractive for practical energy applications [124, 125]. Despite these advantages, the ethanol oxidation reaction (EOR) generally suffers from sluggish kinetics, which remains one of the major drawbacks to the practical performance of direct ethanol fuel cells [124, 125]. Complete oxidation of ethanol to carbon dioxide involves 12 electron transfers [126].



The overall reaction involves multiple adsorption, dehydrogenation, bond-breaking, and oxidation steps, giving rise to a complex reaction network and slow overall kinetics. In particular, complete oxidation is difficult to achieve because it requires cleavage of the C–C bond, which is kinetically demanding on catalysts and depends strongly on the local structure of the catalytic surface [127, 128]. As a result, ethanol is often only partially oxidized, and acetaldehyde and acetic acid are commonly observed as major products [123, 127]. Ethanol oxidation is often described in terms of C₁ and C₂ pathways. In the C₂ pathway, the C–C bond remains intact, and ethanol is oxidized first to acetaldehyde and then to acetic acid. These reactions involve only a fraction of the twelve electrons available from complete oxi-

dation and then lead to a less efficient fuel cell. The C_1 pathway, on the other hand, requires C–C bond cleavage and leads to one-carbon intermediates such as adsorbed CO, which can eventually be oxidized to CO_2 [127, 129]. Improving C–C bond cleavage is therefore an important step toward increasing the efficiency of ethanol oxidation and of the fuel cell device.

Pt is one of the most widely studied catalysts for EOR because it is active for ethanol adsorption and dehydrogenation. Its performance, however, depends strongly on surface structure. Studies on Pt single crystals have shown that different surface orientations and low-coordination sites can lead to large changes in activity and product selectivity [127, 128, 130]. Stepped surfaces, in particular, have been reported to promote C–C bond cleavage more effectively than close-packed terraces [128]. One of the main problems with Pt is poisoning by strongly adsorbed intermediates. C–C bond cleavage can produce CO and other hydrocarbons that bind strongly to Pt and block active sites [129]. These species can be removed at higher potentials when oxygen-containing species become available on the surface, but their accumulation can significantly suppress the activity at lower potentials. Such poisoning further contributes to the sluggish kinetics of EOR on Pt. An effective catalyst therefore needs to promote C–C bond activation without binding the resulting intermediates too strongly.

The local environment of Pt can also be modified by the support. Carbon materials are commonly used because of their conductivity and chemical stability, but they can also influence the electronic structure of supported Pt atoms or clusters [131]. Electrode potential provides another way to change the electronic state of the catalyst. As the surface becomes more positively or negatively charged, the interaction between Pt and adsorbed intermediates can change [21]. This can shift the relative stability of different EOR intermediates and, in turn, affect the preferred reaction pathway [132, 133]. These effects are especially relevant for small Pt structures supported on carbon, where the electronic structure can be

more sensitive to charging than that of bulk Pt surfaces [134, 135].

In this work, the ethanol oxidation reaction on Pt cluster catalysts supported on graphite is studied using density functional theory. The DFT calculations focus on how different Pt configurations and different numbers of hydroxyl groups can affect the stability of reaction intermediates and the competition between C_1 and C_2 pathways.

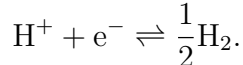
4.2 Methods

4.2.1 Geometry Optimization

Density Functional Theory (DFT) calculations were used for geometry optimizations in the process of searching for stable and metastable Pt_n clusters on graphite and sampling possible configurations under various hydroxyl coverages. We performed the calculations using the projector-augmented-wave (PAW) method and plane-wave basis sets in the Vienna Ab initio Simulation Package (VASP) [61, 62]. The plane-wave kinetic energy cutoff was set at 450 eV. We employed the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with the dDsC dispersion correction to account for van der Waals interactions [67–69]. The Methfessel-Paxton smearing scheme was employed with a broadening value of 0.2 eV [63]. Geometry optimizations were done via ionic relaxation, with the total energy and forces converged to 10^{-6} eV and 0.05 eV/Å, respectively. The model consists of two graphene layers. Both slabs were separated by 12 Å of vacuum along the direction normal to the surface (z-direction) to avoid spurious interactions between any two adjacent unit cells. The Brillouin zone was sampled using a Γ -centered 1x1x1 k-point grid for a 7x7 unit cell.

4.2.2 Hydrogen Electrode Reference

The free-energy changes of electrochemical reaction steps were evaluated using the computational hydrogen electrode (CHE) model developed by Nørskov and co-workers and subsequently widely applied to the thermodynamic analysis of electrocatalytic reactions [21, 132, 133, 136]. Within the CHE framework, the chemical potential of a proton–electron pair is referenced to that of gas-phase hydrogen through the equilibrium



At $U = 0$ V versus the reversible hydrogen electrode (RHE), the electrochemical potential of a proton–electron pair is therefore expressed as

$$\mu(\text{H}^+ + \text{e}^-) = \frac{1}{2}\mu(\text{H}_2).$$

This approach avoids the explicit treatment of solvated protons and electrode electrons while allowing the effect of the applied electrode potential to be incorporated thermodynamically [18, 21]. The Gibbs free-energy change for each elementary reaction step was calculated according to

$$\Delta G = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}},$$

where ΔE_{DFT} is the DFT-calculated electronic energy difference, ΔE_{ZPE} is the zero-point-energy correction, and ΔS is the entropy change. The potential-dependent contribution for a proton-coupled electron-transfer step is given by

$$\Delta G_U = -neU,$$

where n is the number of transferred electrons, e is the elementary charge, and U is the

applied electrode potential. When the electrode potential is referenced to the standard hydrogen electrode (SHE), the pH-dependent contribution is expressed as

$$\Delta G_{\text{pH}} = nk_{\text{B}}T \ln(10) \text{ pH}.$$

When potentials are reported versus RHE, the corresponding pH dependence of the proton–electron couple is incorporated into the electrode-potential reference [18, 21, 136]. Unless otherwise specified, all free energies were evaluated at $T = 298.15$ K.

4.2.3 Surface Charging Method

To account for the effect of electrode charging on the reaction energetics, charged-slab calculations were performed by systematically varying the total number of electrons in the simulation cell. The charged-interface calculations were carried out using the VASPsol implicit solvation framework, in which the surrounding electrolyte is represented by a continuum dielectric medium, providing electrostatic screening for the charged electrode surface [23, 137]. Five charge states were considered for each surface configuration, corresponding to $\Delta N_e = -1.0, -0.5, 0, +0.5$, and $+1.0$ electrons relative to the charge-neutral system. Here, positive ΔN_e denotes electron addition and therefore negative surface charging, whereas negative ΔN_e corresponds to electron removal and positive surface charging. The total energies obtained at these five charge states were fitted to a quadratic function,

$$E(\Delta N_e) = a(\Delta N_e)^2 + b\Delta N_e + c,$$

to construct the characteristic parabolic charging-energy profile of each surface state. The resulting quadratic fits were subsequently used to analyze the energetic response of the adsorbed intermediates to electrode charging.

4.3 Theoretical Investigation

4.3.1 Stability Assessment of Pt_n Cluster on Perfect and Defective Graphite

The defects formed on the highly oriented pyrolytic graphite (HOPG) during the hard-landing approach employed in the experiments are intrinsically difficult to model using state-of-the-art computational tools, including ab initio molecular dynamics (AIMD) [138, 139] and reactive molecular dynamics, such as ReaxFF [140]. In the hard-landing process, the incoming cluster carries sufficient kinetic energy to bombard the pristine graphite surface, eventually inducing the formation of a surface vacancy into which the cluster becomes anchored [138]. However, we took advantage of density functional theory calculations to search for low-energy structures with defects and developed schemes to assess the possibility of vacancy formation in the experiments. We observed that the energy costs of creating a vacancy defect on the pristine HOPG surface increased for every two removed carbon atoms. The energy of the removed carbon atoms is referenced to bulk graphite. This phenomenon can be well explained by the fact that the structure with an even number of removed carbon atoms would undergo restructuring and form 5-membered carbon rings to eliminate dangling carbon atoms due to the defect. Furthermore, we integrated Pt clusters into the defective systems, and the cluster interacted strongly with the defect, and the cost of forming the same defect was significantly reduced. Instead of the weaker π -interaction in the perfect graphite surface, the defects provided the potential opportunity for a much stronger σ -interaction between the dangling carbon atoms and the cluster. The formation energy for defective systems with Pt clusters is shown in Figure 4.1. Therefore, the stabilization effect of Pt clusters was more drastic in the defective system than in the pristine system, which was in good agreement with previous work by Bord et al. [141]. The formation energy reflects the combined contributions from the energy cost of forming a surface vacancy on pristine graphite and the energy gain associated with Pt_n cluster adsorption on the defective graphite surface. The formation of a surface vacancy on HOPG is thermodynamically unfavorable and requires a

substantial energy input [142]. On the other hand, our calculations show that Pt_n clusters can strongly interact with the dangling carbon atoms, substantially stabilizing the defective surface and providing a significant energetic driving force for cluster anchoring, in good agreement with the work of Yumura et al [143]. Noticeably, there were a few cases where the formation energy was close to 0 and one case showing a negative formation energy (Figure 4.2). The small positive formation energy could be potentially offset by the kinetic energy used in the hard-landing experiments, making the formation of these structures promising in the experiments. As larger cluster size could drastically increase the intrinsic complexity and also the computational cost, we continued our investigation with the Pt_3 cluster on the tri-vacancy system.

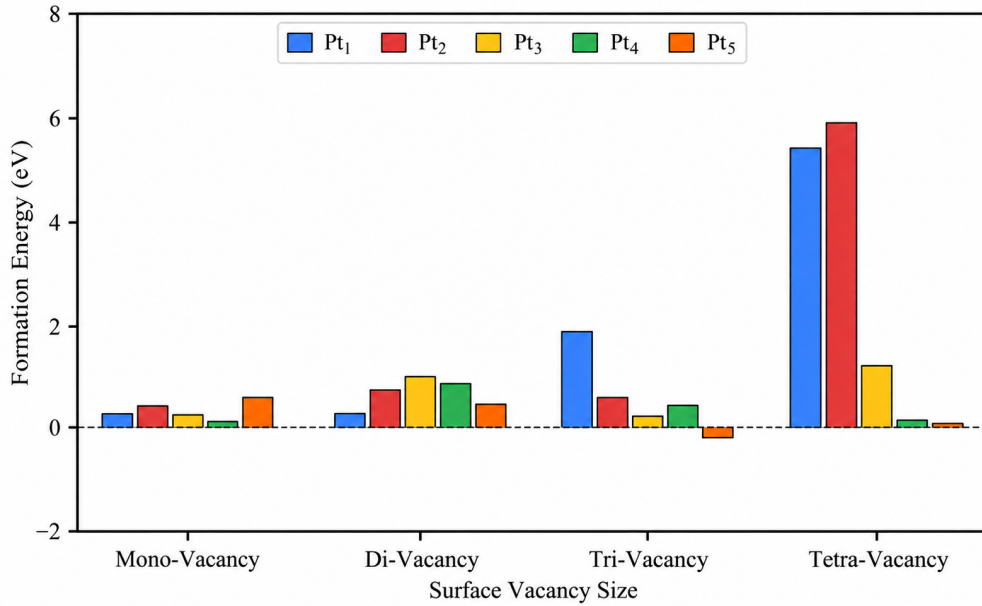


Figure 4.1: Formation energy of various defective surfaces with stabilization of Pt_n clusters. The formation energy is assessed by the equation, $E_{\text{form}} = E_{\text{defective+cluster}} + N * \mu_{\text{graphite}} - E_{\text{pristine}} - E_{\text{cluster}}$, where N is the size of the defect, μ_{graphite} is the chemical potential of one carbon atom in the graphite bulk, E_{form} , $E_{\text{form+cluster}}$, E_{pristine} , and E_{cluster} are the formation energy of the defect, the energy of the defective surface with the Pt cluster, the energy of the pristine surface, and the energy of the Pt cluster, respectively.

