Computational Modeling of the Structure and Catalytic Behavior of Graphene-Supported Pt and PtRu Nanoparticles

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COMPUTATIONAL MODELING OF THE STRUCTURE AND CATALYTIC BEHAVIOR OF GRAPHENE-SUPPORTED PT AND PTRU NANOPARTICLES

A Dissertation Presented

by

RAYMOND GASPER

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

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ACKNOWLEDGEMENTS

To Emily, my family, and my friends, for making this journey a joy
ABSTRACT

COMPUTATIONAL MODELING OF THE STRUCTURE AND CATALYTIC BEHAVIOR OF GRAPHENE-SUPPORTED PT AND PTRU NANOPARTICLES

SEPTEMBER 2018

RAYMOND GASPER

B.S. WORCESTER POLYTECHNIC INSTITUTE

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Directed by: Professor Ashwin Ramasubramaniam

Computer modeling has the potential to revolutionize the search for new catalysts for specific applications primarily via high-throughput methodologies that allow researchers to scan through thousands or millions of potential catalysts in search of an optimal candidate. To date, the bulk of the literature on computational studies of heterogeneous catalysis has focused on idealized systems with near-perfect crystalline surfaces that are representative of macroscopic catalysts. Advancing the frontier to nanoscale catalysis, in particular, heterogeneous catalysis on nanoclusters, requires consideration of low-symmetry nanoparticles with realistic structures including the attendant complexity arising from under-coordination of catalyst atoms and dynamic fluxionality of clusters.

In this thesis, we focus on understanding structure–property–function relationships of Platinum and Platinum-Ruthenium alloy nanoclusters on defective graphene supports, which are highly effective catalysts for methanol fuel cells. In particular, we focus on understanding the interplay between support defects and the electronic structure of supported nanoclusters, and the consequent impact on the thermodynamics and kinetics
of the methanol decomposition reaction (MDR), a reaction of interest for renewable energy technologies such as direct-methanol fuel cells. Using density functional theory (DFT) modeling, we first investigate the adsorption and reaction thermodynamics of MDR intermediates on defective graphene-supported Pt$_{13}$ nanoclusters with realistic, low-symmetry morphologies. We find that the support-induced shifts in catalyst electronic structure correlate well with an overall change in adsorption behavior of MDR intermediates. The reaction thermodynamics are modified by the support interaction to more favorable reaction free energies, suggesting greater catalytic activity. We also show that adsorption energy predictors established for traditional heterogeneous catalysis studies of MDR on macroscopic crystalline facets are equally valid on catalyst nanoclusters (supported or otherwise) with irregular, low-symmetry surface morphologies. To understand the kinetics of MDR on graphene-supported Pt$_{13}$ clusters, we implement and apply a microkinetic model within a batch reactor setup. The microkinetic model predicts high activity for the MDR over nanoparticles that interact strongly with support defects, in comparison to larger nanoparticles that are only weakly influenced by the support which exhibit much lower activity; these results agree with fuel-cell level experimental results. We also find that the support effect induces changes in the most favorable reaction pathway, and in the populations of dominant surface species under realistic reaction conditions. Our studies provide molecular-level insights into experimental observations of enhanced catalytic activity of graphene-supported Pt nanoclusters for MDR and suggest promising avenues for further tuning of catalytic activity through computer-aided-engineering of catalyst–support interactions.
An associated problem with modeling supported nanoclusters involves being able to generate, at the outset, realistic structures of nanoparticles. Using an empirical-potential-based genetic algorithm (developed by my colleague Dr. Hongbo Shi) and DFT modeling, we identify low-energy structures of Pt nanoparticles over the range of 10-100 atoms. We then show that there exists a size window (40–70 atoms) over which Pt nanoclusters bind CO weakly, the binding energies being comparable to those on Pt(111) or Pt(100) facets. The size-dependent adsorption energy trends are, however, distinctly non-monotonic and are not readily captured using traditional descriptors such as $d$-band energies or (generalized) coordination numbers of the Pt binding sites. Instead, by applying machine-learning algorithms (collaborative work with Dr. Hongbo Shi), we show that multiple descriptors, broadly categorized as structural and electronic descriptors, are essential for qualitatively capturing the CO adsorption trends. Our approach allows for building quantitatively predictive models of site-specific adsorbate binding on realistic, low-symmetry nanostructures, which is an important step in modeling reaction networks as well as for rational catalyst design in general. We also extend the Pt-C empirical potential to the Pt-Ru-C system that will allow for future studies of supported Pt-Ru nanoclusters that are among the best known catalysts for MDR. Developing the Pt-Ru-C empirical potential was based on previously established potentials for the Pt-C and Ru-C system. Achieving an accurate Pt-Ru-C potential required careful benchmarking against experimental and DFT data, resulting in targeted adjustment of the Pt-Ru and Ru-C bond parameters.
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CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 MOTIVATION

The field of computational catalysis has grown to rely on the idea that by using simple scaling relations for thermodynamics and kinetics of elementary chemical reactions, we can avoid the need for several expensive density functional theory (DFT) calculations.\textsuperscript{2–6} These scaling relations, commonly referred to as “predictors”, have alleviated computational workloads by orders of magnitude enabling high-throughput studies over large phase spaces of metal alloy surfaces being used for heterogeneous catalysis in a wide variety of chemical reactions. This approach has produced some notable cases where \textit{ab initio} modeling has enabled the computational discovery of novel alloy catalysts that outperformed (or reaffirmed) the best industry standards.\textsuperscript{7} Such key successes hint of a future where catalyst discovery can take place by a fully intentional and data-driven approach, with computational tools predicting and driving the rational design of likely catalysts for further experimentation. The predictor approach has been developed to date by focusing study primarily on high-symmetry, low-Miller-index surfaces of materials for reasons of computational feasibility. In general, these models offer reasonable predictions when representing catalysts of micron size or larger that display prominent crystalline facets. However, the drive to increase the active surface area of catalysts naturally motivates reducing catalyst sizes to the nanoscale where the validity of models developed for low-index crystalline facets becomes questionable. To the best of our knowledge, only one other group has made significant headway in showing the applicability of predictor relationships for small nanoparticles, proving their
effectiveness on symmetric four-atom Ag, Au, Co, Cu, Pt, and Rh nanoparticles for the methanol decomposition reaction (MDR), a chemical reaction significant in methanol fuel cells where methanol decomposes into CO and two H$_2$.\textsuperscript{4} In addition, the catalytic activity of nanoparticles has been shown experimentally to be very sensitive to size and structure: in one case, a low-symmetry twelve-atom Pt nanoparticle was shown to be 2.5 times more active for the oxygen reduction reaction than an icosahedral thirteen atom one.\textsuperscript{8,9} Thus, the development of accurate models of catalytic reactions on nanoscale catalysts is a significant need and challenge for future developments in the field of computational catalysis.\textsuperscript{10–14} Furthermore, nanoparticle catalysts are also very sensitive to electronic perturbations from their supports because a higher percentage of the nanoparticle’s atoms are either directly bonded to or in the proximity of the support. Thus, the development of accurate predictors for nanoscale catalysts must now also be undertaken in the context of the catalyst support, further increasing the complexity of the problem.

### 1.2 RESEARCH QUESTIONS AND OUTCOMES

With the key challenges posed above, we address the following fundamental questions in this dissertation:

1) How do size, composition, and support effects alter the structure–property relationships of graphene-supported Pt nanoparticle catalysts?

2) How do we establish accurate representative structures for low-symmetry, supported nanoparticles in computer simulations?

3) Are the traditional predictors that enable high-throughput calculations on high-symmetry surfaces still valid for low-symmetry nanoparticle surfaces? If
not, why do the traditional predictors fail and how can they be improved or supplanted?

We investigate these questions through the specific problem of the MDR and the adsorption of CO on defective graphene-supported Pt nanoparticles. Pt is known to be the most effective pure metal catalyst for the MDR.\textsuperscript{15,16} However, the activity of pure Pt is plagued by poisoning of the catalyst surface by CO, which is by far the most strongly adsorbed molecule on Pt in the MDR pathway.\textsuperscript{16,17} Allying Ru to the Pt catalyst activates water more readily and allows subsequent oxidation of the CO thus increasing the activity of the catalyst.\textsuperscript{16,18} In addition, experimental evidence suggests a dramatic support effect for these nanoparticle catalysts: for particles approximately 4 nm in size, switching from a conventional carbon black support to a defective graphene support in methanol fuel cells both lowers CO poisoning of the catalyst surface and substantially increases the current density of the fuel cell by a factor of 2.5 for Pt and 7 for PtRu alloy.\textsuperscript{19,20} This is a clear indication of unique support-induced changes in the activity of the nanoparticle catalyst and worthy of further investigation. We hypothesize that significant support interaction is inducing changes in the physical and electronic structures of the Pt nanoparticles, which then positively influences the thermodynamics and kinetics of the MDR.

The first challenge that must be addressed is the choice of proper structural models for computer simulations of nanoparticles. It has been shown conclusively that the ground states of transition metal nanoparticles smaller than ~3 nm are low-symmetry structures, which additionally have many degenerate isomers.\textsuperscript{10,12–14,21} Finding these low-energy structural minima in a high-dimensional energy landscape with many local
minima is computationally demanding and requires the use of effective global search algorithms, for example, genetic algorithms (GA). Unfortunately, when coupled with modeling approaches of high accuracy (e.g., density functional theory; DFT), GAs and other global minimization methods tend to become computationally prohibitive. My coworker, Dr. Hongbo Shi, in order to accelerate the global minimization search for realistic nanoparticle structures, developed a GA that relies on empirical potentials which are intrinsically less accurate but orders-of-magnitude less expensive than DFT. The GA was successfully tested with different empirical potentials (embedded-atom method and Tersoff potentials) as well as with self-consistent-charge density functional tight-binding potentials. In collaboration with Dr. Shi, I have parameterized and tested a Tersoff potential for the ternary Pt-Ru-C system, which will be employed in future work by our research group. Current results indicate quantitative agreement between the potential and DFT for PtRu nanoparticles supported on defective graphene.

With the ability to address the problem of identifying realistic structures for supported and unsupported Pt and PtRu nanoparticles, we can progress to investigations of the catalytic properties of these nanoparticles. As shown in prior work by our group and by others, understanding the size-dependent physical and electronic structure of nanoparticles is crucial as these properties have a significant influence on catalytic activity. A particularly well-known example of size effects is the high activity of gold nanoparticles for various reactions in contrast to bulk gold surfaces that are generally inert. An example of structural dependence that is particularly relevant to our work is the finding by Wang et al. that Pt@Ru (shell@core) nanoparticles are significantly more active for the MDR than PtRu dispersed-alloy nanoparticles. Fully investigating
the changes in catalytic activity caused by different sizes and structures of nanoparticle catalysts using DFT would be computationally prohibitive and as such we must turn to predictor relations fit to carefully selected DFT or experimental data sets.

Predictor relations for adsorption energies of small molecules on metal surfaces are a key element of high-throughput calculations. They allow a small subset of high-accuracy, computationally-expensive calculations to fit a simple correlation that then replaces exhaustive sampling. There are three thermodynamic predictor relations that have stood the test of time and have remained popular in the computational catalysis community: the $d$-band center model,\textsuperscript{31} which correlates the binding energy of a specific molecule to the electronic density of states of a range of metal surfaces; the adsorption energy scaling relation,\textsuperscript{4} which linearly relates the adsorption energies of two similar species, such as a carbon-binding small molecule (e.g. C$_3$H$_7$OH) to CO, on a range of metal surfaces; and the coordination number model,\textsuperscript{5} which correlates the binding energy of a specific molecule to the coordination number of the surface atoms of a specific metal surface.

There are also predictor relations for reaction barriers (kinetics) of small molecules on metal surfaces, which are necessary for high-throughput calculations of catalyst activity. Examples of such kinetic predictors include the Brønsted-Evans-Polanyi (BEP) relationship, which linearly relates the free-energy barrier of a reaction to the corresponding reaction free-energy; the initial-state model, which linearly relates the free-energy barrier of a reaction to the free-energy of the reactant state; and the final-state model, which linearly relates the free-energy barrier of a reaction to the free-energy of the product state.\textsuperscript{7} The predictor relations for barriers are particularly useful as the calculation of reaction barriers is orders of magnitude more computationally intensive
than thermodynamics calculations (such as adsorption energies), making high-accuracy DFT calculations for reaction barriers of complex systems a trying task even with modern supercomputers.

Considering the substantial effect that differences in size and support exert on catalytic activity for Pt nanoparticles, we would like to predict, *ab initio*, a specific size (or limited size range) and specific support for maximum catalytic activity for the MDR. However, full DFT sampling of the MDR on many sizes of Pt nanoparticles with different supports remains a prohibitively computationally expensive task and so we must implement predictors for these systems. As indicated before, the reliability of predictor relationships for adsorption energies and for reaction barriers on supported, low-symmetry nanoparticles has yet to be tested and we take the MDR as a well-understood and technologically important case in the context of which we explore these issues. To study the behavior of MDR intermediates on Pt nanoparticles, we consider a few key reaction pathways identified on Pt(111) under ultra-high vacuum conditions by Greeley and Mavrikakis. These pathways are, in order of overall activity:

*Path 1*: \( \text{H}_3\text{COH} \rightleftharpoons \text{H}_2\text{COH} + \text{H} \rightleftharpoons \text{HCOH} + 2\text{H} \rightleftharpoons \text{CO} + 4\text{H} \),

*Path 2*: \( \text{H}_3\text{COH} \rightleftharpoons \text{H}_2\text{CO} + \text{H} \rightleftharpoons \text{H}_2\text{CO} + 2\text{H} \rightleftharpoons \text{HCO} + 3\text{H} \rightleftharpoons \text{CO} + 4\text{H} \),

*Path 3*: \( \text{H}_3\text{COH} \rightleftharpoons \text{H}_2\text{COH} + \text{H} \rightleftharpoons \text{H}_2\text{CO} + 2\text{H} \rightleftharpoons \text{HCO} + 3\text{H} \rightleftharpoons \text{CO} + 4\text{H} \).

Each step in these pathways is a dehydrogenation step and involves a hydrogen atom attaching to and diffusing away from the reaction site on the Pt surface. In paths 1 & 3, the O-H bond is the first to be broken, followed by successive dehydrogenation steps to CO- note that in path 1 the final step is a concerted double-dehydrogenation step. In path 2, the C-H bond is the first to be broken followed by successive dehydrogenation to CO.
With the addition of the steps HCOH $\rightleftharpoons$ COH + H and COH $\rightleftharpoons$ CO + H to the paths noted above, all possible dehydrogenation steps originating from methanol are included in our reaction network. We show that the (thermodynamic) predictor relations for adsorption energies of MDR intermediates based on the $d$-band center model as well as adsorption energy scaling relationships—conventional descriptors in heterogeneous catalysis—are also reasonably accurate on defective graphene supported Pt$^{13}$. Furthermore, we also show that the initial-state model for prediction of reaction barriers (kinetics) is sufficiently accurate for low-symmetry nanoparticles— we likewise tested the BEP and final-state models, which were not effective for the systems studied herein. However, a key difference is that the low-symmetry surfaces of the nanoparticles requires more careful statistical sampling than on high-symmetry surfaces, and the resulting predictor relationships have an inherent stochasticity.$^{33}$ Using the initial-state model, we develop and apply a microkinetic model to investigate the kinetics for the MDR on unsupported and graphene-supported Pt$^{13}$ nanoparticles, and to compare these results with the conventional Pt(111) surface. The microkinetic model predicts faster reaction rates on small, strongly supported nanoparticles than on larger, weakly supported ones, and also provides insights into the support-induced changes of the reaction network and of the steady-state surface coverages. Our computational approach delivers molecular-level explanation for experimental data and shows that nanometer-scale defective-graphene-supported Pt nanoparticles are more active for MDR than larger Pt nanoparticles on carbon black.

As noted above, the low-symmetry of nanoclusters leads to site-specific variations in the adsorption and dehydrogenation of MDR intermediates. As a first attempt at
quantifying and predicting such site-specific adsorption, we turn to machine-learning model in a search for multiple relevant descriptors. The use of machine learning techniques in materials science is in its infancy and growing, and a few groups have recently explored using machine learning for predictions of adsorbate binding on transition-metal surfaces, reporting modest errors (∼0.1 eV) with respect to DFT. The gradient-boosting algorithm was used recently by Takigawa et al. to accurately predict the $d$-band center of bulk alloys and alloy surfaces based only on mechanical and structural properties, demonstrating the potential usefulness of this machine learning algorithm for computational catalysis research. With the specific example of CO adsorption (which is also the thermodynamic sink for MDR), we develop a machine-learning model that combines electronic-structure and geometric descriptors to achieve predictive capability while still maintaining a transparent connection to the underlying physics at relatively low computational expense. The resulting trained machine-learning model has comparable accuracy to DFT calculation for site-specific adsorption energies on low-symmetry nanoparticle surfaces, with the total CPU-time required for data generation plus the training process taking roughly one one-hundredth the CPU-time of full DFT sampling. A key outcome of this study is the identification of a range of sizes (40-70 atoms) for Pt clusters that bind CO most weakly. While this study was performed only for unsupported Pt clusters, the preceding analysis of MDR thermodynamics and kinetics suggests that the cluster size effect can be combined with support effects to design graphene-supported Pt nanocatalysts that are less prone to CO poisoning and are more active towards MDR than Pt$_{13}$ clusters.
1.3 THESIS ORGANIZATION

This thesis is organized topically, based around our relevant publications. First we present our findings for predictor relationships and thermodynamics for the MDR over defective-graphene supported Pt nanoparticles in Chapter 2. Thereafter, in Chapter 3, we extend our thermodynamic studies to investigate the MDR barriers over defective-graphene supported Pt nanoparticles and employ these barriers along with the thermodynamics discussed in Chapter 2 to build a MATLAB microkinetic model that predicts the performance of an MDR reactor at realistic conditions. In Chapter 4 we present a collaborative project between myself and Dr. Hongbo Shi in which we identify a failure of traditional predictor relationships in the case of CO adsorption onto Pt nanoparticles with realistic structure (generated by Dr. Shi’s genetic algorithm) and over a wide range of sizes, and we show how machine-learning techniques using physically motivated descriptors can be to successfully capture the CO adsorption behavior. Thereafter, we report the parameterization of a new Pt-Ru-C Tersoff-style empirical potential in Chapter 5, which will be employed in future work in our research group for generation of realistic bimetallic supported nanoparticle structures. In Chapter 6, we summarize the overall conclusions of the works as they pertain to the objective of the thesis and discuss some possible future avenues of related work. The appendices contain full texts of the thesis work publications (Appendices A&B, corresponding to Chapters 2 and 4 respectively), two additional publications from projects unrelated to the thesis (Appendices C&D), and supporting information from both the published works (Chapters 2 and 4) and unpublished work (Chapters 3 and 5) contained herein.
CHAPTER 2

THERMODYNAMICS AND ADSORPTION ENERGY SCALING RELATIONS
FOR THE METHANOL DECOMPOSITION REACTION OVER DEFECTIVE-
GRAPHENE SUPPORTED PLATINUM NANOPARTICLES

2.1 INTRODUCTION

Graphene has been demonstrated to be a very effective support for electrocatalysts for methanol and hydrogen fuel cells.\textsuperscript{15,19,40–44} In particular, for direct-methanol fuel cells, graphene-supported platinum clusters have been shown to have high catalytic activity for the methanol decomposition reaction (MDR), and increased resistance to both sintering and CO poisoning.\textsuperscript{15,19,40–44} The details of the binding of Pt nanoclusters to defective graphene supports have been studied extensively. Via computational and experimental work, Pt nanoclusters have been shown to adsorb strongly to point-defect sites in the graphene support.\textsuperscript{42,45,46} Upon binding at point defects, significant charge transfer takes place from the Pt nanoclusters to the graphene support, correspondingly modifying the electronic structure of the nanoclusters.\textsuperscript{12,47–50} This phenomenon suggests the use of predictors based upon electronic structure, in particular the $d$-band center model, which have been used to great effect to allow exploration of pure transition metal surfaces and surface alloys for use as catalysts.\textsuperscript{3,31,51–55} Other predictors for catalytic activity are based on scaling relationships, which correlate, for example, the adsorption of a molecule on different surfaces to the adsorption energy of a simpler probe molecule on the same surface. These have been demonstrated to be accurate in a wide variety of applications.\textsuperscript{3,4,51,56,57} In previous work, we showed that the $d$-band center can be used effectively as a predictor for CO adsorption on unsupported or graphene-supported Pt
nanoclusters, but did not explore any of the MDR intermediates or provide any investigation of adsorption energy scaling relationships. The reduction of CO adsorption energies via support effects offers a possible explanation for the higher tolerance to CO poisoning that supported Pt nanoclusters exhibit, while the strong binding of Pt nanoclusters to defects explains resistance to sintering. However, neither of these observations is sufficient to explain fully the higher catalytic activity for the methanol decomposition reaction (MDR) that is observed in experiments. Thus, the primary goal of this work is to present a detailed density functional theory (DFT) study of the adsorption of MDR intermediates on Pt$_{13}$ nanoclusters with the goal of understanding the role of support effects on reaction thermodynamics. As Pt$_{13}$ nanoclusters (with or without supports) have already been studied in detail, and larger graphene-supported Pt nanoclusters would be computationally unfeasible to study, they serve as a model reference system for further exploration of catalytic reactions. We also seek to further extend the use of the $d$-band center model and adsorption energy scaling relationships from their traditional applications for catalysis at macroscopic crystalline surfaces to more complex supported-cluster reaction networks, thereby expanding the generality of their potential use for rational catalyst design.

Calculations of adsorption energies and reaction thermodynamics on clusters require overcoming difficulties that are not present on high-symmetry surfaces. Due to there being few (if any) symmetry-equivalent adsorption sites on low-symmetry clusters, some form of statistical sampling must be undertaken, which magnifies the effort required to understand a reaction on a single cluster. In addition, clusters adopt different geometries and electronic structures on different supports, requiring separate calculations even for
simple quantities such as adsorption energies. The combination of these factors makes investigation of cluster-support systems for their catalytic potential extraordinarily time- and resource-consuming. Therefore, in order to achieve a broad and/or in-depth investigation of supported catalyst design, circumventing these extensive \textit{ab initio} calculations via robust predictors is highly desirable. In this work, we demonstrate that the \textit{d}-band center model can be extended for use not only as a predictor for CO adsorption, as we have done before,\textsuperscript{58} but more generally as a predictor for the qualitative adsorption behavior of the methanol decomposition reaction across nanoclusters with varying degrees of support interactions.

The MDR has been extensively investigated,\textsuperscript{17,30,57–64} in part due to its value for understanding and improving catalytic performance for direct methanol fuel cells. Pioneering work in the field was performed by Greeley and Mavrikakis, who investigated the reaction on Pt(111) in extensive detail.\textsuperscript{32,65} They showed via a combination of DFT and microkinetic modeling that the most likely pathway for MDR on a Pt(111) single-crystal surface under ultra-high vacuum is $\text{H}_3\text{COH} \rightarrow \text{H}_2\text{COH} \rightarrow \text{HCOH} \rightarrow \text{CO}$ (Path 1), with the first dehydrogenation step being rate-determining. Two other viable, but less favorable, pathways were identified: (i) $\text{H}_3\text{COH} \rightarrow \text{H}_3\text{CO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{HCO} \rightarrow \text{CO}$ (Path 2), with the first step also being the rate determining step, and (ii) $\text{H}_3\text{COH} \rightarrow \text{H}_2\text{COH} \rightarrow \text{H}_2\text{CO} \rightarrow \text{HCO} \rightarrow \text{CO}$ (Path 3), with the first and second steps having approximately the same barriers. In addition to the Pt(111) surface, the MDR pathway has also been fully or partially identified on stepped and defective platinum surfaces,\textsuperscript{54} B\textsubscript{12}N\textsubscript{12} nanocages,\textsuperscript{66} the Cu(111) surface,\textsuperscript{67} the Cu(110) surface,\textsuperscript{59} the ZnO(1010) surface,\textsuperscript{68} among several others.\textsuperscript{61,62,64,69–72} Kandoi \textit{et al.}\textsuperscript{17} showed that the experimental performance of the
Pt(111) surface catalyst for the MDR can be predicted qualitatively by a combination of *ab initio* calculations and microkinetic modeling, along the way reaffirming the dominant pathway established by Greeley and Mavrikakis. In our work, we characterize the adsorption energies and reaction thermodynamics of the three pathways previously identified, considering especially the relationships between the most likely pathways. We believe that the level of understanding in the field, along with the previously identified gap in understanding regarding the effect of supports, makes this reaction-catalyst-support system ideally suited for investigation of predictors for supported catalysis.

Our computational methodology is explained in Section 2.2. Results and discussion on the effect of support binding on the adsorption and reaction thermodynamics of MDR intermediates are presented in Section 2.3. Conclusions and closing remarks are presented in Section 2.4.

### 2.2 METHODOLOGY

Spin-polarized DFT calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP). The core and valence electrons were treated using the projector-augmented wave function method. The Perdew-Burke-Ernzerhof generalized-gradient approximation (PBE) was used to describe electron exchange and correlation. From convergence studies, we chose a kinetic energy cutoff of 400 eV and a first-order Methfessel-Paxton smearing of 0.05 eV. All atomic positions were relaxed with a force tolerance of 0.02 eV/Å.

Initial low-energy Pt$_{13}$ cluster configurations (supported or unsupported) were generated via simulated annealing as reported in Ref. 12. The supports considered were 8×8 single-layer graphene sheets that were either defect free or containing a point defect.
(vacancy or divacancy) at the cluster adsorption site. Graphene planes were separated in the normal direction by 18 Å of vacuum to prevent spurious interaction with periodic images. The Brillouin zone was sampled by a $2 \times 2 \times 1$ $\Gamma$-centered $k$-point mesh, chosen from our convergence studies. Unsupported (Isolated) Pt$_{13}$ clusters were modeled in an 18 Å cube using a single $\Gamma$ point for reciprocal space sampling. Adsorption energies and reaction energies were sampled on five random sites on each cluster, with the results presented as the average result with student-T confidence intervals. We implement a standard average instead of a more chemically relevant procedure such as Boltzmann averaging because the data set is too small to be able to use such a treatment properly. With our data set, a Boltzmann average would essentially select only the upper limit of the adsorption energies- this effect would not disrupt the overall trends identified herein, which can be seen in Figure G.1 in the supporting information. Sampling sites were chosen randomly, with repeated sites or sites hindered by graphene proximity (high steric hindrance) being discarded. Initial configurations for adsorbed molecules were set up to be as close to the Pt(111) adsorption configuration as possible but these eventually relaxed to various local minima as dictated by the local structure of the adsorption sites. Charge transfer analyses were performed using a Bader analysis.$^{81,82}$

Reference Pt(111) surface calculations were performed on a three-layer, $3 \times 3$ surface cell with the bottom two layers frozen in their bulk FCC geometry. Slabs of greater thickness with additional free layers were tested and not found to influence the adsorption energies. The slabs were separated by 18 Å of vacuum normal to the surface to prevent spurious interactions. A $\Gamma$-centered, $5 \times 5 \times 1$ $k$-point mesh was used for Brillouin zone sampling. Dipole-moment corrections were applied normal to the surface.
For adsorption energy \((E_{\text{ads}})\) calculations, the following definitions are employed throughout this paper:

**Supported Clusters:**

\[
E_{\text{ads}} = E_{\text{Pt}_{13} + \text{support} + \text{adsorbate}} - E_{\text{Pt}_{13} + \text{support}} - E_{\text{adsorbate}},
\]

\((2.1)\)

**Isolated Cluster:**

\[
E_{\text{ads}} = E_{\text{Pt}_{13} + \text{adsorbate}} - E_{\text{Pt}_{13}} - E_{\text{adsorbate}},
\]

\((2.2)\)

**Pt(111) Surface:**

\[
E_{\text{ads}} = E_{\text{Pt(111) + adsorbate}} - E_{\text{Pt(111)}} - E_{\text{adsorbate}}.
\]

\((2.3)\)

In Eq. \((2.1)\), \(E_{\text{Pt}_{13} + \text{support} + \text{adsorbate}}\) is the total energy of the relaxed \(\text{Pt}_{13}\) cluster, graphene support, and adsorbate molecule; \(E_{\text{Pt}_{13} + \text{support}}\) is the total energy of the \(\text{Pt}_{13}\) cluster and graphene support relaxed again after adsorbate removal; and \(E_{\text{adsorbate}}\) is the reference energy of the adsorbate isolated in vacuum. In Eq. \((2.2)\), for the isolated cluster, \(E_{\text{Pt}_{13} + \text{adsorbate}}\) is the total energy of the relaxed \(\text{Pt}_{13}\) cluster plus adsorbate, \(E_{\text{Pt}_{13}}\) is the energy of the isolated \(\text{Pt}_{13}\) cluster relaxed after adsorbate removal, and \(E_{\text{adsorbate}}\) is the reference energy of the isolated adsorbate; Eq. \((2.3)\) is analogous to Eq. \((2.2)\) with \(\text{Pt}(111)\) substituting for the \(\text{Pt}_{13}\) cluster. For all molecules considered, the reference state is the molecule in vacuum; for a hydrogen atom, however, the reference state is half the energy of the \(H_2\) molecule. Note that as defined, more negative adsorption energies correspond to a stronger bond between the adsorbate and the catalyst.