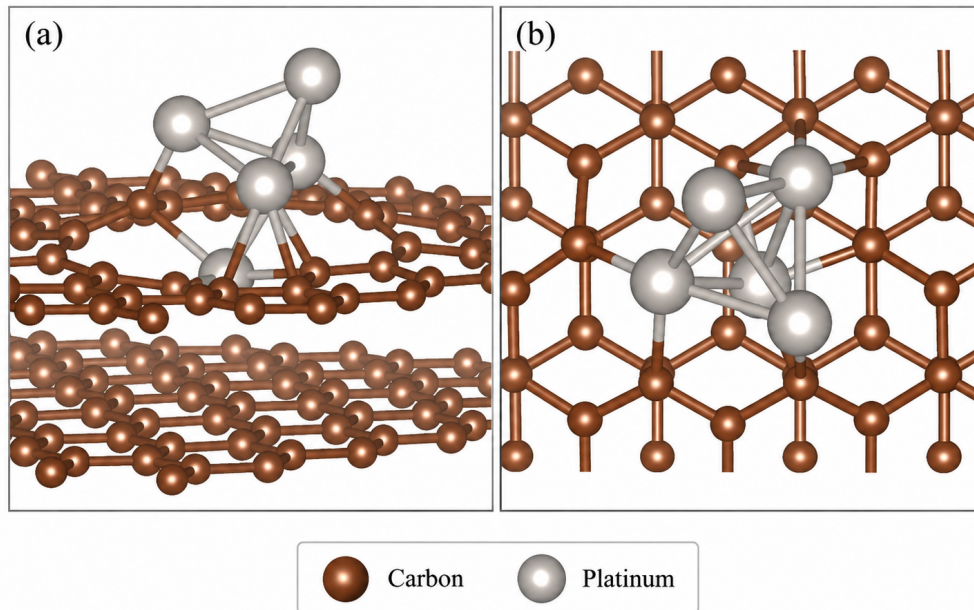


Figure 4.2: Views of the Pt_5 on the tri-vacancy graphite surface. The system shows a negative formation energy. Carbon atoms are colored in brown, and the platinum atoms are colored in grey.

4.3.2 Optimal Coverage of Hydroxyl Groups

To better understand the catalyst under realistic conditions, we carried out calculations to determine the optimal coverage of hydroxyl groups within the EOR potential window, specifically 0.4 to 1.0 V vs SHE under acidic conditions ($\text{pH} = 1$) [144]. The chemical potential of the OH group is determined by the equilibrium with the hydrogen electrode. In determining the optimal coverage of OH, we employed the grand canonical basin hopping method, a Monte Carlo-based method that allowed us to explore the configurational and compositional spaces simultaneously [145, 146]. The free energy is calculated by the following equation.

$$G_{ads} = G_{total} - G_{bare} - n * \mu_{OH}$$

where G_{ads} , G_{total} , and G_{bare} are the free energy of adsorption, the free energy of the catalyst with adsorbed OH groups, and the free energy of the bare catalyst, respectively. n is the number of OH groups adsorbed on the catalyst, and μ_{OH} is the chemical potential of an OH group obtained from the hydrogen electrode reference, $\mu_{OH} = \mu_{H_2O(l)} - \frac{1}{2}\mu_{H_2} + eU - k_B T \ln(10)$. The free energy of adsorption of various coverages (1OH, 2OH, and 3OH) on two distinct cluster configurations (embedded and on-surface) is shown in Fig. 4.4, and the configurations of the two clusters are shown in Figure 4.5

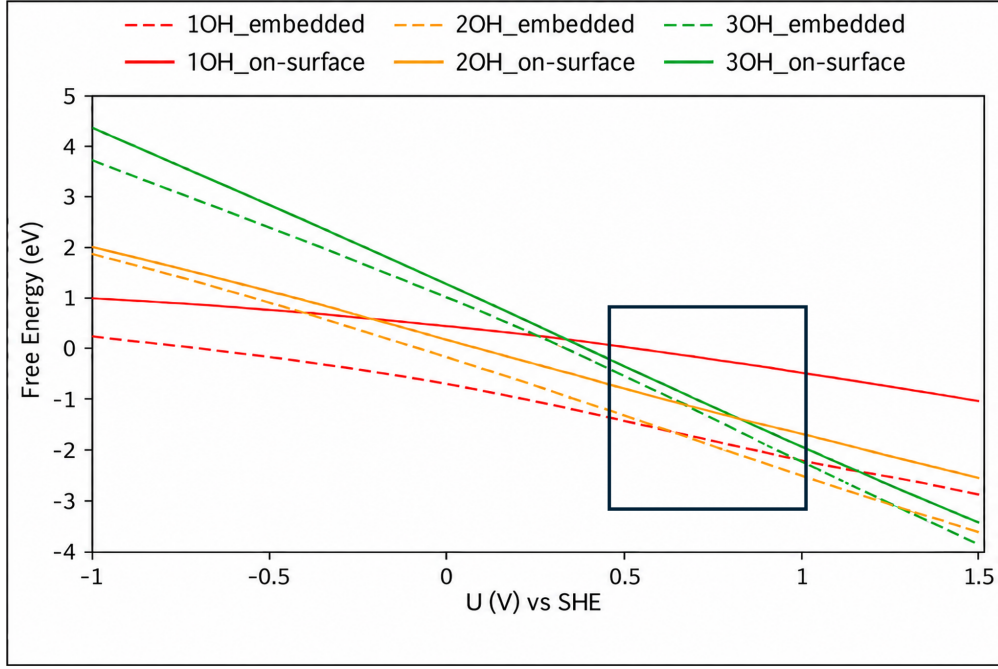


Figure 4.3: Free energy of adsorption of various coverages on two distinct cluster configurations. Three different coverages (1OH, 2OH, and 3OH) and two different cluster configurations (on-surface and embedded) were considered. The detailed configurations are shown in Figure 4.5. The embedded and on-surface clusters are shown in dashed and solid lines, respectively. The potential of interest for EOR is highlighted by the black square.

We observed that all the cases investigated became stabilized as the electrode potential increased. The optimal coverage for each configuration also changed as the potential increased. For example, the 1OH structure was the most stable up to ~ -0.2 V vs SHE for the on-surface cluster. The 2OH structure became the most stable system in the intermediate-potential region. The 2OH structure then intersected with the 3OH structure at ~ 0.8 V vs SHE, and the latter represented the optimal coverage in the high-potential region. Similar transitions occurred for the embedded cluster configuration as well, but the potentials at which the crossing happened were slightly different. Generally, the on-surface cluster configuration had lower adsorption energy across the entire potential range that we have explored. The

embedded cluster shown in Figure 4.5a was buried into the graphene layers, and it had strong interactions with the dangling carbon atoms, which significantly stabilized the defects. However, it became less interactive with the additional adsorbates, in this case, the OH's. On the other hand, the on-surface cluster could interact strongly with the OH groups, making the OH adsorption more favorable. Although the 3OH-covered state can become thermodynamically competitive at higher potentials, such high OH coverage may reduce the number of available Pt active sites and weaken the adsorption of reaction intermediates. Therefore, the subsequent reaction-pathway calculations focused on the 0OH, 1OH, and 2OH coverages. This approach captures the most relevant catalyst states within the EOR potential window while retaining sufficient available Pt sites for adsorption and subsequent reactions.

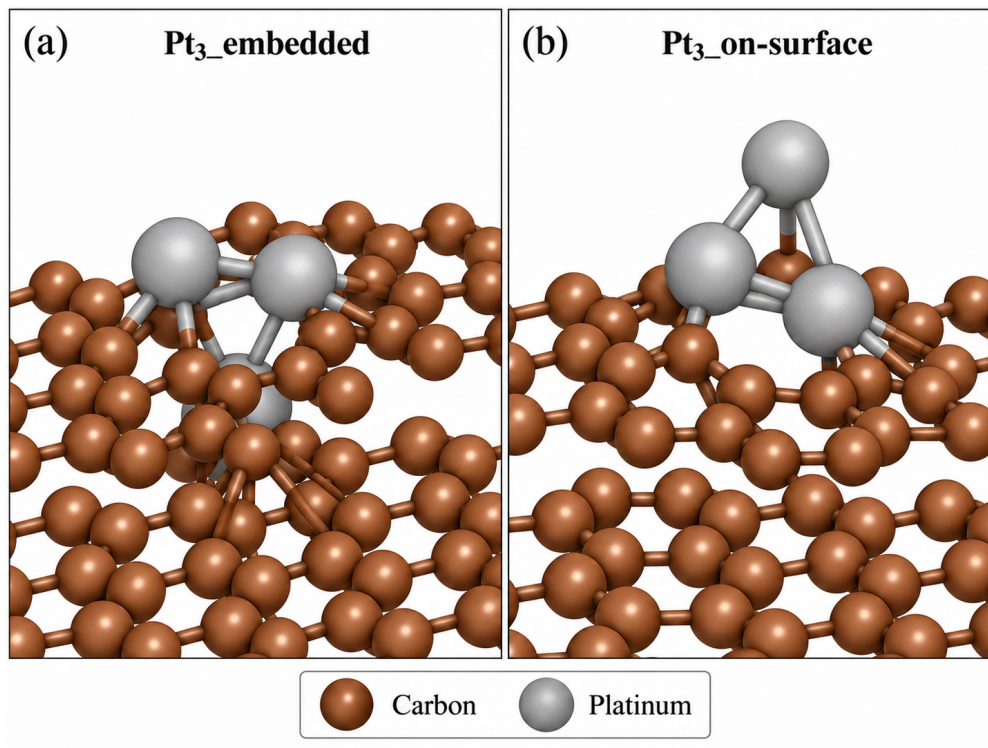


Figure 4.4: Configurations of the two clusters explored in this study. The Pt atoms in the cluster are more penetrated into the graphene layers when in the embedded configuration (a), while they are open to the adsorbates in the on-surface configuration (b). Carbon atoms are colored in brown, and platinum atoms are colored in grey.

4.3.3 Ethanol Oxidation Reaction Pathways

To study the ethanol oxidation reaction pathways, we sampled structures with reaction species in each reaction state, in addition to the OH groups, using the grand canonical basin hopping method [145, 146]. For each reaction state, we considered a total of 6 cases (3 different OH coverages x 2 different cluster configurations = 6 cases). We chose three potentials, 0.6, 0.8, and 1.2 V vs SHE, to represent the low-, intermediate-, and high-potential regions of the ethanol oxidation reaction, respectively. The EOR pathway at 0.6 V vs SHE is shown in Figure 4.5.

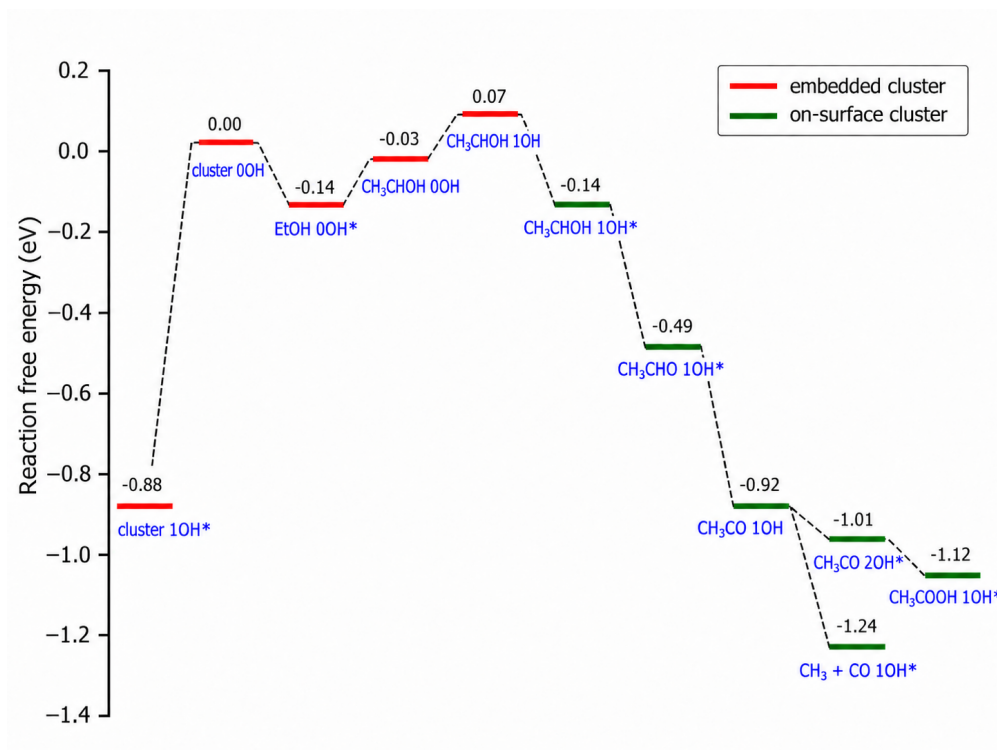


Figure 4.5: Ethanol oxidation reaction pathways at 0.6 V vs SHE. The reaction states labeled with * indicate that they are the most stable among all 6 cases, while other states help transition from one stable state to another. Embedded and on-surface cluster configurations are labeled in red and green, respectively.

The overall free-energy span along the pathway is 0.95 eV, ranging from -0.88 to 0.07 eV. The most stable initial catalyst state is the embedded Pt₃ cluster with one adsorbed OH group. Prior to ethanol adsorption, removal of the OH group leads to the bare embedded cluster, which is used as the reference state for the reaction free energies. Ethanol then adsorbs on the embedded cluster with no OH coverage. An alternative sequence, in which ethanol adsorption precedes OH removal, was also considered but was found to be thermodynamically less favorable. Therefore, the pathway involving OH removal followed by ethanol adsorption is shown in the reaction profile. Subsequent dehydrogenation of ethanol forms

the CH_3CHOH intermediate on the embedded cluster. Adsorption of one OH group then yields the $\text{CH}_3\text{CHOH-1OH}$ state. At this point, restructuring of the Pt_3 cluster from the embedded to the on-surface configuration lowers the free energy from 0.07 to -0.14 eV, corresponding to a stabilization of 0.21 eV. This result demonstrates that the preferred cluster configuration can depend on the adsorbed reaction intermediate. The subsequent oxidation steps proceed on the on-surface cluster without further changes in OH coverage or cluster configuration, leading to CH_3CHO and then CH_3CO .

The acetyl intermediate, CH_3CO , represents a key branching point between the C_1 and C_2 pathways. C–C bond cleavage produces CH_3 and CO , corresponding to the C_1 pathway and ultimately enabling complete oxidation to CO_2 . Alternatively, further oxidation preserves the C–C bond and leads toward acetic acid through the C_2 pathway. At 0.6 V, the C_1 products, $\text{CH}_3 + \text{CO}$, have a relative free energy of -1.24 eV, whereas CH_3COOH lies at -1.12 eV. Thus, the C–C cleavage products are thermodynamically favored by 0.12 eV at this potential, indicating that the complete-oxidation pathway is more favorable than the partial-oxidation pathway under these conditions. Here, the energy difference demonstrates a thermodynamic preference rather than a kinetic preference, as we do not have information on the barriers of these reactions. The free-energy profile presented here describes the thermodynamic preference of the sampled catalyst states and reaction intermediates. Kinetic barriers associated with cluster restructuring were not explicitly calculated. The detailed structures of some key states are shown in Figure C.1.

We also explored the EOR pathway solely on the embedded cluster, meaning no configuration change was allowed. The reaction profile is shown in Figure C.2. Comparing it to Fig. 4.5, they differed only in the second half of the pathway, where the cluster configuration occurred in Figure 4.5. The two pathways had the same free energy range; however, we observed that in the pathway of the embedded cluster, acetic acid had a lower energy than

the C_1 products. Despite missing information on the transition states, the oxidation step could be more favorable than the cleavage step on the embedded cluster. Figures C.3 and C.4 demonstrate the EOR pathway at 0.8 and 1.2 V vs SHE. The two pathways had free energy ranges of 0.87 and 0.63 eV, respectively. The energy ranges decreased with increasing electrode potential. However, the C_1 products formed from acetyl (CH_3CO) became less stable than acetic acid (CH_3COOH), making the complete oxidation not readily accessible. To reach the complete oxidation of ethanol, there were two vital requirements: one was that the potential could not be too high; otherwise, the reaction would undergo partial oxidation; the other was that the cluster configuration was allowed to change.

4.4 Experimental Validation

Our experimental collaborators measured cyclic voltammetry (CV) to study the oxidation and reduction processes in the ethanol oxidation reaction [147]. CV is the most commonly used and versatile technique in electrochemistry to study the mechanism of redox reactions and probe corresponding active species [148, 149]. Figure 4.6 shows the CV results for Pt_4/N -HOPG.

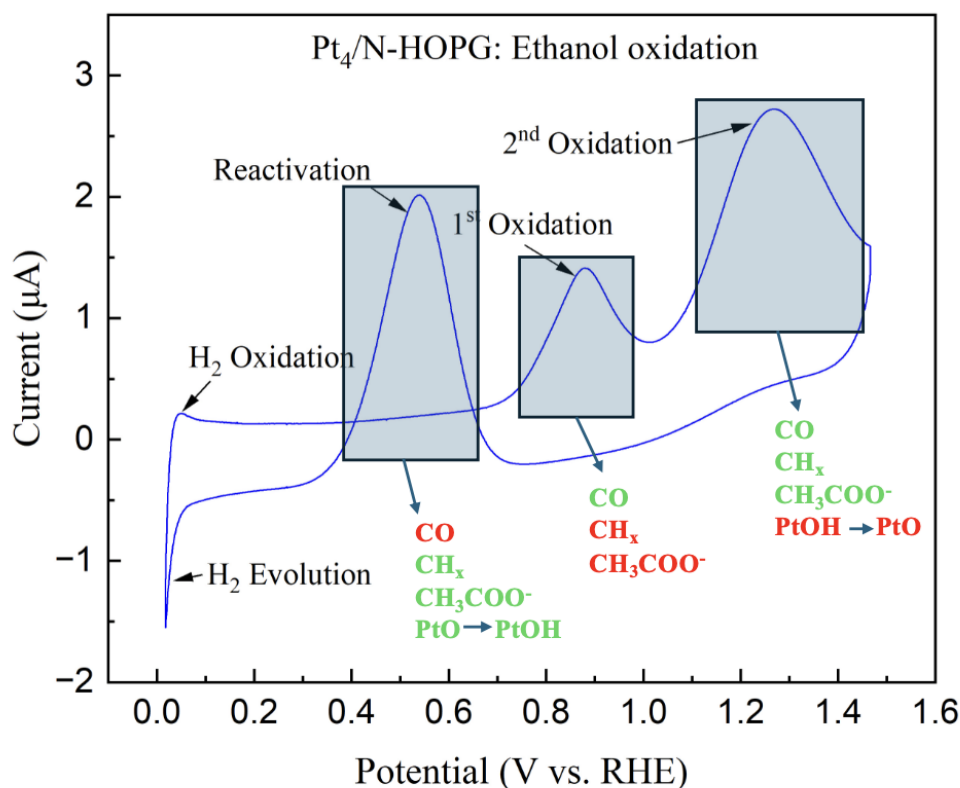


Figure 4.6: Cyclic voltammetry of Pt₄/N – HOPG. Three major peaks were observed: (1) 1st oxidation; (2) 2nd oxidation; and (3) reactivation. In each peak, the species in green are oxidized or reduced, and the species in red poison the catalysts and stop the reactions.

The CV shows three characteristic regions. At intermediate potentials, the first oxidation peak is associated with the oxidation of strongly adsorbed intermediates, including CO-containing species. At higher potentials, a second oxidation peak appears, where more oxidized surface species and ethanol-derived intermediates such as CH_x and acetate-related species can be further oxidized. At the same time, the Pt surface becomes increasingly oxidized. During the reverse scan, reduction of Pt oxide reactivates Pt active sites. However, strongly adsorbed CO can remain on the surface and poison the catalyst, limiting further ethanol oxidation. These experimental results show several qualitative consistencies with our calculations. First, the second oxidation peak appears at high potential, where the

Pt surface becomes more oxidized. This agrees with our calculation that higher potentials stabilize higher OH coverages on the Pt cluster. Second, the stronger oxidation current at high potential is consistent with the much more downhill reaction profile predicted at 1.2 V, indicating a stronger thermodynamic driving force for ethanol oxidation. More importantly, acetate-related species are observed in the high-potential oxidation region. This is consistent with our calculated change in selectivity: at 0.6 V, the C_1 products are more stable, whereas at 1.2 V, the C_2 partial-oxidation products become more favorable. Our calculations also show that the oxidation of adsorbed CO becomes favorable only at higher potentials. This is consistent with the CV, where CO-containing species are oxidized in the intermediate-to-high potential region. At lower potentials, CO can remain strongly adsorbed on the Pt cluster and block active sites, leading to catalyst poisoning.

4.5 Conclusions

In this work, we explored the stability of Pt_n on the pristine and defective graphite surfaces, the optimal coverage of OH on the cluster catalysts, and finally the ethanol oxidation reaction pathways at various potentials. Our study showed that the formation of Pt_n clusters on the defective graphite was feasible given the initial kinetic energy used in the hard-landing experiments. We extended our study to the Pt_3 clusters on the tri-vacancy graphite surface. We computed the reaction profile considering a total of 6 cases for each reaction state, at 3 different potentials. At low potentials, the reaction had to overcome a large overall barrier, but the complete oxidation pathway was favorable. However, at high potentials, the reaction had a reduced barrier, but the C_1 products were higher in energy than the C_2 products. We also found that the conditions required for complete oxidation were harsh - low or intermediate potentials and possible configuration change. Both experiments and calculations showed that CO produced at low potentials could potentially poison the catalyst and could be oxidized at higher potentials.

CHAPTER 5

Conclusions

In this dissertation, we employed DFT calculations to investigate hydrogen reactivity over Pd–Au catalysts in Chapter 2. Our calculations demonstrated that surface hydrogen adsorption was much more stable than subsurface hydrogen adsorption. Therefore, subsurface hydrogen population could only occur after the surface was fully covered. We examined two plausible mechanisms for hydride formation and decomposition and found that the barrier was lower when only one surface vacancy was allowed to form at a time. We also found that hydride decomposition had a higher barrier under He modulation conditions than hydride formation under H₂ incorporation conditions. This observation revealed a pronounced cork effect: once incorporated into the subsurface, hydrogen had to overcome a significantly higher barrier to desorb. This cork effect was also observed experimentally. Hydride decomposition proceeded at a slower rate and exhibited an induction period that was not observed during hydride incorporation. We further found that hydrogen vibrations became increasingly important as the amount of hydrogen incorporated into the system increased, particularly when the surface layer was fully covered and subsurface hydrogen became populated. Under these conditions, accounting for vibrational entropy and zero-point energy corrections could potentially improve the prediction of the optimal hydrogen coverage under experimental conditions. Finally, we found that the stability region of hydride structures became broader as the Pd thickness increased. Under the experimental modulation conditions, some models with smaller Pd thickness would not undergo the corresponding modulation, suggesting that Pd thickness plays an important role in determining the accessibility and stability of the hydride phase.