The thermodynamics of the MDR were calculated using the following definitions of reaction energies:

**Supported Clusters:**
\[ \Delta E_{\text{rxn}} = E_{Pt_{13}+\text{support}+\text{product}} + N_H \left[ \frac{1}{2} E_{H_2(g)} + \overline{E_{\text{ads},H}} \right] - E_{Pt_{13}+\text{support}+\text{reactant}}, \]  

(2.4)

Isolated Cluster:

\[ \Delta E_{\text{rxn}} = E_{Pt_{13}+\text{product}} + N_H \left[ \frac{1}{2} E_{H_2(g)} + \overline{E_{\text{ads},H}} \right] - E_{Pt_{13}+\text{reactant}}, \]  

(2.5)

Pt(111) Surface:

\[ \Delta E_{\text{rxn}} = E_{Pt(111)+\text{product}} + N_H \left[ \frac{1}{2} E_{H_2(g)} + \overline{E_{\text{ads},H}} \right] - E_{Pt(111)+\text{reactant}}, \]  

(2.6)

where \( N_H \) is the number of hydrogen atoms being removed from the intermediate in a particular reaction step (\( N_H = 1 \) in all steps except for the semi-concerted removal of two H atoms from HCOH where \( N_H = 2 \)), \( E_{H_2(g)} \) is the DFT energy of an \( H_2 \) molecule, and \( \overline{E_{\text{ads},H}} \) is the average adsorption energy of hydrogen on the system being considered [Pt\(_{13}\), the exact value can be used on Pt(111)]. By way of benchmarking, this approach was compared with the more conventional approach wherein the products of a reaction step (i.e., the MDR intermediate and the leaving H atom) are co-adsorbed on the catalyst surface and the reaction thermodynamics calculated with respect to this configuration. Selected tests on Pt(111) and on the isolated Pt\(_{13}\) cluster (Fig. G.5) reveal that both approaches provide consistent and reliable estimates of the reaction thermodynamics. On the Pt(111) surface both approaches yield nearly identical results; on the isolated Pt\(_{13}\) cluster, the results coincide to within the bounds of statistical error, indicating that neglecting adsorbate-adsorbate interactions will not affect the significance of the overall results. Thus, employing the average value for hydrogen adsorption energy facilitates reaction thermodynamics analyses at half the computational cost of the co-adsorption.
approach while also minimizing the influence of variations in energy of the relaxed cluster and support, which causes excessive noise in the calculations without lending improved understanding. No entropic contributions or zero-point energies were included in this study but are included in the full kinetic analysis of the MDR in Chapter 3.

2.3 RESULTS AND DISCUSSION

2.3.1 ADSORPTION OF MDR INTERMEDIATES OVER DEFECTIVE-GRAPHENE SUPPORTED PT NANOPARTICLES

The graphene-supported Pt$_{13}$ clusters used for this study are shown in Figure 2.1. Initial configurations for the systems used were taken from previous work. The systems chosen for this study are an isolated Pt$_{13}$ cluster, a pristine-graphene supported Pt$_{13}$ cluster, a Pt$_{13}$ cluster supported on a graphene sheet with a single vacancy, and a Pt$_{13}$ cluster supported on a graphene sheet with an unreconstructed divacancy. These systems were chosen due to previous work indicating that they provided a broad range of support interaction, leading to significant shifts in $d$-band center and CO adsorption behavior between the systems. The structures of the Pt-graphene systems are generated by

![Figure 2.1: Relaxed Pt$_{13}$ clusters that are a) isolated, b) on a pristine graphene support, c) bound at a vacancy defect in graphene, and d) bound at a divacancy defect in graphene. (C – brown spheres; Pt – gray spheres)](image)
simulated annealing and correspond to realistic MDR catalysts at reaction conditions. The support size was increased relative to our previous work to an 8\times8 graphene supercell to accommodate larger adsorbed molecules without spurious image interaction.

As discussed in previous work, with the increasing size of point defects in the graphene support, both the binding strength and charge transfer between the Pt cluster and graphene–support increase.\textsuperscript{12} This charge transfer induces a change in the electronic structure of the clusters, manifested by a downshift in the $d$-band center value. The $d$-band centers of the clusters from Fig. 2.1 are listed in Table 2.1 and reaffirm these conclusions. The details of the charge transfer and its effects on the $d$-band can be found in work by Drs. Fampiou and Ramasubramaniam.\textsuperscript{12} The $d$-band centers of the unsupported cluster and the pristine-graphene-supported cluster (weak cluster–support interactions) are significantly higher than that of the Pt(111) surface; however, sufficiently strong support interaction in the divacancy case lowers the $d$-band center below the Pt(111) level. The $d$-band model then suggests that the adsorption energy of molecular adsorbates on these catalysts should be correlated consistently with respect to the $d$-band shift between the differently supported Pt\textsubscript{13} nanoparticles. Indeed, for the case of CO adsorption on graphene-supported or unsupported Pt\textsubscript{13} clusters, we have shown previously that trends in adsorbate binding (as well as oxidation barriers) can be rationalized in terms of the $d$-band shifts.\textsuperscript{58,83} Through this metric we will further unravel the relationship between support effects and adsorption for MDR intermediates below.
Table 2.1: Positions of $d$-band centers ($\varepsilon_d$) of Pt$_{13}$ clusters and Pt(111) surface (relative to the Fermi level).

<table>
<thead>
<tr>
<th>System</th>
<th>$\varepsilon_d$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>-2.58</td>
</tr>
<tr>
<td>Isolated cluster</td>
<td>-2.25</td>
</tr>
<tr>
<td>Cluster on pristine graphene</td>
<td>-2.42</td>
</tr>
<tr>
<td>Cluster bound at vacancy in graphene</td>
<td>-2.49</td>
</tr>
<tr>
<td>Cluster bound at divacancy in graphene</td>
<td>-2.62</td>
</tr>
</tbody>
</table>
Unlike macroscopic crystal surfaces or faceted nanoparticles, it is impossible to identify a small set of symmetry-equivalent adsorption sites on our low-symmetry, graphene-supported Pt$_{13}$ nanoclusters. Thus, in order to understand the adsorption behavior, five randomly chosen sites were sampled on each cluster–support system. Sample converged configurations of various adsorbates on the Pt$_{13}$ cluster and graphene support are displayed in Figs. 2.2 and 2.3. Despite variations in local cluster geometry, the most favorable site for H$_3$CO adsorption on the supported clusters is the same as on Pt(111) at the on-top site. Such agreement is not universally true, however, and variations in adsorption configurations, likely dictated by variations in local cluster morphology, are seen for other adsorbate molecules. This is seen, for example, in Fig. 2.3 where atomic configurations of various adsorbates are displayed at a single adsorption site on a Pt$_{13}$ cluster: H$_3$COH, H$_3$CO, HCO, and H$_2$COH all adopt the same adsorption configuration as
on a Pt(111) surface (on-top site), but $\text{H}_2\text{CO}$ does not; instead, $\text{H}_2\text{CO}$, which adopts a Pt-C-O-Pt bridge configuration on Pt(111), can adopt either this configuration, an on-top configuration, or a Pt-C-Pt bridge configuration on Pt$_{13}$ clusters. As another example, CO, which adsorbs most strongly to the fcc site on the Pt(111) surface (as per DFT calculations; the disagreement with experiment is well known$^{84,85}$), adopts on-top, bridge, and hollow low-energy adsorption configurations on Pt$_{13}$ clusters.

![Diagram](image)

Figure 2.3: Top row: selected MDR intermediates on Pt(111) surface. Bottom row: same selected MDR intermediates on a single adsorption site of divacancy graphene-supported Pt$_{13}$. a) $\text{H}_3\text{COH}$, b) $\text{H}_3\text{CO}$, c) HCO, d) $\text{H}_2\text{CO}$, e) $\text{H}_2\text{COH}$. (C – brown spheres; Pt – gray spheres; O – red spheres; H – white spheres)

To extend understanding of the MDR on nanoclusters, we sample all intermediates of the favorable pathways for the methanol dehydrogenation reaction under UHV conditions. To do this we consider the following adsorbate molecules: $\text{H}_3\text{COH}$, $\text{H}_3\text{CO}$, $\text{H}_2\text{CO}$, HCO, $\text{H}_2\text{COH}$, HCOH, CO, and H. This selection is based on the molecules that participate in the most likely UHV reaction pathways identified by Greeley & Mavrikakis,$^{32}$ Paths 1, 2, and 3 in our current nomenclature (see Section 2.1). In addition, monatomic carbon and oxygen are also studied to establish adsorption energy scaling relationships as was done previously for crystalline surfaces.$^{16,17,22-24}$ Figure 2.4 displays the average adsorption energies of each MDR intermediate on all four Pt$_{13}$ clusters (220
calculations in total) plotted as a function of the corresponding molecular adsorption energy on Pt(111). For each system (i.e., isolated cluster or cluster and support), a linear fit of all adsorption energies (not just average values) versus the adsorption energy of the same molecule on Pt(111) was performed, with best-fit parameters listed in Table 2.1. Despite statistical variation, the adsorption behavior for every system versus Pt(111) shows a very consistent trend: to a very good approximation, all linear fits essentially have the same slope as the dashed 1:1 line (Fig. 2.4) suggesting that the support induces rigid shifts in the adsorption energies of MDR intermediates on the Pt\textsubscript{13} nanoclusters. These rigid shifts can be quantified by the y-intercepts of the best-fit lines and, as shown in the inset of Fig. 2.4, are inversely correlated to the calculated cluster d-band centers. In other words, as the cluster d-band center approaches that of Pt(111), so do the adsorption energies of MDR intermediates on the cluster (to within statistical variations). This is a noteworthy result as it suggests that by knowing (a) the adsorption energy of an intermediate on Pt(111), and (b) the d-band center for the cluster of interest (supported or unsupported), one may readily calculate the average adsorption energy for that intermediate on the cluster. Detailed statistical sampling over cluster adsorption sites is thus eliminated in favor of a simple scaling relationship. This finding could open up the potential use of support effects as a new control parameter for exploration when conducting high-throughput computational studies of supported catalysts. Systematic exploration of cluster size effects and their interplay with support effects will be reported elsewhere. Bifunctional support effects require special consideration but are not of relevance for our present study. (Consideration of more adsorbate molecules that were
not in favorable reaction pathways is provided in the Supporting Information, the general trends identified here are still applicable.)

Figure 2.4: Adsorption energies of MDR intermediates on supported and unsupported Pt$_{13}$ nanoclusters versus adsorption energies on Pt(111). Data points are averages of all sampled adsorption sites on that system and error bars are calculated from Student-T 95% confidence intervals. Lines represent linear fits of all (not just average) molecular adsorption energies for each Pt$_{13}$ cluster. The dashed 1:1 line is plotted as a guide to the eye. The inset shows the shift (y-axis intercept) of the adsorption data fits for each system versus their respective $d$-band centers; the dashed line is a linear fit that serves as a guide to the eye.
Table 2.2: Linear best-fit parameters for adsorption energies (Eads) of MDR intermediates on Pt13 nanoclusters to their Pt(111) values (Fig. 2.4).

<table>
<thead>
<tr>
<th>System</th>
<th>Slope</th>
<th>y-Intercept (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated cluster</td>
<td>0.97</td>
<td>-0.55</td>
</tr>
<tr>
<td>Cluster on pristine graphene</td>
<td>1.01</td>
<td>-0.34</td>
</tr>
<tr>
<td>Cluster bound at vacancy in graphene</td>
<td>0.97</td>
<td>-0.32</td>
</tr>
<tr>
<td>Cluster bound at divacancy in graphene</td>
<td>0.94</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

For completeness, the adsorption energies and trends in adsorption energy were checked against a multitude of other potential descriptors including charge transfer from the Pt13 cluster to the support, charge transfer from the adsorbate to the Pt13 cluster, the Fermi level shift of the supported Pt13 clusters versus the unsupported case and versus Pt(111), and the d-band center of the Pt13 clusters relative to the vacuum level; none of these descriptors proved useful. The excellence of the d-band center position (relative to the Fermi level) as a predictor of average adsorption behavior on catalyst nanoclusters appears to be unique.

Given the successful past use of adsorption energy scaling relationships for heterogeneous catalysis on macroscopic crystalline surfaces,\textsuperscript{3,4,57,86} it is natural to inquire whether such relations work on nanoclusters. To the best of our knowledge, beyond a recent series of studies of four-atom unsupported clusters,\textsuperscript{2,4,87} this question has received scant attention and certainly not for supported, low-symmetry nanoclusters. In Fig. 2.5, we display the adsorption energies of the MDR intermediates on the unsupported and supported Pt13 nanoclusters as a function of the adsorption energy of either monatomic
carbon or monatomic oxygen; the probe atom (C or O) was chosen depending upon whether the intermediate adsorbed most frequently to the cluster via a C-Pt or an O-Pt bond. In all cases, the most frequently observed cluster–adsorbate bond was the same as that on the Pt(111) surface. For H₂CO, which was seen to bind via C, O, or both simultaneously, O was chosen as the probe molecule due to a superior agreement. As seen from Fig. 2.5, for the most part, the adsorption energy of an intermediate correlates very well with that of the relevant probe molecule leading to a set of robust scaling relationships. The correlation for HCO and H₂COH appears somewhat less robust, but the outlying data for these two cases are contributed by the isolated Pt₁₃ clusters. To the extent that the isolated Pt₁₃ cluster merely sets the “zero” for probing support interactions and is not relevant as a catalyst, we deem these couple of outliers to be unimportant. The trend of adsorption energies for the C atom on the clusters may initially appear erratic, but actually is very similar to the results for carbon-binding molecules on the clusters. Within statistical error, adsorption energies for the isolated, pristine, and vacancy cases are fairly similar; adsorption in the divacancy case is significantly weaker though and in many cases the data even lie above the Pt(111) values. Just as for the d-band center model, the internal variation caused by the low-symmetry cluster sampling does not disrupt the general trends that make adsorption energy scaling relationships an effective predictor.
As seen above, the scaling relationships are fairly robust for all adsorbates and cluster–support systems despite local variations in geometry and the corresponding variations in adsorption energies. By substituting the average C and O adsorption energies into the linear fit equations for the various adsorbates (see Fig. 2.5), one can “predict” the average adsorption energies of the MDR intermediates. The predicted adsorption energies for the MDR intermediates can then be compared to the DFT-

![Scaling relationships for adsorption energies of MDR intermediates versus adsorption energies of monatomic carbon or oxygen. Points are average adsorption energies for each system whereas linear fits are to all adsorption data. (The Pt(111) value for HCO overlaps with that for H$_2$COH making the symbols indistinguishable.)](image)

Figure 2.5: Scaling relationships for adsorption energies of MDR intermediates versus adsorption energies of monatomic carbon or oxygen. Points are average adsorption energies for each system whereas linear fits are to all adsorption data. (The Pt(111) value for HCO overlaps with that for H$_2$COH making the symbols indistinguishable.)