In Chapter 3, we extended our investigation of the impact of subsurface hydrogen content on hydrogen–deuterium exchange reactions. We explored the temperature-dependent adsorption energies of our Pd–Au models and observed that the most stable configuration transitioned gradually from 4 ML to 1 ML as the temperature increased. For the hydrogen desorption process, we found that the 1L Pd model exhibited a significantly higher barrier. This can be primarily attributed to the absence of subsurface hydrogen atoms that could migrate to the surface and fill the vacancy created during desorption, resulting in a substantial destabilization of the surface. In contrast, thicker models could benefit from subsurface hydrogen atoms to stabilize the surface during desorption, leading to lower barriers and, consequently, higher desorption rates. Among thicker models, we found that the stability region of hydride structures broadened with increasing numbers of Pd layers, indicating the capability of accommodating more hydrogen content in the subsurface and, eventually, higher desorption rates. Our computational results explained the trend observed in the experiments, where TOFs increased with increasing Pd thickness, from 1L up to 6L. Additionally, we performed enthalpy barrier analysis to compare with experiments, and we found that temperature-dependent enthalpy and temperature-dependent H coverage imposed opposite effects. Both effects were quite small and within the DFT accuracy, and it was not possible to determine which effect was the dominant factor.

In Chapter 4, we switched the topic to the electrocatalytic oxidation of ethanol on Pt_n cluster supported on graphite. We first studied the stability of the defective graphite surfaces. Our calculations elucidated that the cost of forming vacancies increased for every two carbon atoms that were removed from the pristine surface. We also observed that the Pt_n clusters interacted strongly with the defective surface, curing the defects by forming bonds with the dangling carbon atoms. Yet, the stabilization effects from the cluster could barely offset the cost of forming the defects. Some cases showed very small overall formation energy,

which was very promising considering the initial kinetic energy imposed on the cluster in the hard-landing experiments that could help offset the small formation energy. Additionally, we studied the ethanol oxidation reaction pathway at various EOR potentials by using the CHE model and the surface charging method. We found that at low potentials (eg., 0.6 eV vs SHE), the overall free energy range was quite large (0.95 eV), but the complete oxidation pathway was more favorable, considering that the C_1 products were 0.12 eV lower in energy. Nonetheless, at high potentials (eg., 1.2 V vs SHE), the overall free energy range was reduced to 0.63 eV, but the C_1 products were higher in energy in this case, indicating a potential partial oxidation pathway. Our calculations provided more insight into the three current peaks measured in the experiments, where the calculations suggested that the CO produced at low potentials would poison the catalysts and could not be removed until higher potentials were reached.

Altogether, in this dissertation, we utilized computational tools to explore the hydrogen reactivity on transition metal catalysts and the ethanol oxidation reaction on cluster catalysts, encompassing both thermal catalysis and electrocatalysis. The former topic was important for the design, development, and improvement of catalysts used in hydrogenation and dehydrogenation reactions. The latter encountered several challenges. Not only are the reaction kinetics slow and complete oxidation difficult to achieve, but the liquid-phase environment also poses significant challenges for computational modeling with existing methods. Through the studies presented in this dissertation, we demonstrated how computational approaches could provide molecular-level insights into these complex catalytic processes and help identify the factors governing catalyst reactivity and reaction pathways. Together, these results highlighted the value of computational modeling as a complementary yet necessary tool for understanding and ultimately improving catalytic systems.

APPENDIX A

Supplementary Information for Chapter 2

A.1 Computational Details

In addition to the computational methods detailed in Chapter 2, we also examine the dissociative adsorption energy of H_2 on Pd(111), defined as the change in energy from an isolated slab and a gas-phase H_2 to a combined system interacting as atomic H adsorbed on the slab:

$$E_{ads} = E[H_{(ads)}/Pd(111)] - E[Pd(111)] - \frac{1}{2}E[H_{2(g)}]$$

PBE-dDsC provides an H adsorption energy of -0.60 eV at the low-coverage limit, within 0.13 eV of the experimental benchmark of -0.47 eV [150]. Based on these results, we conclude that PBE-dDsC is an appropriate reference functional that can provide a reasonable comparison with experimental data for H_2 chemisorption on the Pd-Au system.

We perform transition state modeling using the VASP Transition State Tool (VTST) as well. Transition state pathways are first optimized via the climbing-image nudged elastic band (CI-NEB) method, using three intermediate images generated by linear interpolation using a spring constant of $5 \text{ eV}/\text{\AA}^2$ [151, 152]. The total forces, defined as the sum of the spring force along the chain and the true force orthogonal to the chain, are converged to $0.05 \text{ eV}/\text{\AA}$. Then, the image with the highest energy is fully optimized to a first-order saddle point via the dimer method, this time converging the total energy and forces to 10^{-7} eV and $0.01 \text{ eV}/\text{\AA}$, respectively [153]. We confirm that the normal modes of all transition states contain one and only one imaginary frequency by calculating the Hessian matrix within the

harmonic approximation, using a central difference of 0.01 Å at the same level of accuracy as the dimer method.

Vibrational frequencies are obtained for all relaxed structures by calculating the Hessian matrix similarly. Given the large difference in the masses of the adsorbates and the metal substrate, only the adsorbate degrees of freedom are considered in the calculations. If any imaginary frequencies are present, the structure is displayed along the normal mode of the largest imaginary frequency and re-optimized by converging the total energy and forces to 10^{-7} eV and 0.01 eV/Å, respectively. The process is repeated until all imaginary frequencies are eliminated.

Conversion from the electronic energy at 0 K (E_{DFT}) to the Gibbs free energy (G) at a given temperature T and pressure P is given by:

$$G(T, P) = E_{DFT} + E_{ZPC} + \int_0^T (c_V + k_B) dT - T \cdot S(T, P)$$

See **Table A.1** for the statistical thermodynamic expressions of integrated constant-volume heat capacity (c_V) and the entropy (S). Translational and rotational degrees of freedom are included for gas-phase H₂ only. Zero-point energy correction (E_{EPC}) is given by:

$$E_{ZPC} = \frac{1}{2} \sum_i h\nu_i$$

where h is the Planck constant, k_B is the Boltzmann constant, and ν_i is the non-imaginary vibrational frequency of normal mode i . See **Figure A.1** for the calculations of the Gibbs free energy of surface formation.

A.2 Entropy Calculations in DFT

Table A.1: Statistical thermodynamic expressions of the translational, rotational, and vibrational components of the integrated constant-volume heat capacity ($\int_0^T c_V dT$) and the entropy (S) employed for free energy conversion [154]. m = molecular mass, I = principal moment of inertia, σ = symmetry number ($\sigma = 2$ for H_2).

Component	$\int_0^T c_V dT$	S
Translational (3D)	$\frac{3}{2}k_B T$	$k_B \left\{ \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \right] + \frac{5}{2} \right\}$
Rotational (linear)	$k_B T$	$k_B \left\{ \ln \left[\frac{8\pi^2 I k_B T}{\sigma h^2} \right] + \frac{3}{2} \right\}$
Vibrational (harmonic)	$\sum_i \frac{h\nu_i}{e^{h\nu_i/(k_B T)} - 1}$	$k_B \sum_i \left[\frac{h\nu_i/(k_B T)}{e^{h\nu_i/(k_B T)} - 1} - \ln (1 - e^{-h\nu_i/(k_B T)}) \right]$

A.3 Free Energy of Formation Calculations

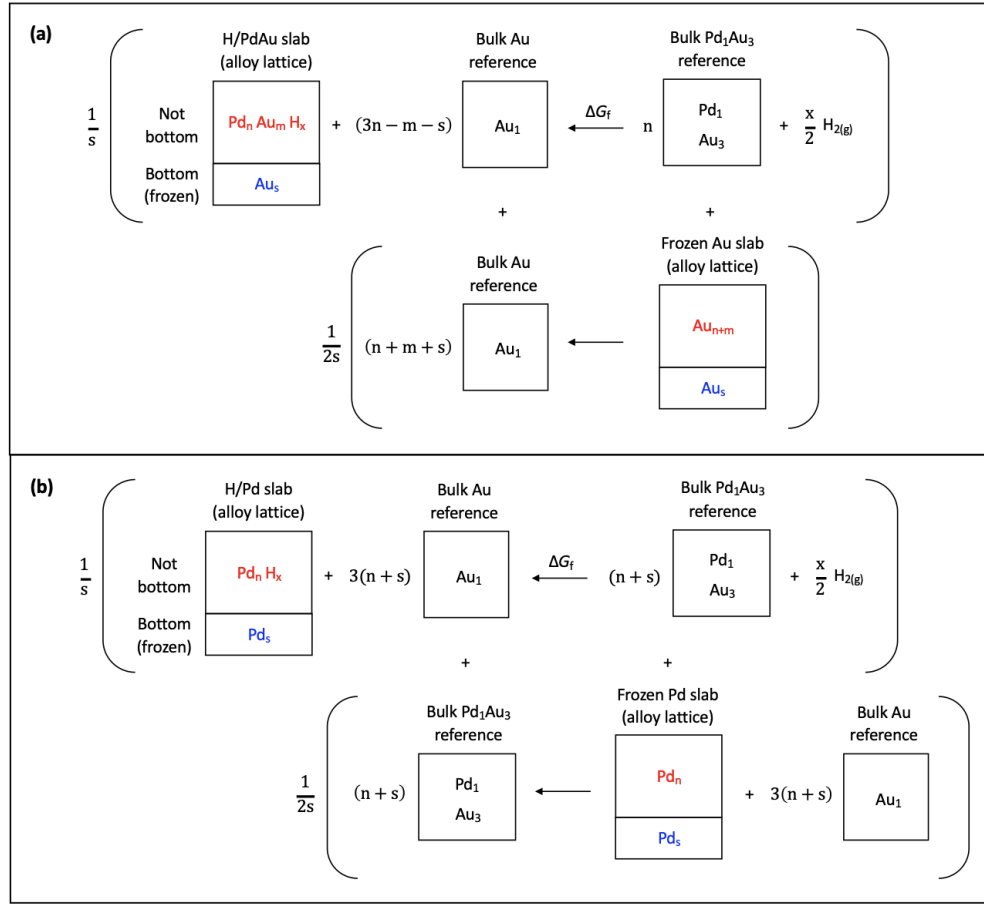


Figure A.1: Formulation of the Gibbs free energy of surface formation, normalized by the number of surface atoms (s), for slab models of (a) H/PdAu and (b) H/Pd. Bulk Au and Pd_1Au_3 alloy and gas-phase H_2 are chosen as reference. The surface energy associated with the frozen bottommost layer of the slab (blue) is subtracted out using a corresponding frozen monometallic slab.

A.4 Stability Assessment

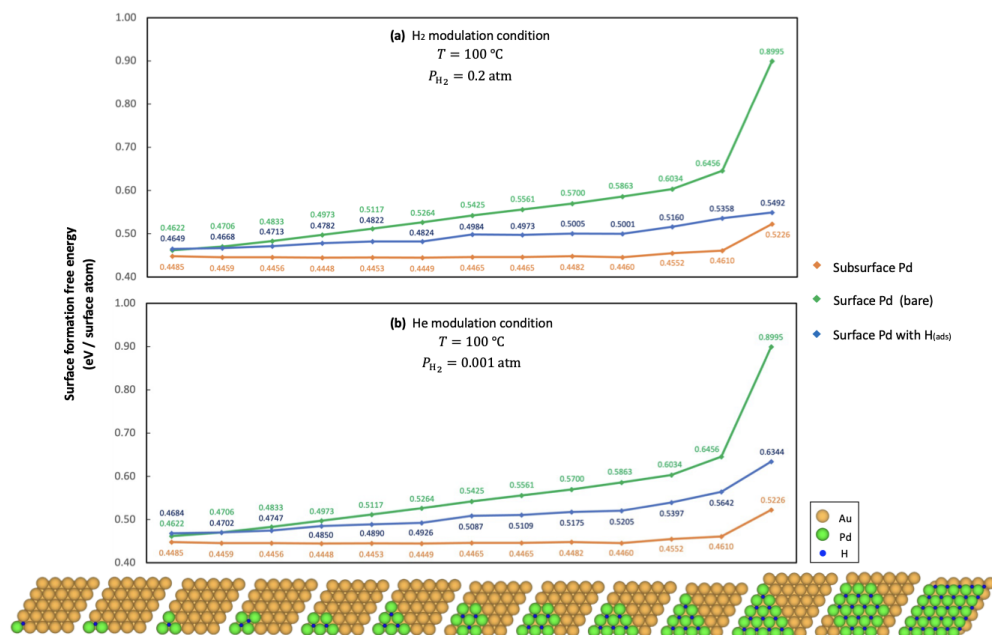


Figure A.2: DFT-computed Gibbs free energy of surface formation (eV/surface atom, see **Figure A.1**) of slab models for localized Pd ensembles of varying sizes under the two modulation conditions of interest. Surface Pd with chemisorbed H (blue points) becomes relatively close in stability to subsurface Pd (orange points) under the H₂ modulation condition only for the extended Pd monolayer (rightmost structure). Under the He modulation condition, subsurface Pd remains thermodynamically favored.