As seen above, the scaling relationships are fairly robust for all adsorbates and cluster–support systems despite local variations in geometry and the corresponding variations in adsorption energies. By substituting the average C and O adsorption energies into the linear fit equations for the various adsorbates (see Fig. 2.5), one can “predict” the average adsorption energies of the MDR intermediates. The predicted adsorption energies for the MDR intermediates can then be compared to the DFT-
calculated adsorption energies to assess the overall quality of the correlations. As seen from Fig. 2.6, the scaling relationships based on C and O adsorption energies (Fig. 5) function as excellent predictors across the entire spectrum of MDR intermediates and cluster–support systems. The deviation between values predicted by the scaling relationships and calculated from DFT is relatively small throughout the range of adsorption energies being considered. Indeed, the performance of these scaling relationships at predicting the average adsorption energies is surprisingly good given the variation in adsorption geometries and energies between systems and points to the general robustness of the chosen predictors, inspired from studies on crystalline facets, even for low-symmetry clusters.
The thermodynamics of the MDR have been explored quite thoroughly on a variety of surfaces and through a variety of methods, as discussed in Section 2.1. Here we perform an initial investigation of the MDR thermodynamics on low-symmetry supported Pt\textsubscript{13} nanoclusters.

Figure 2.6: Adsorption energies of MDR intermediates on all systems predicted by fitted scaling relationships based on C and O adsorption energies versus their DFT calculated values. Error bars are Student-T 95\% confidence intervals of the DFT-calculated adsorption energies. Equality line is plotted as a guide to the eye.

### 2.3.2 MDR THERMODYNAMICS

The thermodynamics of the MDR have been explored quite thoroughly on a variety of surfaces and through a variety of methods, as discussed in Section 2.1. Here we perform an initial investigation of the MDR thermodynamics on low-symmetry supported Pt\textsubscript{13} nanoclusters.
On Pt(111) Greeley and Mavrikakis identified the pathway $H_3COH \rightarrow H_2COH \rightarrow HCOH \rightarrow CO$ (Path 1) as the most dominant one for the MDR.\textsuperscript{32} Two additional pathways, $H_3COH \rightarrow H_3CO \rightarrow H_2CO \rightarrow HCO \rightarrow CO$ (Path 2) and $H_3COH \rightarrow H_2COH \rightarrow H_2CO \rightarrow HCO \rightarrow CO$ (Path 3), were identified as possible but relatively noncompetitive as, in comparison to the other two pathways, the rate limiting step of Path 1 has both a significantly lower barrier and higher reverse barrier, yielding an effective rate that is orders of magnitude higher than Paths 2 and 3. COH was shown to be present as a spectator species, with high barriers of formation and decomposition, but also high adsorption energy, leading to a minor poisoning effect on the catalyst surface. Since we used a different exchange-correlation functional (and a different DFT program) than Greeley and Mavrikakis, we revisited their proposed MDR pathways on Pt(111) and obtained essentially the same conclusions. The calculated reaction thermodynamics (Eqs. 4-6) for the Pt(111) surface as well as for a Pt\textsubscript{13} cluster bound at a divacancy in graphene are displayed in Fig. 2.7. (Results for other cluster–support systems are displayed in Figure S4.)
The thermodynamics of Path 1 are relatively unchanged between the Pt(111) surface and the divacancy-bound Pt$_{13}$ cluster. The statistical nature of our analysis does mean that some reactive sites on the cluster will exhibit reaction energies lower than average, indicating the possibility of outlier sites that contribute significant fractions of the total activity, analogous to the way that step-edges and defects have been shown to contribute significant activity and dominate the overall reaction on larger, faceted nanoparticles. The other two pathways (Paths 2 & 3), however, present interesting differences from the Pt(111) surface. Path 2 (H$_3$COH → H$_3$CO → H$_2$CO → HCO → CO) on Pt(111) is unfavorable due to higher reaction energy and barrier for the first reaction step (H$_3$COH → H$_3$CO).
However, on the divacancy-bound Pt$_{13}$ cluster, this first step is less uphill. Because of these interactions we believe that the second pathway could be more active on the graphene-divacancy-bound Pt$_{13}$ cluster than on the Pt(111) surface. Path 3 ($H_3CO \rightarrow H_2COH \rightarrow H_2CO \rightarrow HCO \rightarrow CO$) is less active on Pt(111), once again because of the unfavorable and high barrier for the $H_2COH \rightarrow H_2CO$ step. Again, for the divacancy-bound Pt$_{13}$ cluster case this step is significantly less unfavorable, with average reaction energy of essentially zero, and thus Path 3 could become much more active on the graphene-divacancy-bound Pt$_{13}$ cluster than on the Pt(111) surface. This finding is tested in Chapter 3 using the reaction barriers and microkinetic modeling. Overall, the interaction between the three MDR pathways appears to be significantly changed on the divacancy-bound Pt$_{13}$ cluster with respect to the Pt(111) surface: instead of having one dominant pathway contributing most of the catalytic activity as on the Pt(111) surface, the reaction thermodynamics suggest a mildly dominant pathway (that is possibly more active on the divacancy-bound Pt$_{13}$ cluster than on the Pt(111) surface), with two competing pathways also generating significant activity. As all reaction energies are statistical distributions rather than precise values on the low-symmetry supported Pt$_{13}$ clusters, the possibility of contributed activity from extraordinarily active outlier sites on the cluster is also a matter of future interest.

The thermodynamics and adsorption of COH are also of some interest in the graphene-divacancy-bound Pt$_{13}$ case. On Pt(111), COH has a very high adsorption energy, a high barrier of formation, and a very high barrier for decomposition into CO and H. It was found that this combination led to COH being a minor poison to reaction, occupying roughly 10% of available surface sites.$^{32}$ However, on the divacancy-bound
Pt\textsubscript{13} cluster, the energetics are very different. COH still has a high adsorption energy, but it is about 1 eV lower than the Pt(111) case (see Table S3 and Fig. S1). The reaction energy for forming COH from HCOH is much higher on the divacancy-bound Pt\textsubscript{13} cluster than on Pt(111), becoming thermodynamically even more unfavorable. This higher reaction energy then suggests the potential of an even higher barrier of formation, and means that the backwards reaction becomes thermodynamically favorable. Finally, the reaction energy for decomposition of COH into CO and H is dramatically more favorable on the divacancy-bound Pt\textsubscript{13} cluster than on the Pt(111) surface. Considering all of these factors, it seems plausible that less COH would be formed on the divacancy-bound Pt\textsubscript{13} cluster to begin with, and any COH that is formed could be hydrogenated, dehydrogenated, or desorbed more easily than on the Pt(111) surface, having the net effect of increasing the availability of reaction sites.

The other graphene-supported Pt\textsubscript{13} clusters also exhibit interesting reaction thermodynamics. More information on their specific details can be found in Figure S3 and Table G.5, but a few salient points will be discussed here. First, similarly to the graphene-divacancy-bound Pt\textsubscript{13} case, it seems likely that on all the Pt\textsubscript{13} clusters COH either would not be formed in appreciable amounts or would be able to hydrogenate/dehydrogenate to HCOH/CO, and not behave as a minor poison/spectator. Second, in general, most reaction steps have more negative reaction energies on all Pt\textsubscript{13} clusters relative to Pt(111). Furthermore, the reaction energies are also correlated with the strength of adsorption of the reactants and products on the supported Pt\textsubscript{13} clusters: weaker/stronger adsorption leads to smaller/larger reaction energies. To the extent that the adsorption energies of intermediates are in turn correlated with the cluster $d$-band
centers, which are sensitive to support defects, the support effect is then manifested on the reaction thermodynamics through this sequence of correlations. This suggests the possibility of different rate-limiting steps for certain pathways on the clusters, and for overall lower barriers assuming that BEP relationships hold for this novel system. Finally, some of the reaction steps have fairly large uncertainties, which suggests the possibility that the non-uniformity of the clusters could offer a non-zero concentration of sites with much lower barriers, therefore increasing the effective reaction rate of the system in a way that the average values would not indicate; however, it is impossible currently to make any conclusions based on this and more in-depth analysis is surely required.

2.4 CONCLUSIONS

We investigated the adsorption of MDR intermediates and examined the thermodynamics of several MDR pathways on Pt$_{13}$ nanoparticles with varying amounts of interaction with a graphene support. The average adsorption energies of the intermediates of the MDR experienced a rigid shift relative to Pt(111) as a result of support interaction, and this shift could be correlated well with the $d$-band center of the system, which is in turn influenced by the strength of support interaction. In addition, scaling relationships and $d$-band center correlations established on high-symmetry crystal surfaces appear to be successful for predicting the average adsorption behavior of molecules on supported Pt$_{13}$ clusters. A comparison of the MDR thermodynamics between the Pt(111) and divacancy graphene-supported Pt$_{13}$ suggest shifts in the interactions between the favorable reaction pathways, and may indicate overall higher activity for graphene-supported Pt$_{13}$ clusters compared to the Pt(111) surface. Overall,
our studies indicate that defective graphene-supported Pt$_{13}$ is a promising MDR catalyst and possesses qualitatively different adsorption and reaction thermodynamics from the Pt(111) surface, which may further explain the high activity seen in defective graphene-supported Pt nanoparticles.

The findings in this work suggest new questions that should be addressed next to move results towards the goal of rational design of MDR catalysts. Specifically, it remains to be investigated whether the reaction barriers on the supported clusters are different than those on single-crystal surfaces, and if those differences match expectations from experimental work. The validity of BEP-like relationships between the reaction barriers and reaction thermodynamics for these supported-cluster systems remains a significant open question. Confirmation of BEP-like relationships would greatly facilitate computationally inexpensive calculation of the reaction barriers for the full reaction network on the low-symmetry supported Pt$_{13}$ clusters, which could enable further investigation into the interplay of multiple support effects under realistic conditions.
CHAPTER 3

KINETICS OF THE METHANOL DECOMPOSITION REACTION OVER
DEFECTIVE-GRAPHENE SUPPORTED PT NANOPARTICLES: A MULTI-
SCALE COMPUTATIONAL STUDY

3.1 INTRODUCTION

Graphene has been demonstrated to be a very effective support for
electrocatalysts for methanol and hydrogen fuel cells.\textsuperscript{15,19,40–44} In particular, for direct-
methanol fuel cells, defective-graphene supported platinum clusters have been shown to
have high catalytic activity for the methanol decomposition reaction (MDR), and
increased resistance to both sintering and CO poisoning compared to more weakly
supported clusters on graphite and carbon black.\textsuperscript{15,19,40–44} The details of the binding of Pt
nanoclusters to defective graphene supports have been studied extensively- Via
computational and experimental work, Pt nanoclusters have been shown to adsorb
strongly to point-defect sites in the graphene support.\textsuperscript{42,45,46} Upon binding at point
defects, significant charge transfer takes place from the Pt nanoclusters to the graphene
support, correspondingly modifying the electronic structure of the nanoclusters.\textsuperscript{12,47–50}
This phenomenon suggests the use of predictors based upon electronic structure, in
particular the $d$-band center model, which have been used to great effect to allow
exploration of pure transition metal surfaces and surface alloys for use as catalysts.\textsuperscript{3,31,51–
55} Other predictors for catalytic activity are based on scaling relationships, which
correlate, for example, the adsorption of a molecule on different surfaces to the
adsorption energy of a simpler probe molecule on the same surface. These have been
demonstrated to be accurate in a wide variety of applications.\textsuperscript{3,4,51,56,57} In our previous
works, we have shown that support-induced shifts in the $d$-band center of defective-graphene supported Pt nanoparticles can be correlated with both CO adsorption energies and MDR intermediates adsorption energies in general.$^{33,58}$ The reduction of CO adsorption energies via support effects offers a possible explanation for the higher tolerance to CO poisoning that graphene-supported Pt nanoclusters exhibit. Other past work in our group also showed significant reduction in CO oxidation barriers on defective-graphene supported Pt nanoparticles, further unearthing the fundamental causes of the increased CO resistance.$^{83}$ The strong binding of Pt nanoclusters to support defects in graphene also explains the observed resistance to catalyst sintering. However, neither of these observations is sufficient to explain fully the higher catalytic activity for the methanol decomposition reaction (MDR) that is observed in experiments. Thus, the primary goal of this chapter is to present a detailed density functional theory (DFT) and microkinetic modeling study of the MDR over on defective-graphene supported Pt$_{13}$ nanoclusters with the goal of elucidating the role of support effect on MDR activity.

Calculations of any catalytic property (adsorption energies, transition states, etc.) on clusters require overcoming difficulties that are not present on high-symmetry surfaces. Due to there being few (if any) symmetry-equivalent adsorption sites on low-symmetry clusters, some form of statistical sampling must be undertaken, which magnifies the effort required to understand a reaction on a single cluster. In addition, clusters adopt different geometries and electronic structures on different supports, requiring separate calculations even for simple quantities such as adsorption energies. The combination of these factors makes exploration of cluster–support systems for their catalytic potential extraordinarily time-consuming and resource intensive. Therefore, in order to achieve a
broad and/or in-depth exploration of supported catalyst design, circumventing these extensive \textit{ab initio} calculations via robust predictors is highly desirable.

The MDR has been investigated extensively\cite{17,30,57,59–64}, in part due to its value for understanding and improving catalytic performance of direct-methanol fuel cells. Pioneering work in the field was performed by Greeley and Mavrikakis, who investigated the MDR on Pt(111) in detail\cite{32,65}. They showed via a combination of DFT calculations and microkinetic modeling that the most likely pathway for MDR on a Pt(111) single-crystal surface under ultra-high vacuum is $\text{H}_3\text{COH} \rightarrow \text{H}_2\text{COH} \rightarrow \text{HCOH} \rightarrow \text{CO}$ (henceforth, Path 1), with the first dehydrogenation step being rate-determining. Two other viable, but less favorable, pathways were identified: (i) $\text{H}_3\text{COH} \rightarrow \text{H}_3\text{CO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{HCO} \rightarrow \text{CO}$ (Path 2), with the first step also being the rate determining step, and (ii) $\text{H}_3\text{COH} \rightarrow \text{H}_2\text{COH} \rightarrow \text{H}_2\text{CO} \rightarrow \text{HCO} \rightarrow \text{CO}$ (Path 3), with the first and second steps having approximately the same barriers. In addition to the Pt(111) surface, the MDR pathway has also been fully or partially identified on stepped and defective platinum surfaces\cite{54}, $\text{B}_{12}\text{N}_{12}$ nanocages\cite{66}, the Cu(111) surface\cite{67}, the Cu(110) surface\cite{59}, the ZnO(10\overline{1}0) surface\cite{68}, among several others\cite{61,62,64,69–72}. Kandoi \textit{et al}.\cite{17} showed that the experimental performance of the Pt(111) surface catalyst for the MDR can be predicted qualitatively by a combination of \textit{ab initio} calculations and microkinetic modeling, along the way reaffirming the dominant pathway established by Greeley and Mavrikakis. In this work, we investigate the transition states of the MDR over Pt$_{13}$ nanoparticles. We show that the initial-state model for prediction of transition states is an accurate descriptor for the MDR barriers over defective-graphene supported Pt$_{13}$ nanoparticles (the BEP and final-state models were also tested and found to be ineffective for these system) and,
using the barrier data from this DFT-derived predictor relationship and previous results for MDR thermodynamics, (Ref 31) we proceed to implement a microkinetic model that allows for extensive exploration of support effects on the MDR over graphene-supported Pt nanoclusters at realistic conditions.

Microkinetic models are frequently used to quantify the combined effects of chemical thermodynamics and kinetics for a catalytic system at realistic operating conditions.4,17,52,89–92 The microkinetic model employed here is generally based on previous work for the MDR on Pt(111) by Kandoi et al.,17 with modifications aimed at improving accuracy for adsorption-desorption kinetics based on findings in more recent literature,93 as well as incorporating our own DFT data for Pt13 nanoclusters. One key limitation is that the present model does not include oxidation reactions, which are likely significant at realistic reaction conditions. We neglect oxidation reactions because including the presence of oxygen or water molecules would be prohibitively complicated and computationally expensive for our systems; nevertheless, we can directly compare our results to ultra-high vacuum systems studied in the literature.4,17

Our computational methodology is explained in Section 3.2. Results and discussion on the effect of support binding on the MDR activity and favorable pathways are presented in Section 3.3. Conclusions and closing remarks are presented in Section 3.4.

3.2 COMPUTATIONAL METHODOLOGY

3.2.1 DENSITY FUNCTIONAL THEORY CALCULATIONS

Spin-polarized DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP).73–76 The core and valence electrons were treated using the
projector-augmented wave function method.\textsuperscript{77,78} The Perdew-Burke-Ernzerhof generalized-gradient approximation (PBE) was used to describe electron exchange and correlation.\textsuperscript{79} From convergence studies, we chose a kinetic energy cutoff of 400 eV and a first-order Methfessel-Paxton smearing\textsuperscript{80} of 0.05 eV. All atomic positions were relaxed with a force tolerance of 0.02 eV/Å.

Initial low-energy Pt$_{13}$ cluster configurations (supported or unsupported) were generated via simulated annealing as reported in Ref. 11. The supports considered were 8×8 single-layer graphene sheets that were either defect free (pristine) or containing a point defect (vacancy or divacancy) at the cluster adsorption site. Graphene planes were separated in the normal direction by 18 Å of vacuum to prevent spurious interaction with periodic images. The Brillouin zone was sampled by a 2×2×1 Γ-centered $k$-point mesh, chosen from convergence studies. Unsupported Pt$_{13}$ clusters were modeled in an 18 Å cube using a single Γ point for reciprocal space sampling. Transition states were sampled on five random sites on each cluster—details on this process are included below. Sampling sites were chosen randomly, with repeated sites or sites hindered by graphene proximity (high steric hindrance) being discarded. The transition states are sampled on the same sites as investigated for adsorption characteristics in our previous work,\textsuperscript{33} with the “leaving” hydrogen in each dehydrogenation step moving to the ‘top’ site on the nearest possible surface Pt atom and the initial configurations for all transition states are interpolated from the adsorbed configurations found in that work.

Reference Pt(111) surface calculations were performed on a three-layer, 3×3 surface cell with the bottom two layers frozen in their bulk FCC geometry. Slabs of greater thickness with additional free layers were tested and not found to influence the adsorption
energies or transition states. The slabs were separated by 18 Å of vacuum normal to the surface to prevent spurious interactions. A Γ-centered, 5×5×1 k-point mesh was used for Brillouin zone sampling.

Transition states were determined using both the climbing-image nudged-elastic-band (CI-NEB) method and the dimer method. Transition-state searches in all cases were initiated with a NEB that was interpolated from converged adsorption configurations and run until the NEB pathway settled into a smooth energy profile with a single maxima, at which point the CI-NEB or dimer methods were implemented. Due to the highly fluxional nature of the surface, the NEB spring force was adjusted between 5-10 eV/Å on a case-by-case basis. Similarly, the dimer method and CI-NEB did not perform uniformly on the full set of sampled reaction steps, so calculations were switched between the different algorithms on a case-by-case basis. In some cases, the CI-NEB was constrained down to a single image with the limits being reset to the images adjacent to the transition state. If a CI-NEB image converged to a local minimum that was more stable than the initial reactant or product states, the pathway was reset to the new limits and restarted as a NEB calculation. Transition states were optimized until all forces were less than 0.02 eV/Å, and then validated by the existence a single imaginary vibrational frequency. For the Pt(111) surface, three of the 14 transition states were found to be in agreement (both energy barrier and vibration frequencies) with the work of Greeley & Mavrikakis, and the remaining barriers are taken from their work.

Of the various possible transition-state predictor relationships, we consider three linear relationships in this work that are described as follows:
BEP relationship:

\[ E_a = m \cdot \Delta E_{rxn} + b \]  

(3.1)

Initial-state model:

\[ E_{TS} = m \cdot E_{IS} + b \]  

(3.2)

Final-state model:

\[ E_{TS} = m \cdot E_{FS} + b \]  

(3.3)

where, for a given reaction step, \( E_a \) is the activation energy, \( \Delta E_{rxn} \) is the reaction energy of the given step, \( E_{TS} \) is the energy of the transition state, \( E_{IS} \) is the energy of the reactant state, and \( E_{FS} \) is the energy of the product state.

### 3.2.2 DEVELOPMENT OF A MICROKINETIC MODEL FOR MDR OVER DEFECTIVE-GRAFENESUPPORTED Pt\(_{13}\) NANOPARTICLES

The microkinetic model to be used for this research is based on previous work for the MDR on the Pt(111) surface by Mavrikakis and coworkers.\(^{17}\) The reaction network being considered encompasses the three pathways listed in Chapter 1 as well as adsorption steps for methanol, carbon monoxide, and hydrogen from the gas phase; the relevant elementary reactions are listed in Table .1. All other intermediates are considered to exist only on the Pt(111) surface, which is qualitatively reasonable considering that carbon balance for the real reactor shows 97\% of the product carbon is either CO or CH\(_4\).\(^{17}\) The CH\(_4\) production under realistic operating conditions is less than one-tenth the CO production on Pt(111), and is
assumed negligible both in this work and others since DFT calculations consistently show C-O bond activation to be very unfavorable over catalysts that are active for the MDR.\textsuperscript{2,4,17,65}

Table 3.1: Elementary reaction steps of the MDR on Pt(111) and Pt\textsubscript{13} nanoparticles being considered in the microkinetic model. An asterisk is used to represent an adsorption site on the Pt surface.

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH\textsubscript{3}OH(g) + * ↔ CH\textsubscript{3}OH*</td>
</tr>
<tr>
<td>2</td>
<td>CH\textsubscript{3}OH* + * ↔ CH\textsubscript{2}O* + H*</td>
</tr>
<tr>
<td>3</td>
<td>CH\textsubscript{2}O* + * ↔ CH\textsubscript{2}O* + H*</td>
</tr>
<tr>
<td>4</td>
<td>CH\textsubscript{2}O* + * ↔ HCO* + H*</td>
</tr>
<tr>
<td>5</td>
<td>HCO* + * ↔ CO* + H*</td>
</tr>
<tr>
<td>6</td>
<td>CO(g) + * ↔ CO*</td>
</tr>
<tr>
<td>7</td>
<td>H\textsubscript{2}(g) + 2* ↔ 2H*</td>
</tr>
<tr>
<td>8</td>
<td>CH\textsubscript{3}OH* + * ↔ CH\textsubscript{2}OH* + H*</td>
</tr>
<tr>
<td>9</td>
<td>CH\textsubscript{2}OH* + * ↔ CHOH* + H*</td>
</tr>
<tr>
<td>10</td>
<td>CHOH* + * ↔ CO* + H*</td>
</tr>
<tr>
<td>11</td>
<td>COH* + * ↔ CO* + H*</td>
</tr>
<tr>
<td>12</td>
<td>CHOH* + 2* ↔ CO* + 2H*</td>
</tr>
<tr>
<td>13</td>
<td>CH\textsubscript{2}OH* + * ↔ CH\textsubscript{2}O* + H*</td>
</tr>
<tr>
<td>14</td>
<td>CHOH* + * ↔ HCO* + H*</td>
</tr>
</tbody>
</table>

The species thermodynamics are determined entirely by DFT calculation in order to have a consistent basis. Gas phase enthalpies are corrected for zero-point energies; standard entropies and heat capacities of the species are calculated using partition functions with translation, rigid rotor, and harmonic oscillator contributions as\textsuperscript{17}

\[
S^0_{\text{gas}} = S^0_{\text{trans,3D}} + S^0_{\text{rot}} + S^0_{\text{vib}},
\]

\[
S^0_{\text{trans,3D}} = k_B \left[ \ln \left( \frac{(2\pi m k_B T)^{3/2}}{h^3} \right) + \ln \left( \frac{k_B T}{p} \right) + \frac{5}{2} \right],
\]

where \( m \) is the mass of the molecule of interest, \( R \) is the universal gas constant, \( k_B \) is the Boltzmann constant, \( h \) is the Planck constant, \( T \) and \( P \) are the temperature and pressure of the system, respectively,
\[ S_{\text{rot}}^0 = k_B \left[ \ln \left( \frac{8\pi^2 \sqrt{8\pi^4 I_{x1} I_{x2} I_{x3}}}{\sigma_r h^3} \right) + \frac{3}{2} \right], \] (3.6)

where \( I_{x1}, I_{x2}, \) and \( I_{x3} \) are the moments of inertia of the molecule about the three principal axes, and \( \sigma_r \) is the rotational symmetry number, and

\[ S_{\text{vib}}^0 = k_B \sum_{i}^{\text{all modes}} x_i \ln \left( \frac{x_i}{e^{x_i} - 1} \right) , x_i = \frac{\hbar \nu_i}{k_B T} . \] (3.7)

The heat capacity is defined similarly as

\[ c_p = C_{\text{trans},3D} + C_{\text{rot}} + C_{\text{vib}}, \] (3.8)

\[ C_{\text{trans},3D} = C_{\text{rot}} = \frac{3}{2} k_B, \] (3.9)

\[ C_{\text{vib}} = k_B \sum_{i}^{\text{all modes}} \exp \left( \frac{x_i}{e^{x_i} - 1} \right) , x_i = \frac{\hbar \nu_i}{k_B T} , \] (3.10)

where \( \nu_i \) is a vibrational frequency of the species of interest. The enthalpy of any given surface species is then given by

\[ H_{\text{surface}}^0 = H_{\text{gas}}^0 + E_{\text{ads}} + \Delta ZPE, \] (3.11)

where \( E_{\text{ads}} \) is the adsorption energy calculated for an MDR intermediate and \( \Delta ZPE \) is the change in zero-point energy upon adsorption. The entropy of an adsorbed species is determined by the relation

\[ S_{\text{ad}}^0 = 0.70 S_{\text{gas}}^0 - 3.3 k_B, \] (3.12)

where \( S_{\text{gas}}^0 \) is the standard entropy of the gas phase species. This relation was found by Campbell et al.\(^93\) to be significantly more accurate at describing the surface entropy of adsorbed molecules than traditional statistical mechanics calculations. The gas-phase enthalpies of H (assumed to be one-half the enthalpy of H\(_2\)) and CO at 298K are used as a consistent thermodynamic reference states for all other molecules. The equilibrium constants for each reaction step are calculated as
\[ K_{i,eq} = \frac{k_{i,f}}{k_{i,r}} = e^{\frac{\Delta G_i}{k_BT}}, \] (3.13)

where \( \Delta G_i \) is the change Gibbs free energy between the products and reactants of the elementary step, calculated using the “average-H” simplification discussed previously, \( k_{i,f} \) is the forward rate constant for the reaction step, and \( k_{i,r} \) is the reverse rate constant for the reaction step.

For the adsorption-desorption steps (steps 1, 6, and 7 in Table 3.1), the kinetics are based on the work of Campbell, et al.\(^9\) The desorption reaction constant is defined as

\[ k_{\text{des}} = \frac{k_BT}{h} \exp \left( \frac{S^0_{\text{gas}} - S^0_{\text{gas,1D-trans}} - S^0_{\text{ad}}}{k_B} \right), \] (3.14)

where \( S^0_{\text{gas}} \) is the standard entropy of the gas phase species, \( S^0_{\text{gas,1D-trans}} \) is the one-dimensional translation contribution to the standard entropy of the gas phase species (assumed to be simply 1/3 the total translational entropy), \( S^0_{\text{ad}} \) is the standard entropy of the adsorbed surface species calculated using Eq. (3.12). The adsorption constant can then be defined using the thermodynamic equilibrium constant for the adsorption/desorption step as seen in Eq. (3.13). For the surface dehydrogenation steps the forward rate constant is calculated as

\[ k_i = A e^{\frac{E_{a,i}}{k_BT}}, \] (3.15)

where \( A \) is the pre-exponential factor and \( E_{a,i} \) is the ZPE-corrected activation energy of that elementary step. The activation energies used are from DFT calculations where possible (all reaction steps on the Pt(111) slab and 19 reaction steps on the unsupported Pt\(_{13}\) nanoparticles) and in all other cases are generated using the initial-state model discussed previously. The pre-exponential factor of each reaction step is calculated as
\[
A = \frac{k_B T}{h} \exp \left( \frac{S_{TS}^{TS} - \sum_k S_{\nu l b}}{k_B} \right),
\]

(3.16)

where \( S_{TS}^{TS} \) is the vibrational entropy of the transition state, and \( \sum_k S_{\nu l b} \) is the sum of the vibrational entropies of the reactants of the elementary step. This is the typical harmonic-transition-state-theory expression assuming that the reactant and the transition state have the same mass, which is true in all reaction steps for the MDR. The reverse reaction rate can then be calculated using the equilibrium constant for that elementary step.