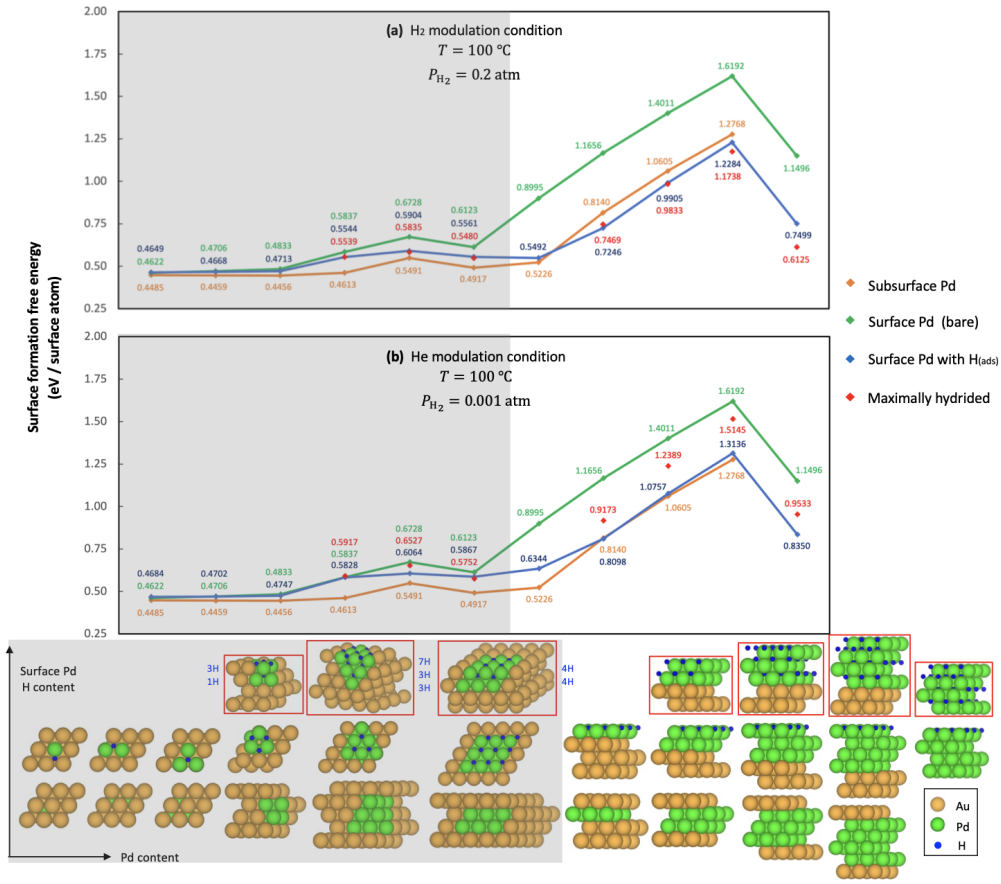


Figure A.3: DFT-computed Gibbs free energy of surface formation (eV/surface atom, see **Figure A.1**) of slab models with varying surface/subsurface Pd and H concentrations under the two modulation conditions of interest. Localized Pd ensembles are shaded in gray. Maximally hydride structures are boxed in red. For a given type of structure, surface Pd with chemisorbed H (blue points) becomes more stable than subsurface Pd (orange points) under H₂ modulation condition only for the extended Pd structures (Pd bilayers and beyond), with maximally hydride surface Pd (red points) being slightly more stable. Under the He modulation condition, subsurface Pd remains slightly more thermodynamically favored.

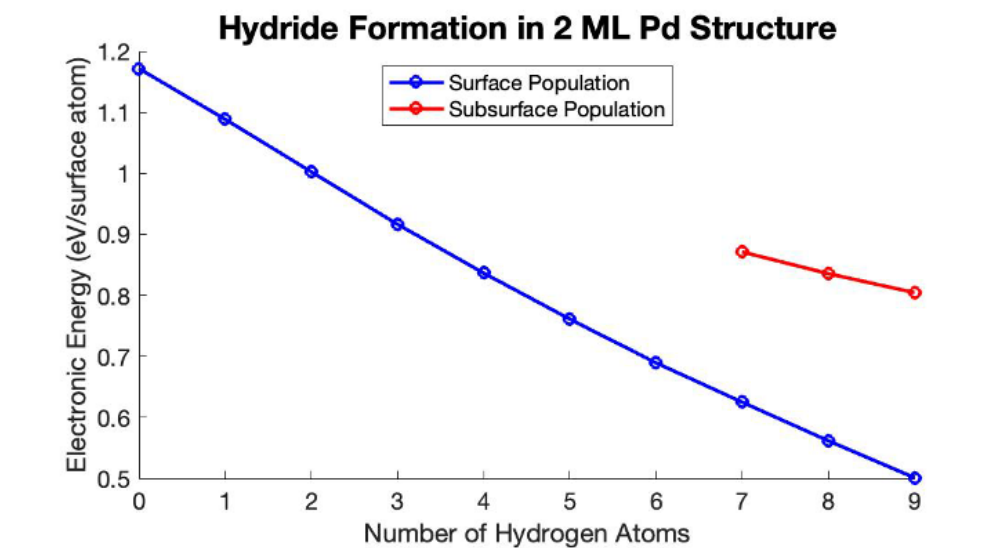


Figure A.4: Hydride formation energy as a function of hydrogen coverages for the 2ML Pd structure. The blue line represents the hydrogen atoms that situated in the surface, and the red line represents the hydrogen atoms that situated in the subsurface. Stable subsurface populations are not located under low coverages.

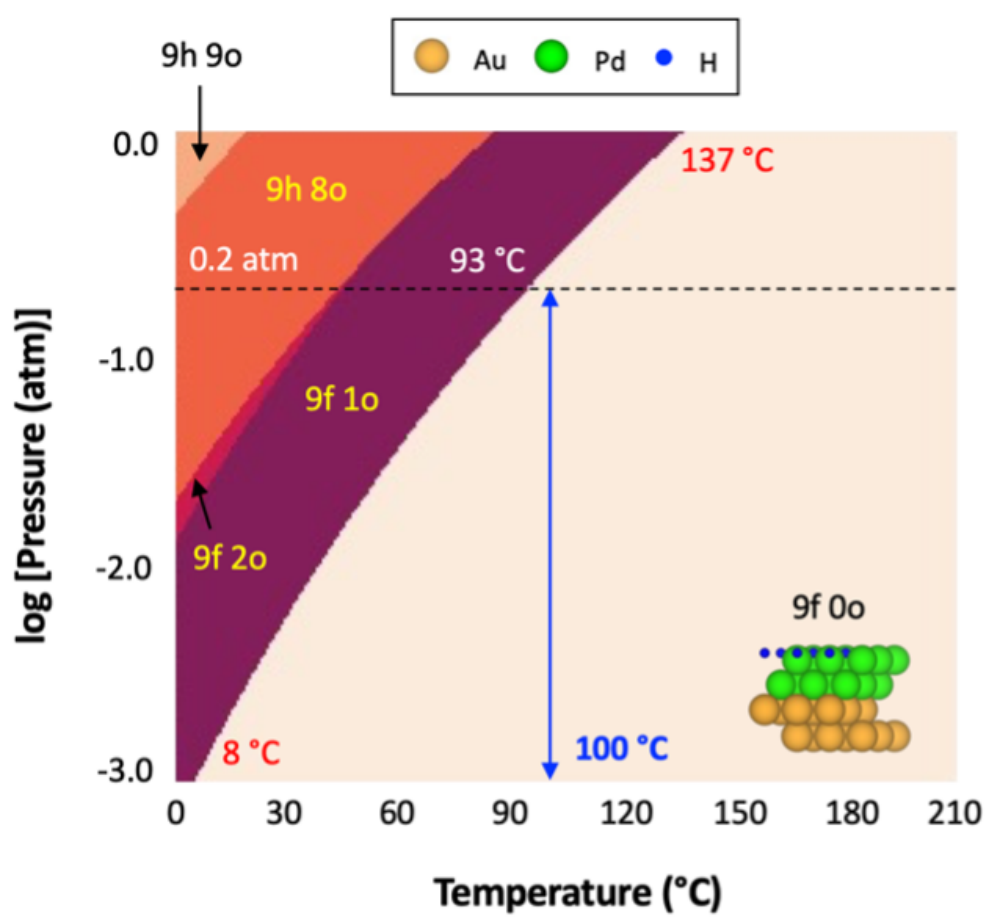


Figure A.5: Stability diagram computed from ab initio thermodynamics for the Pd bilayer structure with varying surface/subsurface H concentrations. The blue arrow indicates the experimental modulation conditions at 100 °C. Each layer can have a maximum of 9 H atoms in the 3×3 unit cell employed in the simulation.

A.5 Hydride Decomposition Process

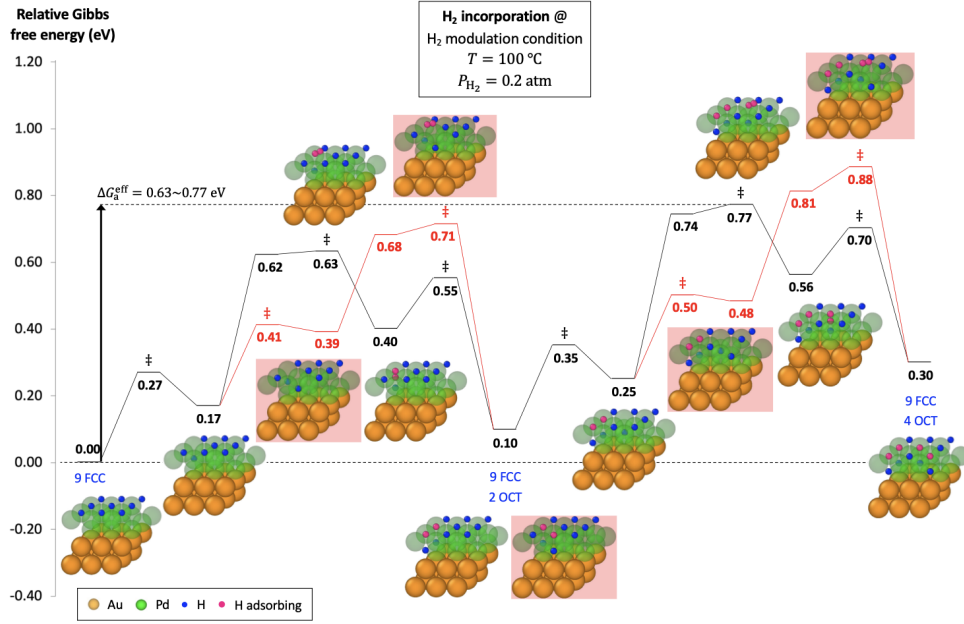


Figure A.6: DFT-computed pathway for H incorporation into the subsurface of Pd bilayer structure under the H₂ modulation condition. The Gibbs free energy of surface-chemisorbed structure (9 FCC) and gas-phase H₂ is set as the reference. The overall process of adding 4H is endergonic by 0.30 eV, and the effective free energy barrier is 0.77 eV. Two possible pathways are considered for each 2H addition: creation of a surface vacancy followed by H₂ activation and concerted downward migration (black pathway); or creation of two surface vacancies followed by H₂ activation (red pathway). Pd atoms are semi-transparent to allow subsurface H atoms to be visible. Each intermediate structure is indicated by the number of H atoms and the corresponding type of site. Each layer can have a maximum of 9 H atoms in the 3×3 unit cell employed. FCC = FCC hollow site; OCT = subsurface octahedral site.