The microkinetic model software was written in MATLAB. The code is reproduced in Appendix E and is also available online at [github.com/rgasper/MDR-MKM](https://github.com/rgasper/MDR-MKM). The model is not intended to produce results in strict agreement with experiments, but to allow for quantitative comparison between the different catalysts considered in this study at relevant conditions. Briefly, the reactor is modeled with non-dimensional quantities and could represent either a batch-flow or plug-flow reactor (PFR) depending on the normalization of the dimensionless time parameter. We normalize units of time by a factor of \( k_B T / h \) (\( \approx 10^{13} \)) and normalize units of concentration (both gas and surface coverage) by the total gas concentration at reactor conditions. The reactor is operated at 473 K and 1 bar, which are reasonable conditions for a methanol fuel cell.\(^{17}\) There are three ordinary differential equations (ODEs) for the time-dependent concentration of the gas species (methanol, CO, and H\(_2\)), nine differential equations for fractional coverages of the surface intermediates, and one site-balance equation. The ODEs are integrated via the “ode15s” stiff ODE solver in MATLAB until the coverage of the surface species and hydrogen production rate stabilize, which occurs in \( 2 \times 10^8 \) time steps (approximately \( 1 \times 10^{-4} \) seconds) after introduction of methanol gas to the reactor for the Pt(111) and divacancy-graphene supported Pt\(_{13}\). (The other three catalyst–support systems don’t show
appreciable catalytic activity as discussed in section 3.3.2.) The initial condition is a concentrated feed of methanol gas with the remaining gas balance being inert filler gas. The initial condition is a concentrated feed of methanol gas with the remaining gas balance being inert filler gas. The solution of the ODEs yields the gas concentrations and surface coverages. The model accounts for the effects of adsorbate-adsorbate interactions only in the case of CO adsorption. CO coverage dominates the surface and it has been shown experimentally that high CO coverage reduces CO adsorption energy. DFT calculation has shown that the effect of CO coverage on the adsorption energies of other MDR intermediates is negligible, so a full accounting of adsorbate-adsorbate interactions is neglected. The CO adsorption energy of each system is calculated using the expression

\[
E_{ads,CO} = A + B \exp(-4.79 \theta_{CO}),
\]

where A and B are parameters fit to the CO adsorption energy spread reported for each system by Fampiou and Ramasubramaniam. \( E_{ads,CO} \) is the adsorption energy of CO, and \( \theta_{CO} \) is the unitless coverage of CO, the particular values of which are shown below in Table. This equation gives a smooth interpolation between CO adsorption energies at 0% and 100% coverage. In addition, the adsorption energy of COH for all systems is adjusted by +2.5%, as the unchanged DFT value produces unreasonable results for the well-studied Pt(111) system. This modification is in the same vein as Kandi et al.’s approach and has a negligible effect on the Pt13 systems, which the model predicts to have near-zero coverages of COH.
Table 3.2: Parameter fits for CO adsorption energy curve based to match proportional CO adsorption energy drop shown by Fampiou and Ramasubramaniam.\textsuperscript{83}

<table>
<thead>
<tr>
<th>System</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>-1.89</td>
<td>0.0065</td>
</tr>
<tr>
<td>Unsupported Pt$_{13}$</td>
<td>-2.44</td>
<td>0.003</td>
</tr>
<tr>
<td>Pristine-Graphene Supported Pt$_{13}$</td>
<td>-2.60</td>
<td>0.0035</td>
</tr>
<tr>
<td>Vacancy-Graphene Supported Pt$_{13}$</td>
<td>-2.45</td>
<td>0.002125</td>
</tr>
<tr>
<td>Divacancy-Graphene Supported Pt$_{13}$</td>
<td>-1.74</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

Finally, we also conduct a simple sensitivity analysis for the MDR over divacancy-supported Pt$_{13}$. To this end we calculate the change in hydrogen gas production resulting from a small change in one of the model parameters. The parameters considered are the adsorption energies of each species involved, and the barriers of the thirteen reaction steps. The adsorption energies were changed by $\pm \frac{1}{4}$ the error (95\% Student-T confidence interval) identified in our previous publication,\textsuperscript{33} and the reaction barriers were adjusted by $\pm 5\%$.

3.3 RESULTS AND DISCUSSION

3.3.1 INITIAL-STATE MODEL FOR PREDICTION OF METHANOL DECOMPOSITION REACTION TRANSITION STATES ON DEFECTIVE-GRAPHENE SUPPORTED PT NANOPARTICLES

As discussed in Chapter 1, having a predictor relationship to calculate reaction barriers without requiring numerous DFT transition-state calculations is essential for modeling the MDR on low-symmetry supported nanoparticles. Therefore, we have
undertaken select MDR reaction barriers calculations for our systems in order to understand and quantify the influence of the graphene support on overall MDR kinetics.

Just as with the fitting of predictor relationships for adsorption energies of MDR intermediates on low-symmetry, supported nanoparticles, the fitting of predictor relations for reaction barriers is extremely challenging due to the highly deformable nature of the low-symmetry cluster. The low-symmetry surface requires some form of statistical sampling, and correctly interpreting the results requires taking into account the inherent variability of the surfaces. To fit predictor relationships for the defective-graphene supported Pt$_{13}$ nanoparticles, we use DFT data for the MDR barriers over the Pt(111) surface and from a sampling of barriers over the unsupported Pt$_{13}$ nanoparticle surface. Significant effort was made to converge barrier calculations on the divacancy-graphene supported Pt$_{13}$ surface and this effort is ongoing. The highly fluxional nature of the nanoparticle surface combined with the larger system size necessary to accommodate the graphene support makes the convergence of reaction barriers extremely tedious. The average DFT-calculated reaction barriers on the unsupported Pt$_{13}$ and the Pt(111) surface that were used for fitting of the predictor relationships are shown below Table 3.3. The full table of sampled barriers on the unsupported Pt$_{13}$ can be found in Table F.3.
Table 3.3: DFT-sampled barriers for the MDR over the unsupported Pt$_{13}$ nanoparticles and the Pt(111) surface. Pt$_{13}$ results are average values. Steps with no entry had no converged transition state among the sampled reaction steps. Values in eV. No barriers are reported for steps one, six, and seven as these are adsorption/desorption reactions and assumed to have no barrier, as is consistent with the MDR literature.$^{4,17}$ The full set of sampled barriers on unsupported Pt$_{13}$ is in Table F.1.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Pt(111)</th>
<th>Pt$_{13}$ Averages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$OH(g) + * ⇌ CH$_3$OH*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$OH* + * ⇌ CH$_3$O* + H*</td>
<td>0.47</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$O* + * ⇌ CH$_2$O* + H*</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>4</td>
<td>CH$_2$O* + * ⇌ HCO* + H*</td>
<td>0.05</td>
<td>0.65</td>
</tr>
<tr>
<td>5</td>
<td>HCO* + * ⇌ CO* + H*</td>
<td>0.12</td>
<td>1.19</td>
</tr>
<tr>
<td>6</td>
<td>CO(g) + * ⇌ CO*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$(g) + 2* ⇌ H* + H*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>CH$_3$OH* + * ⇌ CH$_2$OH* + H*</td>
<td>0.51</td>
<td>0.62</td>
</tr>
<tr>
<td>9</td>
<td>CH$_2$OH* + * ⇌ CHO* + H*</td>
<td>0.43</td>
<td>1.22</td>
</tr>
<tr>
<td>10</td>
<td>CHO* + * ⇌ CO* + H*</td>
<td>0.59</td>
<td>0.58</td>
</tr>
<tr>
<td>11</td>
<td>COH* + * ⇌ CO* + H*</td>
<td>0.80</td>
<td>0.61</td>
</tr>
<tr>
<td>12</td>
<td>CHO* + 2* ⇌ CO* + 2H*</td>
<td>0.24</td>
<td>0.91</td>
</tr>
<tr>
<td>13</td>
<td>CH$_2$OH* + * ⇌ CH$_2$O* + H*</td>
<td>0.29</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>CHO* + * ⇌ HCO* + H*</td>
<td>-</td>
<td>1.13</td>
</tr>
</tbody>
</table>

For the MDR over Pt(111), we use the DFT-calculated barriers taken from Greeley and Mavrikakis’ work.$^{32}$ These barriers include zero-point energy corrections. We have independently verified, using our own calculations, the validity of a small sample of these transition states and their corresponding vibrational frequencies. Furthermore, we have calculated 19 transition states on the unsupported Pt$_{13}$ nanoparticle along with the associated ZPE-corrections. These ZPE-corrected transition states, combined with the Pt(111) MDR transition states from literature, supply us with the data for fitting various predictor relationships.
We attempted to fit all three common transition-state predictor models to our DFT transition-state data—the BEP, the initial-state model, and the final-state model. The models are simple linear relationships, with the definitions contained in section 3.2.1. The BEP relationship and final-state model did not provide accurate fits. The initial-state model, however, fit well for both the individual data sets and combined data set of the unsupported Pt\textsubscript{13} and Pt(111) transition states, especially considering the inherent variability of the unsupported Pt\textsubscript{13} surface. The quality of the fit can be seen below in Figure 3.1. The activation energy for each reaction step can be observed as the vertical height of each datum above the parity line. The average activation energies of the individual steps show a wide range between 0.15–1.2 eV and the initial-state model is seen to fit the data accurately over this range, with the activation energies corresponding to the highest/lowest energy initial states being fit most accurately. With this particular data sampling, it appears that the initial-state model is predicting barriers that are modestly larger than their true values. Given the acceptable quality of the initial-state energy as a predictor for reaction barriers over two very different systems—the Pt(111) surface and isolated Pt\textsubscript{13} nanoclusters that are two extreme cases of the systems considered here—we assume for now that the initial-state model fit to the Pt(111) and unsupported Pt\textsubscript{13} data is a reasonable descriptor for the defective-graphene supported Pt\textsubscript{13}. This assumption is supported by the Sabatier principle, which states that a strongly (weakly) bound reactant will have a low (high) barrier for reaction. We also note that the adsorption energies of MDR intermediates on defective-graphene supported Pt\textsubscript{13} nanoparticles are intermediate to those of the Pt(111) slab and the unsupported Pt\textsubscript{13} clusters and thus, we may expect the same of the reaction barriers.
3.3.2 BEHAVIOR OF THE METHANOL DECOMPOSITION REACTION OVER PT(111) AND DEFECTIVE-GRAPHENE SUPPORTED PLATINUM NANOPARTICLES

With the initial-state predictor relation at hand, we use the equations listed in Section 3.2 to calculate the reaction barriers and rates that are required for the microkinetic model. The microkinetic model was run using thermodynamic and kinetic information from all the systems, but only produced useful results for the MDR over the Pt(111) and the graphene divacancy-bound Pt$_{13}$. For the other three systems (unsupported Pt$_{13}$ clusters, pristine graphene-supported Pt$_{13}$, and graphene vacancy-bound Pt$_{13}$), the overall adsorption energies are too strong and cause the percentage of free sites to tend towards zero resulting in negligible MDR turnover; this is consistent with a different kinetic
model in the literature suggesting a nominal turnover frequency for the MDR of \(\sim 10^{15}\) over Pt nanoparticles.\(^4\)

Comparing the results of the MDR over divacancy-graphene supported Pt\(_{13}\) to that over the Pt(111) slab, the model suggests similar (within an order of magnitude) surface-area-normalized reaction rates for the MDR. This is a notable result, as these two systems are structurally quite different, and reported turnover frequencies for ultra-small Pt nanoparticles are very low.\(^4\) However, the most active pathway is different between the two systems. The gas phase behavior is similar for both systems as well, with the model predicting that the divacancy-graphene supported Pt\(_{13}\) system produces H\(_2\) gas at approximately 1/3 the rate (surface-area normalized) of the Pt(111) system, and neither produce significant quantities of CO gas. Additionally, the abundance of free sites is nearly the same between the two systems, about 4%. The reaction rates of the MDR over Pt(111) and over divacancy-graphene supported Pt\(_{13}\) are displayed in Figs. 3.2 & 3.3. For Pt(111), we find the same most-active pathway as Kandoi \textit{et al.}\(^{17}\) – H\(_3\)COH \(\rightarrow\) H\(_2\)COH \(\rightarrow\) HCOH \(\rightarrow\) CO. However, the most active pathway on the divacancy-graphene supported Pt\(_{13}\) is H\(_3\)COH \(\rightarrow\) H\(_2\)COH \(\rightarrow\) H\(_2\)CO \(\rightarrow\) HCO \(\rightarrow\) CO. The dominant and secondary pathways have similar reaction rates for the two systems. A significant difference between the MDR network on the two catalysts is that the net rate of COH formation is an order of magnitude lower on divacancy-graphene supported Pt\(_{13}\) than on Pt(111); the irreversible reaction directions favor COH decomposition on the former and COH accumulation on the latter. The result of these differences is that the coverage of COH on Pt(111) is around 15%-20%, depending on temperature and pressure, whereas the coverage of COH on divacancy-graphene supported Pt\(_{13}\) is much lower, around 4%.
In short, COH is a secondary catalyst poison on Pt(111) but does not poison the divacancy-graphene supported Pt\textsubscript{13}; however, the coverage of CO is higher on the divacancy-graphene supported Pt\textsubscript{13} than on Pt(111), making up for the difference. Both the COH coverage and free-site coverage for Pt(111) we report here are different from what has been reported in the literature previously\textsuperscript{17}; however, given that these results are calculated using an entirely different expression for adsorption-desorption reactions (found to be more accurate than traditional harmonic transition state theory)\textsuperscript{93}, and that these results are exquisitely sensitive to the relative adsorption energies of COH and CO on the Pt(111) surface, we do not see this as evidence of a failure in the model.

Figure 3.2: MDR reaction rates over Pt(111) catalyst surface. Surface-area-normalized reaction rates are dimensionless and rounded to the nearest power of ten. The most favorable reaction pathway is indicated with green arrows (see legend for details). Hydrogen atoms stacked vertically alongside the intermediates represent those that are adsorbed onto the catalyst surface.
Figure 3.3: MDR reaction rates over divacancy-graphene supported Pt$_{13}$ catalyst surface. Surface-area-normalized reaction rates are dimensionless and rounded to the nearest power of ten. The most favorable reaction pathway is indicated with green arrows (see legend for details). Hydrogen atoms stacked vertically alongside the intermediates represent those that are adsorbed onto the catalyst surface.