A.6 Hydrogen Penetration Process

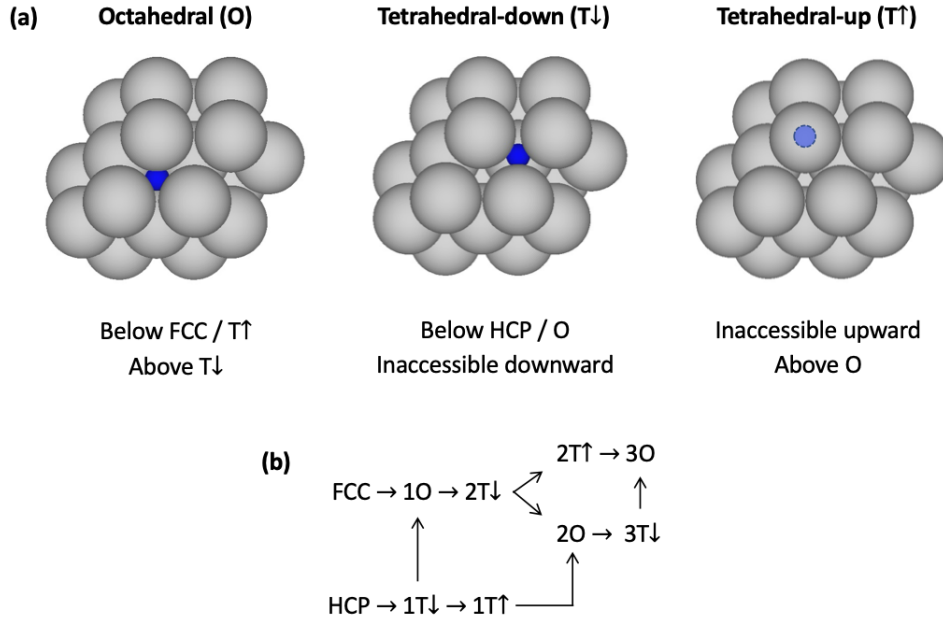


Figure A.7: Subsurface sites for hydrogen atoms and pathways for hydrogen penetration from surface to subsurface. (a) Three types of subsurface sites considered in mechanistic modeling of diffusion at the dilute limit. (b) Ideal pathways for migration from surface sites (FCC or HCP hollow) to subsurface sites, numbered by the layer number.

APPENDIX B

Supplementary Information for Chapter 3

B.1 Hydrogen Desorption on the 1L Pd System

The hydrogen desorption process is investigated on the 1L Pd system. The calculations are performed on a 3x3 periodic slab, and the structure consists of a 3-layer Au core with a 1-layer Pd shell on top and 9 hydrogen atoms in fcc positions. The process starts with molecular desorption from a fully covered structure with 9 fcc hydrogen atoms, with an energy barrier of 1.35 eV. Afterward, two adjacent surface vacancies form. A hydrogen migration process is followed to separate the vacancies, and the final structure is 0.09 eV more stable than the counterpart with adjacent vacancies. The energy values reflect the conditions at 150 °C and 0.20 atm. The vibrational effects are not included because the number of hydrogen atoms is not large enough. The free energy profile is shown in **Figure B.1**. The transition states are obtained using the method described in **Appendix A.1**.

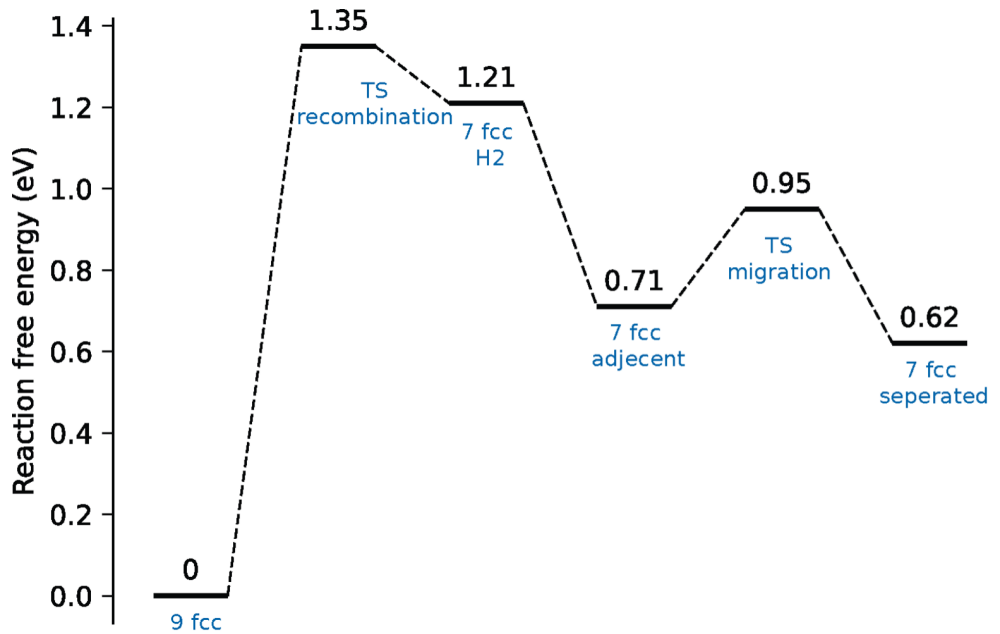
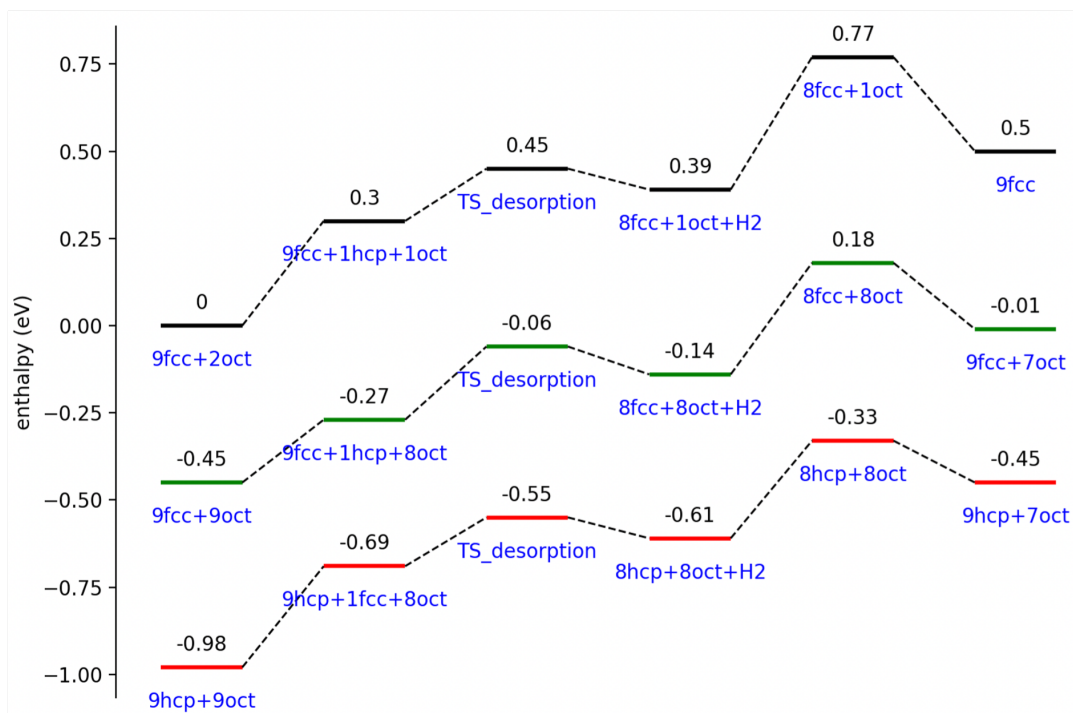


Figure B.1: Energy barrier calculations on a 1L Pd system. DFT-computed reaction free energy profile for the hydrogen desorption process on a 1L Pd shell.

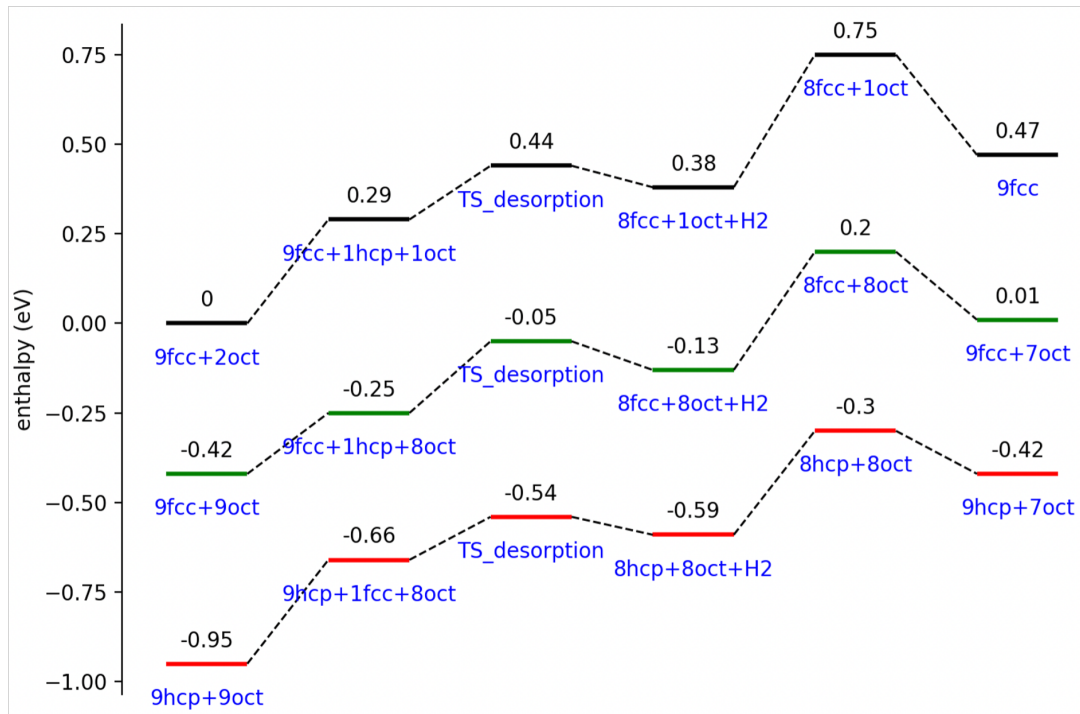
B.2 Hydrogen Desorption on the 5L Pd System

The hydrogen desorption process is also studied on the 5L Pd system. We propose three different cases: the 9fcc+2oct structure to the 9fcc structure; the 9fcc+9oct structure to the 9fcc+7oct structure; and the 9hcp+9oct structure to the 9hcp+7oct structure, shown in black, green, and red, respectively. The process starts with a hydrogen migration - a subsurface octahedral hydrogen moving to a surface site, forming a metastable structure beyond full coverage. A molecular H₂ desorption occurs in a very similar fashion to that on the 1L Pd system. The enthalpy profiles for the three cases are calculated at 100 °C, 150 °C, and 200 °C, shown in panels (a), (b), and (c) of **Figure B.2**, respectively. The enthalpy barriers of the three pathways are summarized in **Table B.1**, and the values are extracted from **Figure B.2**. The transition states are obtained using the method described in **Appendix A.1**.