A sensitivity analysis conducted on the divacancy-graphene Pt$_{13}$ system shows that the most impactful reaction barrier is the C-H bond breakage to form H$_2$COH from H$_3$COH. This is the same as has been reported for the MDR over Pt(111), and is a sensible result as this step is integral in both primary and secondary reaction pathways. The sensitivity analysis also shows that the most impactful species adsorption energy is hydrogen, because adjusting the hydrogen adsorption energy affects both the overall reaction equilibrium (thus the thermodynamic driving force) and every single dehydrogenation reaction on the catalyst surface.
3.4 CONCLUSIONS

In summary our DFT-based microkinetic model for MDR shows that the divacancy-graphene supported Pt\textsubscript{13} system produces H\textsubscript{2} gas at approximately 1/3 the rate (surface-area normalized) of the Pt(111) system. Considering that Pt nanoparticles supported on defective graphene are more resistant to sintering than those on carbon black, and thus retain high surface area, our results suggests that defective-graphene supported Pt nanoparticles could have similar or greater activity for the MDR than carbon-black supported Pt nanoparticles. Additionally, oxidation of CO on defective-graphene supported Pt\textsubscript{13}, which has not been considered here, has been shown by Fampiou and Ramasubramaniam\textsuperscript{83} to have a low barrier that is similar in magnitude to the barriers in the most active MDR pathways over the divacancy-graphene supported Pt\textsubscript{13}. Given that the model currently predicts a similar abundance of free sites between the systems (≈4%) and that the model reports significantly higher CO coverage on the divacancy-graphene supported Pt\textsubscript{13} than the Pt(111), it is plausible that under realistic operating conditions with an oxygen source present (e.g., water) the defective-graphene supported nanoparticles will display a higher rate of CO oxidation and thus, greater abundance of free sites than on carbon-black supported nanoparticles. This expectation would also corroborate with the greater change in activity observed in experiments for PtRu nanoparticles on defective-graphene supports,\textsuperscript{19,20} as Ru is known to activate water under reaction conditions.\textsuperscript{16,18} Overall, our DFT-based microkinetic model now offers a mechanistic explanation- that strong binding of Pt nanoclusters to graphene defects stabilizes ultra-small nanoclusters with high surface area, and that these are made more active for the MDR via charge transfer from the Pt to the graphene- for the role of
defective graphene supports in enhancing the catalytic activity of ultra-small Pt nanoclusters and opens the door to defect-engineering of supports as another dimension of rational catalyst design.
CHAPTER 4

ADSORPTION OF CO ON LARGER PT NANOPARTICLES AND IMPROVED PREDICTORS VIA MACHINE LEARNING

My contributions to research in this chapter included sampling of CO adsorption energies on the Pt nanoparticles and the energy decomposition analysis thereof, as well as partial development of the machine-learning model. The generation of low-energy structures of Pt nanoparticles and implementation of the machine learning model was performed by Dr. Hongbo Shi. Here, I provide a description of my contributions; complete details can be found in our publication,\textsuperscript{39} included in Appendix B.

4.1 INTRODUCTION

Platinum nanoparticles are extensively used as catalysts for electrochemical reactions, being among the best catalysts for hydrogen and methanol fuel cells.\textsuperscript{15,16} While it is generally desirable to prepare nanoparticles with sizes as small as possible in order to attain high electrocatalytic surface area while optimally utilizing the precious metal, ultra-small (~1 nm) nanoparticles begin to present significant deviations in properties relative to their larger, bulk-like counterparts. Examples of such behavior have been shown in many cases experimentally and computationally,\textsuperscript{97-99} with the particularly well-known example of gold, which is normally inert, turning into an effective catalyst in its nanocluster form.\textsuperscript{24,28,29} In addition, it has been observed that ultra-small nanoparticles become exquisitely sensitive to the particle structure, adding more complexity to the issue.\textsuperscript{24-27} Hence, in this work we seek to understand the properties of sub-nanometer Pt clusters, as they correlate with changing particle size, and attempt to find suitable
predictors for adsorbate binding energies that can help circumvent expensive density functional theory (DFT) calculations. Multiple computational groups have also addressed this topic but with a key limitation, namely, focusing only on high-symmetry cluster morphologies.\textsuperscript{99–102} Experimental evidence and computational modeling have shown that real nanoparticles do not adopt high-symmetry structures, and instead adopt somewhat disordered low-symmetry structures.\textsuperscript{103–105} The effects of such morphological variations on the electronic structure are particularly noticeable at small size clusters, as shown in our previous work on supported and unsupported Pt\textsubscript{13} nanoclusters.\textsuperscript{10,58} In this work, we present a systematic analysis of the influence of cluster size and morphology on adsorbate binding using the well-known catalyst poison, carbon monoxide, as an example.

There have been several investigations into the trends of adsorbate binding energies with size on Pt nanoparticles. Li \textit{et al}.\textsuperscript{99} studied CO and O adsorption on selected surface sites on Pt nanoclusters and showed that the adsorption energies with respect to cluster size converge to the bulk values rapidly (at \textasciitilde 147 atoms) and monotonically. Toyoda \textit{et al}.\textsuperscript{100} showed experimentally that the $d$-band center of Pt nanoparticles tends to shift towards the Fermi level with decreasing size, and correlated this shift with a change in electrocatalytic activity; unfortunately, their analysis did not extend into the sub-nanometer size range, where we would expect deviations from quantum size effects to arise. Calle-Vallejo \textit{et al}.\textsuperscript{102} showed on a few truncated octahedral Pt nanoparticles that coordination number is linearly correlated with O, O$_2$, OOH, H$_2$O, and H$_2$O$_2$ adsorption energies across size range but also pointed out that the $d$-band center model can fail on nanocluster systems. Yudanov \textit{et al}.\textsuperscript{98} investigated explicitly the relationship of CO
adsorption energy with size on various high-symmetry Pd nanoparticles, densely sampling sizes below 116 atoms. They observed a definite minimum in CO adsorption energy around a size of 40 atoms, and a linear dependence of cluster $d$-band center with size. Han et al.\textsuperscript{101} showed that the $d$-band center model is accurate for predicting adsorption behavior of O and OH on the facets of cuboctahedral clusters, but fails to predict the edge and vertex adsorption behavior accurately. In short, small molecule adsorption on nanoclusters of different geometries have led to contradictory conclusions: monotonic convergence with respect to size\textsuperscript{99} versus the existence of local minima,\textsuperscript{98} and evidence that simple linear prediction models are accurate \textsuperscript{24} versus their breakdown.\textsuperscript{101,102} These examples from literature form a contradictory picture, possibly because the properties of nanocluster catalysts can exhibit significant sensitivity to both size and structure. Hence, we seek to investigate in more detail the trends of CO adsorption energy with size of Pt nanoclusters that have realistic, global minimum geometries at all sizes considered; this is necessary in order to fully understand whether the conclusions arrived at are truly due to size effects and not merely due to variations in arbitrarily selected particle geometries. Furthermore, beyond addressing the issue of structure sensitivity, we also explore whether single-predictor models (e.g., based on $d$-band centers or coordination number) are sufficient to quantify adsorbate binding energies on low-symmetry, low-energy clusters or if multiple-predictor models are essential for quantitative accuracy.

The first key feature of our current work – at variance with previous studies\textsuperscript{99–102} – is that we conduct CO adsorption calculations on low-symmetry, low-energy nanoclusters. These cluster morphologies are obtained by the application of an empirical bond-order
potential driven Genetic Algorithm (GA), described in previous by Shi et al.\textsuperscript{10} As shown in that work, the empirical-potential-based GA reliably predicts low-energy, low-symmetry cluster morphologies as confirmed by subsequent verification via DFT calculations across a range of cluster sizes. Hence, this approach both allows us to examine realistic minimum-energy structures for any given size of nanoparticle, and eliminates having to decide between the fitness of various arbitrary, high-symmetry geometries. Once low-energy cluster morphologies are obtained from the GA at relatively low computational cost, the remainder of the computational effort can be expended in higher-level DFT calculations of adsorbate binding on these clusters. One of the main challenges of investigating adsorbate binding on these low-symmetry structures is that they generally do not possess symmetry-equivalent sites unlike bulk-terminated crystal facets and high-symmetry clusters. Hence, some form of statistical sampling must be undertaken for calculating even simple adsorption properties, requiring a compromise between accuracy and computational effort spent on repeatedly sampling the same cluster. Thus, it becomes extremely useful to be able to predict both average as well as site-specific adsorption energies on these disordered structures using relatively simple structural metrics and/or limited electronic structure information without having to undertake full-blown DFT adsorption calculations on every available surface site. In order to approach this challenging problem, the second key feature of our work is the application of a machine learning tool \textsuperscript{106,107} to the prediction of CO adsorption energies on sub-nanometer Pt clusters. The use of machine learning techniques in materials science is in its infancy and growing,\textsuperscript{7,108} and a few groups have recently explored using machine learning for predictions of adsorbate binding on transition-metal surfaces,
reporting modest errors (~0.1 eV) with respect to DFT.\textsuperscript{35,37} The gradient-boosting algorithm was used recently by Takigawa \textit{et al.} \textsuperscript{38} to accurately predict the \textit{d}-band center of bulk alloys and alloy surfaces based only on mechanical and structural properties, demonstrating the potential usefulness of machine learning approaches for computational catalysis research. To the best of our knowledge, machine-learning algorithms have yet to be applied to predict adsorbate binding on clusters and our work represents an early example of the promise of this approach to this class of problems.

\textbf{4.2 COMPUTATIONAL METHODS}

\textbf{4.2.1 GENETIC ALGORITHM AND MINIMUM-ENERGY NANOPARTICLE MORPHOLOGIES}

Realistic structures for Pt\textsubscript{N} (\(N = 4-147\)) clusters were obtained by sampling the hyper-dimensional energy surface using a Genetic Algorithm (GA), the details of which are reported in Ref. 10; GA calculations were performed by Dr. Hongbo Shi. Pt-Pt interactions were described using Albe \textit{et al.}’s Tersoff-style empirical potential.\textsuperscript{109} As shown previously,\textsuperscript{10} minimum-energy structures found by the GA consistently displayed low symmetry and were confirmed via DFT to be lower in energy than icosahedral and cuboctahedral clusters, indicating the robustness of the GA and the accuracy of Albe \textit{et al.}’s potential. The GA-optimized clusters were then used as the starting point for subsequent DFT calculations of CO adsorption. The combined empirical-potential-based GA and DFT approach allows us to investigate the coupled effects of morphology and size on the catalytic activity of the clusters.
4.2.2 DENSITY FUNCTIONAL THEORY CALCULATIONS

Non-spin-polarized DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP).\textsuperscript{73–76} The core and valence electrons were treated using the projector-augmented wave method.\textsuperscript{77,78} The Perdew-Burke-Ernzerhof (PBE) form of the generalized-gradient approximation was used to describe electron exchange and correlation.\textsuperscript{79} From convergence studies, we chose a kinetic energy cutoff of 400 eV and a second-order Methfessel-Paxton smearing\textsuperscript{80} of 0.05 eV. All atomic positions were relaxed with a force tolerance of 0.01 eV/Å. The Brillouin zone was sampled using a single \Gamma point.

Initial structures for the Pt\textsubscript{N} clusters were taken from the empirical bond-order potential based GA described above and subjected to an additional conjugate-gradient minimization in VASP to generate the low-energy DFT reference state. While the empirical-potential and DFT potential energy surfaces (PES) are not identical, we have shown previously\textsuperscript{10} that the ordering of low-energy structural isomers is almost always consistently preserved between the empirical potential and DFT, which justifies our approach of simply importing the GA structure into DFT without further exhaustive sampling of the PES. High-symmetry icosahedral (\textit{I}h) and cuboctahedral (\textit{O}h) clusters were also sampled at discrete “magic-number” sizes (13, 55, and 147 atoms). For the purposes of this study, sampling of CO adsorption was only undertaken at the on-top adsorption sites as this configuration has been found to generally be the most favorable site for CO adsorption on Pt nanoclusters.\textsuperscript{58} The CO molecule was placed initially at a distance of 1.88 Å from the selected Pt atom along the radial direction as defined by a vector directed from the nanocluster center-of-mass to the Pt atom. This Pt-C bond
distance was chosen from initial test calculations of CO adsorption on clusters that showed this to be the converged Pt-C bond length, on average. CO binding on PtN clusters was calculated at numerous on-top sites (between 8-20 per cluster) to sample the full range of d-band center positions and coordination numbers available on the cluster. The high-symmetry Ik and Oh clusters were sampled at all the symmetry-inequivalent sites and cluster averages were calculated with weights corresponding to the site multiplicity.

The adsorption energy \( \left( E_{ads} \right) \) of a CO molecule on a PtN cluster is calculated as

\[
E_{ads} = E(Pt_N + CO) - E(Pt_N) - E(CO)
\]

where \( E(Pt_N + CO) \) is the total energy of the N-atom Pt cluster with one adsorbed CO molecule, \( E(Pt_N) \) is the energy of the isolated N-atom Pt cluster, and \( E(CO) \) is the energy of the isolated CO molecule. To separate out the contributions from charge redistribution during CO chemisorption from strain relaxation in the molecule and/or the cluster, we employ three distinct definitions adsorption energy. In the first instance, the adsorption energy \( \left( E_{ads}^{AF}; AF \text{ – all frozen} \right) \) is calculated at the starting adsorption configuration as discussed above by keeping all atoms (Pt cluster and CO) frozen. In the second instance, only the CO molecule is allowed to fully relax while the Pt cluster is frozen; the resulting adsorption energy \( \left( E_{ads}^{FC}; FC \text{ – frozen cluster} \right) \) now quantifies the ligand effect. Finally, the adsorption energy is calculated by allowing for complete relaxation of the cluster and the molecule and the resulting quantity \( \left( E_{ads}^{AR}; AR \text{ – all relaxed} \right) \) accounts for all the underlying processes including the ligand effect as well as strain relaxation in the cluster. The utility of these three definitions in separating out (approximately) the various
physical effects upon adsorbate binding as well as their utility as descriptors will be discussed in more detail below.

4.2.3 MACHINE LEARNING ALGORITHM AND TRAINING

For prediction of site-specific CO adsorption energies over the low-symmetry Pt nanoparticle surfaces, we selected the gradient-boosted regression (GBR) algorithm, a tree-based multivariate regressor, as implemented in the SK-Learn package in Python.\(^\text{106,107}\) All the model settings were left at their default parameters. In total, 195 CO adsorption sites were sampled, with 75% of the data used for training the GBR and 25% used for testing the quality of the model’s predictive performance. A stratified five-fold validation was used to avoid bias in data partitioning, in which the data set for each cluster sampled was split into five different train-test sets, thus ensuring every datum is in a test set at least once. The performance of all of the five resulting models is averaged for the final performance score, the absolute mean error of the models (AME).