(a)



(b)



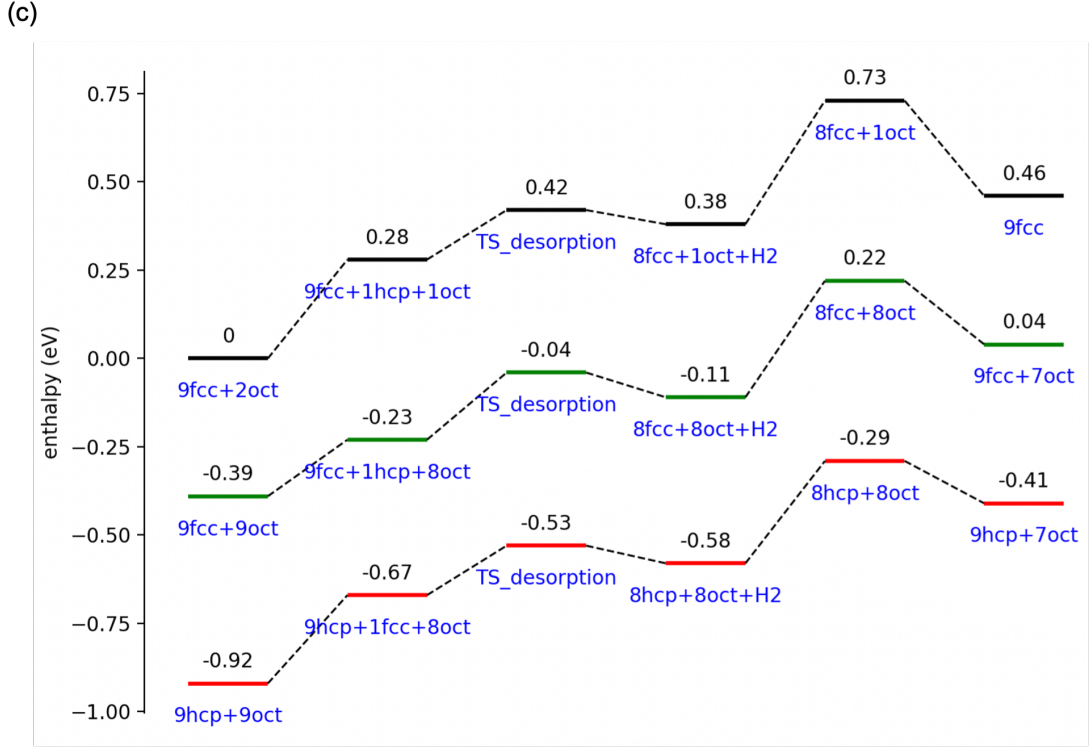


Figure B.2: Enthalpy profiles of the hydrogen desorption process on the 5L Pd model. (a) at 100 °C, (b) at 150 °C, and (c) at 200 °C. The black, green, and red pathways represent the enthalpy profiles of H_2 desorption for the 9fcc+2oct structure, the 9fcc+9oct structure, and the 9fcc+9hcp structure, respectively.

Table B.1: Calculated enthalpy barriers of the three different desorption pathways for the 5L Pd model. Enthalpy barriers for different structural transformations at 100, 150, and 200 °C.

	100 °C	150 °C	200 °C
9fcc + 2oct $\rightarrow$ 9fcc	0.45 eV	0.44 eV	0.42 eV
9fcc + 9oct $\rightarrow$ 9fcc + 7oct	0.40 eV	0.37 eV	0.35 eV
9hcp + 9oct $\rightarrow$ 9hcp + 7oct	0.43 eV	0.41 eV	0.39 eV

B.3 Model Schematic, Nomenclature, and Possible Configurations of Structures with Different Occupations

Figure B.3 demonstrates the schematics of the 5L Pd model. The nomenclature is defined according to which interlayers are occupied in the structure. We explore all the possible configurations with different interlayer occupations for 2 H-layers, 3 H-layers, and 4 H-layers. The internal energies of adsorption are listed in **Table B.2**, with the most stable conformation colored in green. The only exception is among the 2H-layer structures, where the fcc + partial 2nd + partial 3rd structure is slightly more stable than the fcc + 3rd interlayer structure. To maintain simplicity and consistency, we continue the study with the fcc + 3rd interlayer structure.

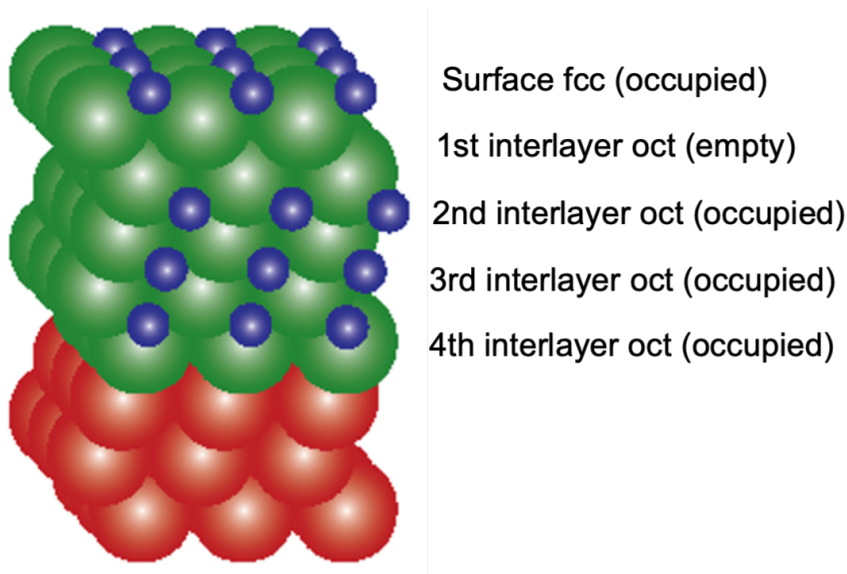


Figure B.3: Model schematic and nomenclature of the hydride structures. The schematic represents the fcc + 2nd + 3rd + 4th interlayer structure. The surface hydrogen can occupy the fcc hollow or the hcp hollow sites, but the subsurface hydrogen will only occupy the oct sites. H, Pd, and Au atoms are colored in blue, green, and red, respectively.

Table B.2: DFT-computed internal energies of adsorption with different interlayer occupations for 2 H-layers, 3 H-layers, and 4 H-layers. The table follows the nomenclature detailed in Figure B.3. The adsorption energy refers to a (3x3) unit cell, i.e., 9 H atoms per layer.

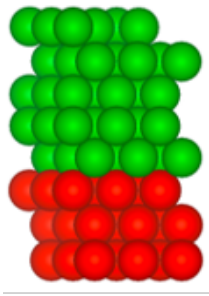
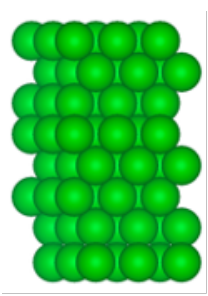
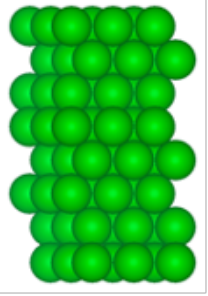
2 H-layers			
Occupied layers	Energy (eV)	Occupied layers	Energy (eV)
fcc + 1st interlayer	-6.7051	hcp + 1st interlayer	-6.7191
fcc + 2nd interlayer	-7.8688	hcp + 2nd interlayer	-7.4897
fcc + 3rd interlayer	-8.2010	hcp + 3rd interlayer	-7.5065
fcc + 4th interlayer	-7.5262	hcp + 4th interlayer	-7.0034
fcc + partial 2nd + partial 3rd interlayers	-8.2874		
3 H-layers			
Occupied layers	Energy (eV)	Occupied layers	Energy (eV)
fcc + 1st + 2nd interlayers	-8.5720	hcp + 1st + 2nd interlayers	-8.6569
fcc + 1st + 3rd interlayers	-9.3175	hcp + 1st + 3rd interlayers	-9.4430
fcc + 1st + 4th interlayers	-9.2709	hcp + 1st + 4th interlayers	-9.2457
fcc + 2nd + 3rd interlayers	-10.3589	hcp + 2nd + 3rd interlayers	-10.1037
fcc + 2nd + 4th interlayers	-10.6836	hcp + 2nd + 4th interlayers	-10.2194
fcc + 3rd + 4th interlayers	-10.2113	hcp + 3rd + 4th interlayers	-9.6125

4 H-layers			
Occupied layers	Energy (eV)	Occupied layers	Energy (eV)
fcc + 1st + 2nd + 3rd interlayers	-11.0879	hcp + 1st + 2nd + 3rd interlayers	-11.3192
fcc + 1st + 2nd + 4th interlayers	-11.5411	hcp + 1st + 2nd + 4th interlayers	-11.7389
fcc + 1st + 3rd + 4th interlayers	-11.8243	hcp + 1st + 3rd + 4th interlayers	-11.8519
fcc + 2nd + 3rd + 4th interlayers	-12.3615	hcp + 2nd + 3rd + 4th interlayers	-12.2409

B.4 Strain Effects on Pd-Au and Pure Pd(111)

To study the strain effects on Pd-Au bimetallic systems, we employ DFT calculations to assess the free energy of adsorption of hydrogen for three different models: PdAu(111) with an Au lattice, pure Pd(111) with an Au lattice, and pure Pd(111) with a Pd lattice. The normalized adsorption free energies are shown in **Table B.3**. The stability diagram of the pure Pd(111) system with the Pd lattice is shown in **Figure B.4**.

Table B.3: DFT-computed internal adsorption energies of three different models. The first column shows the hydrogen adsorption energies of PdAu(111) (5 layers of Pd on 3 layers of Au) with an Au lattice spacing, representing the Au-Pd core-shell catalysts. The second and third columns show pure Pd(111) (8 layers) with the Au lattice and the Pd lattice constant, respectively. Hydrogen adsorption energies are displayed in eV/atom.

			
H coverage	PdAu(111) with Au lattice	Pure Pd(111) with Au lattice	Pure Pd(111) with Pd lattice
1 ML	-0.64	-0.66	-0.55
2 ML	-0.46	-0.45	-0.34
3 ML	-0.40	-0.40	-0.28
4 ML	-0.34	-0.35	-0.22

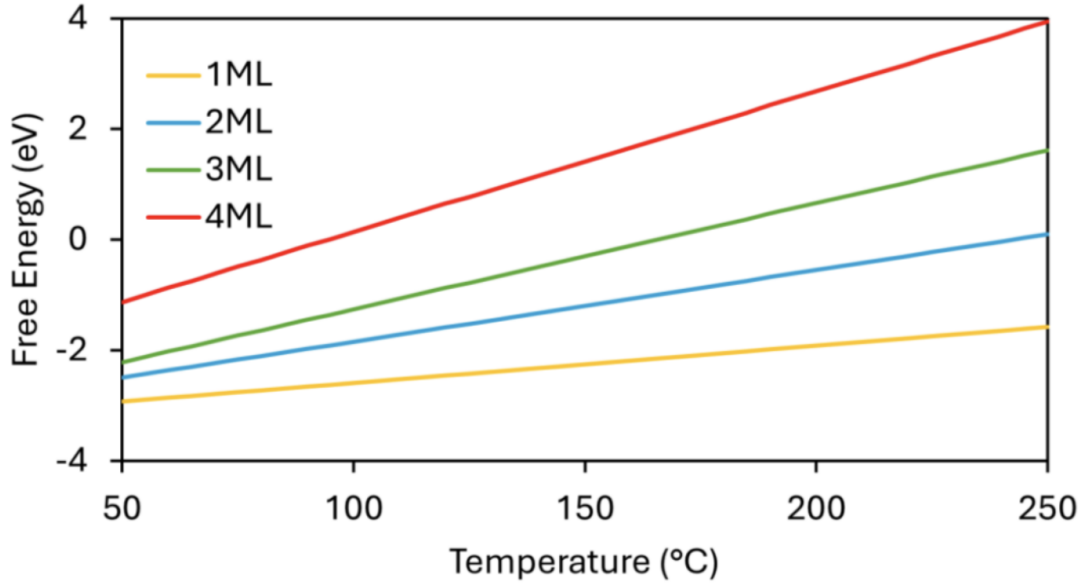


Figure B.4: Stability diagram of the pure Pd(111) system with the Pd lattice. The free energy of adsorption is calculated by $G_{\text{ads}} = G_{\text{total}} - G_{\text{clean}} - \frac{n}{2}\mu_{\text{H}_2}$, where G_{ads} , G_{total} , and G_{clean} are the free energy of adsorption, the free energy of the slab with adsorbed hydrogen contents, and the free energy of the clean slab, respectively, n is the number of hydrogen atoms adsorbed, and μ_{H_2} is the chemical potential of the gas-phase hydrogen molecule. Here, vibrations of hydrogen atoms in both adsorbed states and the gas phase are included. The calculations were performed with a hydrogen pressure of 0.2 atm.

APPENDIX C

Supplementary Information for Chapter 4

C.1 EOR Pathway at 0.6 V vs SHE

The configurations of some key intermediates for the pathway shown in **Figure 4.5** are shown in **Figure C.1**.

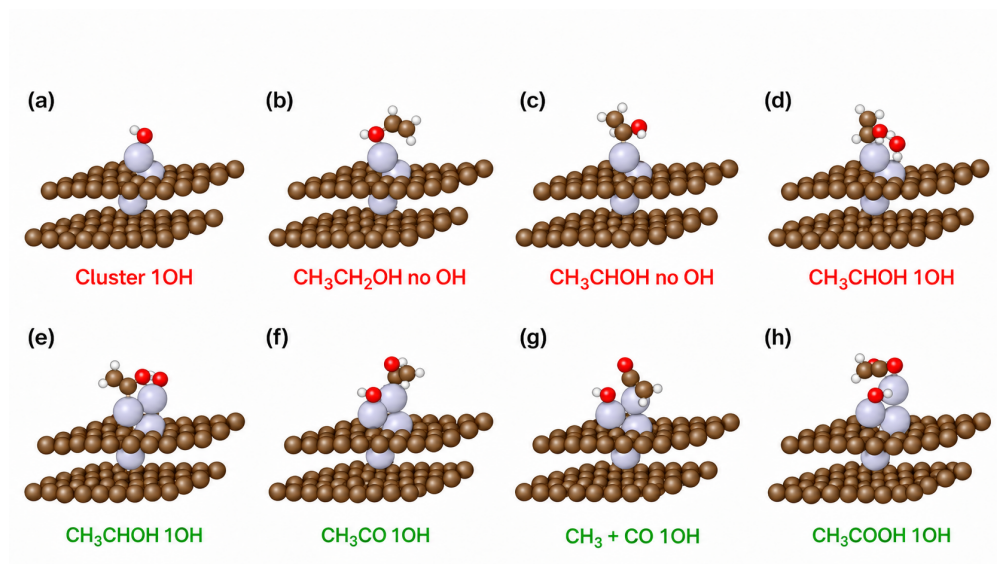


Figure C.1: Configurations of key intermediates for the EOR pathway at 0.6 V vs SHE. (a) cluster with 1OH on the embedded cluster; (b) $\text{CH}_3\text{CH}_2\text{OH}$ with 0OH on the embedded cluster; (c) CH_3CHOH with 0OH on the embedded cluster; (d) CH_3CHOH with 1OH on the embedded cluster; (e) CH_3CHOH with 1OH on the on-surface cluster; (f) CH_3CO with 1OH on the on-surface cluster; (g) $\text{CH}_3 + \text{CO}$ with 1OH on the on-surface cluster; and (h) CH_3COOH with 1OH on the on-surface cluster. Carbon, hydrogen, oxygen, and platinum atoms are colored in brown, white, red, and grey, respectively. Red and green text labels indicate the embedded and on-surface cluster configurations, respectively.

The constrained and unconstrained pathways of EOR at 0.6 V vs SHE are shown in **Figure C.2**.

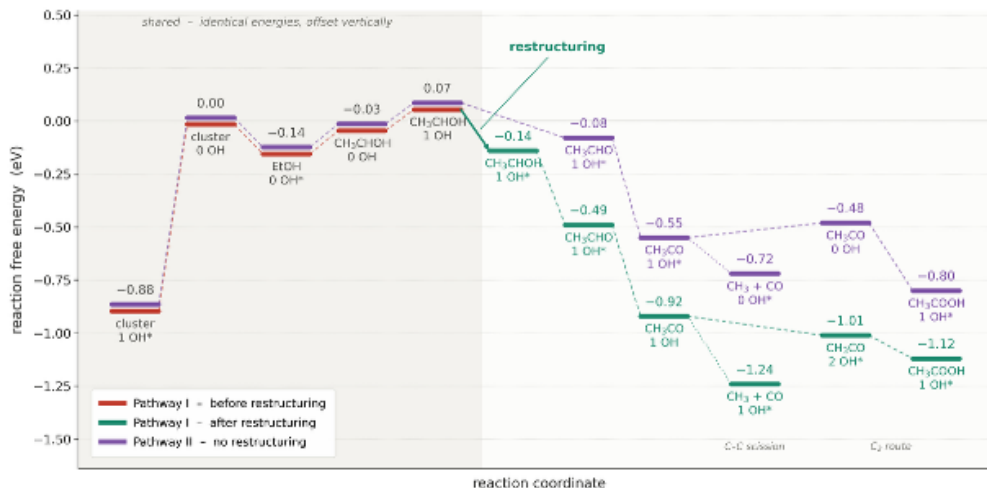


Figure C.2: Comparison between constrained and unconstrained pathways of EOR at 0.6 V vs SHE. The constrained pathway is colored in purple, and the unconstrained pathway is colored in red and green, with red representing the embedded cluster configuration and green representing the on-surface cluster configuration. The reaction states labeled with * indicate that they are the most stable among all 6 cases, while other states help transition from one stable state to another.

C.2 EOR Pathway at 0.8 V vs SHE

The EOR pathway at 0.8 V vs SHE on the embedded cluster is shown in **Figure C.3**.

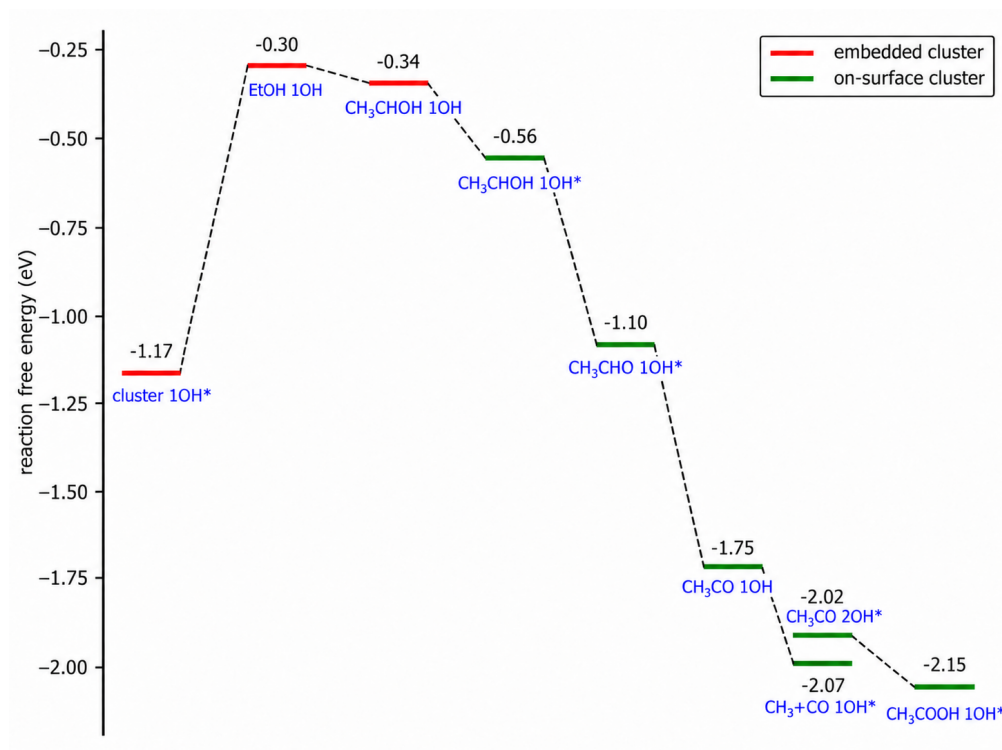


Figure C.3: Ethanol oxidation reaction pathways at 0.8 V vs SHE. The reaction states labeled with * indicate that they are the most stable among all 6 cases, while other states help transition from one stable state to another. Embedded and on-surface cluster configurations are labeled in red and green, respectively.

C.3 EOR Pathway at 1.2 V vs SHE

The EOR pathway at 1.2 V vs SHE on the embedded cluster is shown in **Figure C.4**.

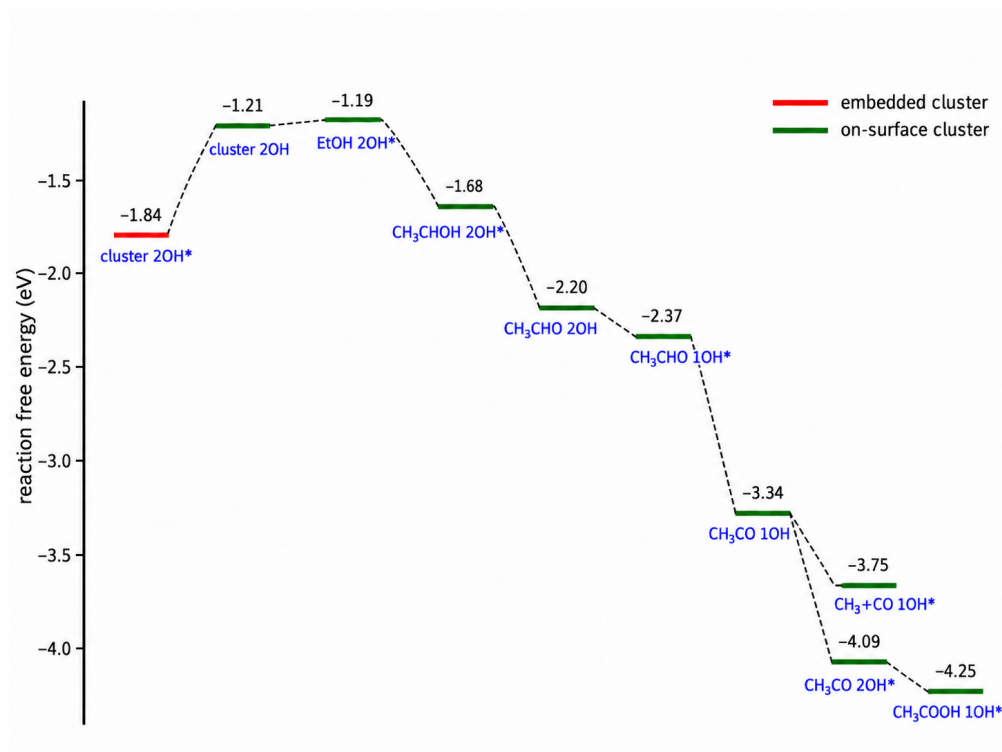


Figure C.4: Ethanol oxidation reaction pathways at 1.2 V vs SHE. The reaction states labeled with * indicate that they are the most stable among all 6 cases, while other states help transition from one stable state to another. Embedded and on-surface cluster configurations are labeled in red and green, respectively.

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