4.3 RESULTS AND DISCUSSION

4.3.1 CLUSTER-SIZE-DEPENDENCE OF D-BAND CENTER ENERGIES

The low-energy structures of Pt nanoparticles and their surface-average \(d\)-band centers (\(e_{d\text{surf}}\)) were calculated by Dr. Hongbo Shi. Detailed results and analysis of his work can be found in our publication\(^\text{39}\) contained in Appendix B. A brief description of his results as relevant to the analysis contained herein follows.

The average \(d\)-band center energies of the surface atoms (\(e_{d\text{surf}}\)) for Pt\(_{N}\) (\(N = 4-147\)) clusters corresponding to particle diameters of 0.4-1.5 nm were calculated and analyzed to identify size-dependent trends, as well as variations between low-symmetry and high-
symmetry (Ih and Oh) morphologies. $\epsilon_{d}^{\text{sur}}$ decreases monotonically with cluster size for high-symmetry cluster geometries, agreeing with literature results. However, the more stable low-symmetry clusters have a non-monotonic trend of $\epsilon_{d}^{\text{sur}}$ with respect to size, with a minimum $\epsilon_{d}^{\text{sur}}$ around $N = 100$ atoms. The distribution of $\epsilon_{d}^{\text{sur}}$ on the low-symmetry nanoparticle surfaces is quite broad and so the minimum at $N=100$ does not indicate a exact size for an optimal Pt$_N$ nanoscale catalyst. We therefore conduct extensive sampling of CO adsorption energy on both the low- and high-symmetry Pt nanoparticles across the entire size range, as the CO adsorption energy is an important thermodynamic descriptor for MDR catalysts and a direct measure of the propensity for CO poisoning.

**4.3.2 CLUSTER-SIZE-DEPENDENT CO ADSORPTION ENERGIES AND THEIR CORRELATION WITH D-BAND CENTER ENERGIES**

We sampled single-molecule CO adsorption energies across a wide range of GA-optimized Pt$_N$ ($N = 4$-$147$) clusters considering approximately 200 adsorption sites in total that span the full range of both coordination number and site-specific $d$-band centers that the surfaces offer. High-symmetry $I_h$ and $O_h$ structures were also studied for comparison against their low-symmetry counterparts as these structures are often used as models for catalyst clusters.

Figure 4.1 displays the results for average CO adsorption energies, $\overline{E_{ads}}$, (with full relaxation of the adsorbate and cluster) as a function of cluster size and morphology. While the sample size for high-symmetry $I_h$ and $O_h$ clusters is limited by geometric considerations to 13, 55, and 147 atoms – the Pt$_{309}$ cluster being too large for detailed adsorption studies – it is nevertheless possible to draw some key distinctions relative to
the GA-optimized clusters. Firstly, we find that with increasing cluster size, the CO adsorption energies monotonically approach the values for bulk surfaces although the results are still far from converged to the bulk values at these cluster sizes. In contrast, the GA-optimized Pt clusters show the presence of a local maximum in the CO adsorption energy (less negative implying weaker adsorbate binding) at a cluster size of $N = 55$ for which the CO adsorption energy is almost equal, within statistical error, to that of the Pt(111) surface. As before, taking into account the statistical errors, we see that within a size range of approximately 40-70 atoms, the Pt nanoclusters bind CO molecules as strongly as the Pt(100) or (111) facets. Secondly, for all sizes considered, the low-symmetry Pt nanoclusters bind CO less strongly than the high symmetry ones. This result can be understood as resulting from the increased stability of the low-symmetry structures relative to the high-symmetry ones, manifested through fewer undercoordinated atoms and lower $d$-band centers. This gap in adsorption energies becomes smaller as cluster size increases and is expected to eventually close at large sizes once the cluster surface is dominated by crystalline facets. Nevertheless, in the sub-nanometer range, the differences are certainly non-negligible, ranging from 0.1-1.0 eV, thus justifying the need for proper optimization of cluster morphology via global minimization techniques as opposed to ad hoc choices of structures.
Figure 8: Average adsorption energy ($\overline{E_{ads}^{AR}}$) of a single CO molecule as a function of cluster size on lower-energy, low-symmetry, GA-optimized Pt clusters found, and on high-symmetry icosahedral and cuboctahedral clusters. The CO molecule and Pt clusters are fully relaxed in these calculations. Statistical error bars represent Student-T 95% confidence intervals with the exceptions of the 4-atom cluster and the high-symmetry clusters, in which every adsorption site was sampled and we report the standard deviation; error bars for the high-symmetry clusters are too small to be visible in this plot. Horizontal dashed lines indicate the reference adsorption energy values on bulk-terminated, FCC Pt(111) and (100) surfaces. The corresponding data for this plot are listed in Table H.2.

To understand more fully the trends of CO adsorption energy with size, and to quantify the relative magnitudes of the ligand and strain effects, we decompose the adsorption process into three distinct steps, as described in Section 4.2.2. Briefly, we calculate adsorption energies for entirely frozen CO molecules and Pt clusters ($E_{ads}^{AF}$) when the CO molecule is placed at a typical C-Pt bond length at an on-top site, relaxed CO molecules but frozen Pt clusters ($E_{ads}^{FC}$), and fully relaxed CO molecules and Pt...
clusters ($E_{ads}^{AR}$). As the Pt cluster is frozen in the calculation of $E_{ads}^{FC}$, this definition of the adsorption energy quantifies the ligand effect. The difference $\overline{E_{def}} = \overline{E_{ads}^{AR}} - \overline{E_{ads}^{FC}}$ is a measure of the contribution from the energy of deformation of the Pt cluster (strain effect) to the total adsorption energy $E_{ads}^{AR}$. Figure displays these various quantities, averaged over clusters surface sites with the relevant data being summarized in Table H.2. As seen from Figure (a) the trends in average adsorption energies with constrained molecular/cluster configurations ($E_{ads}^{FC}$, $E_{ads}^{AR}$) are quite similar to the fully relaxed adsorption energies ($E_{ads}^{AR}$), displaying a local maximum for the Pt$_{55}$ cluster. As before, we note that the statistical errors are large enough here that the trends are more indicative of a size range for clusters with lower CO binding energy rather than a precise cluster size. We also observe from the relative magnitude of $\overline{E_{ads}^{FC}}$ to the difference $\overline{E_{def}} = \overline{E_{ads}^{AR}} - \overline{E_{ads}^{FC}}$ [Figure (b)] that the ligand effect dominates the CO adsorption process. Interestingly, while the calculated values of $\overline{E_{def}}$ are rather noisy – exacerbated by being a difference of two noisy quantities – the calculated cluster deformation energies exhibit essentially a constant value, lying between 0.2-0.5 eV for the range of sub-nanometer Pt clusters studies here. This suggests that the relaxation process is a fairly localized in the vicinity of the adsorbate as opposed to being a large-scale deformation of the cluster as a whole.

The existence of a preferred size range, as seen in Figure 4.1 & Figure , over which low-symmetry Pt nanoclusters bind CO more weakly is a noteworthy result of our adsorption calculations as it points to useful design principle for robust, CO-tolerant Pt nanocatalysts. (Other practical considerations including, for example, support effects that can be taken into consideration in the future using similar methods.) Yet, arriving at this
conclusion has required full-blown DFT simulations of CO adsorption and it is useful to inquire whether simpler descriptors based on cluster geometry and/or electronic structure might be developed to arrive at similar conclusions with much less computational effort. To this end, a quick comparison of the surface $d$-band center and CO binding shows that the optimal cluster size for low CO binding, $N \approx 55$, does not coincide with the minimum in the average surface $d$-band center at $N \approx 100$. The coordination number of surface atoms, another potential descriptor, grows monotonically with size and approaches that for the low-energy facets, and hence cannot by itself capture the local maximum in the adsorption energy curve. These problems in arriving at a single-descriptor based model are magnified even further if one attempts to consider site-specific adsorption energies rather than surface averages. Moreover, the inability of single-descriptor models to capture the adsorption energy trends accurately cannot be attributed to unusual relaxation effects in these sub-nanometer clusters as the adsorption energy trends persist even for the frozen cluster calculations [Figure (a)]. Hence, we turn next to more systematic approaches based on machine-learning algorithms that can help us arrive at robust multi-descriptor models.
Figure 4.2: (a) Average single-molecule CO adsorption energies on Pt clusters calculated with a fully frozen configuration $(E_{ads}^{AF})$, relaxed CO but frozen Pt clusters $(E_{ads}^{FC})$, and fully relaxed configurations $(E_{ads}^{AR})$. (b) $E_{def} = E_{ads}^{AR} - E_{ads}^{FC}$ as a function of cluster size, which accounts approximately for the contribution from cluster deformation (strain effects) to the adsorption energy. Error bars are Student-T 95% confidence intervals with the exception of the 4-atom cluster where every site was sampled and we report standard deviation; only a few representative error bars are shown in (a) for clarity. The exact values with confidence intervals on every data point are reported in Table H.2.
4.3.3 PREDICTION OF CO ADSORPTION ENERGIES VIA MACHINE LEARNING

Having established that single-descriptor models are of limited use in accurately predicting CO adsorption energies, we resort to the application of machine-learning (ML) tools in the search for suitable multi-descriptor models. The machine-learning model was implemented by Dr. Hongbo Shi, with assistance from myself in algorithm design choices and results analysis. The major conclusions are summarized here below, and the detailed results can be found in our publication.39

We first explored a wide variety of possible predictors, including traditional options like the $d$-band center, the local coordination number, and also more exotic options such as the generalized $d$-band center (an average over the local environment of the Pt atom in question), $s$- and $p$- band centers, $s$, $p$, and $d$-band widths, the average Pt-Pt bond distance between the Pt atom in question and its nearest neighbors, the radius of gyration of the whole cluster, and the all-frozen adsorption energy. A figure of the gradient-boosted regression (GBR) performance with importances with this myriad of predictors can be seen in Figure H.3. We found that many of these predictors either had redundant correlations with the CO adsorption energy (electronic band widths with their corresponding band centers, generalized $d$-band center and $d$-band center) or simply had little correlation with CO adsorption energy and thus low importance in the fitted GBR model. We therefore excluded all but the five most significant predictors- the all-frozen CO adsorption energy ($E_{ads}^{AF}$), the generalized $d$-band center ($g\epsilon_d$) and coordination number ($gcn$), the radius of gyration of the particle ($R_g$), and average Pt-Pt bond distance ($d_{Pt-Pt}$). These descriptors have clear physical relevance and, taken together, require at least 100x less computer time to calculate than the fully-relaxed CO adsorption energy.
Figure 4.3 shows the GBR performance with all five of these highly impactful predictors, along with the GBR performance on subsets of the predictor set.

Figure 4.3: DFT-calculated CO adsorption energies on the surface sites of Pt clusters versus the prediction from GBR model with different sets of descriptors: (a) Generalized d-band center, (b) Type 2 descriptors, (c) $E_{\text{ads}}^{AF}$ alone, (d) Generalized d-band center and Type 2 descriptors (e) all three descriptor types (5 descriptors total). Reported AME (absolute mean error) of the model predictions are the average over six-fold cross validation to avoiding splitting bias. The displayed data points are from one such randomly split dataset. Insets in (b), (d) and (e) show the relative importances of the descriptors in the models.
Using these descriptors and our CO adsorption data samples as training data, the GBR can predict the site-specific fully-relaxed CO adsorption energy on Pt nanoparticles with an absolute mean error of 0.12 eV, which is near DFT accuracy. Using this combination of predictors with the gradient-boosted regression, this prediction takes around 1% of the CPU-time as the full-accuracy DFT adsorption energy sampling.

4.4 CONCLUSIONS

We studied Pt nanoclusters, ranging from 0.2–1.5 nm in diameter, to understand size-dependent trends in the energetics of CO binding, and to correlate these with morphological and electronic descriptors. An important aspect of our approach was to employ a genetic algorithm to determine unambiguously the low-energy morphologies of the Pt nanoclusters, which uniformly adopt low-symmetry structures for the sizes considered here. GA-optimized clusters show a non-monotonic trend of surface $d$-band centers with respect to size, going from very high values at small sizes to a minimum around Pt$_{100}$, before slowly asymptoting towards the Pt(111) surface value. This is in clear contrast to the essentially monotonic behavior of high-symmetry, cuboctahedral and icosahedral morphologies, which are not true low-energy structures for sub-nanometer Pt clusters. The CO adsorption behavior on GA-optimized clusters also presents similar non-monotonic behavior with a global maximum at around Pt$_{55}$.

By employing machine learning algorithms, we showed that the non-monotonic trends in CO adsorption energies are not accurately captured by traditional single descriptor models based on $d$-band center energies or coordination number. Multi-descriptor models based on $d$-band centers and structural information (coordination number, bond lengths, cluster size) do not perform much better either. By adding a new
descriptor to our models, namely, the “all-frozen” adsorption energy ($E_{ads}^{AF}$), which partially incorporates some of the features of CO-Pt bond formation, we were able to achieve significant improvement in the machine-learning model. We suggest that this descriptor, $E_{ads}^{AF}$, which can be calculated at minimal computational overhead, might be broadly applied across other systems to predict site-specific adsorption energies with higher accuracy; studies along these lines will be pursued elsewhere.

Overall, our work demonstrates the potential for developing accurate, predictive models of adsorbate binding on realistic nanocluster morphologies by integrating robust structural optimization methods with machine learning algorithms. Progress along these lines can significantly aid rational design of nanoscale catalysts, particularly in the sub-nanometer range where both structural and electronic properties differ fundamentally from those at larger length scales.
CHAPTER 5
PARAMETERIZATION OF A PT-RU-C TERSOFF POTENTIAL

5.1 INTRODUCTION

In the previous chapter, we showed unambiguously that the properties of realistically structured low-symmetry Pt nanoparticles (generated by Dr. Hongbo Shi’s genetic algorithm (GA)) cannot be approximated effectively using high-symmetry \( \text{I}_h \) and \( \text{O}_h \) nanoparticle constructions. In particular, the \( d \)-band center and CO adsorption energy both showed distinctly non-monotonic trends w.r.t. particle size on the GA-generated Pt nanoparticles, whereas the \( \text{I}_h \) and \( \text{O}_h \) nanoparticles showed monotonic trends w.r.t. particle size. Given their relevance for real-world MDR catalysts,\(^{16,19}\) we would like to apply similar approaches to study PtRu bimetallic nanoparticles supported on defective graphene as well. Sampling large, bimetallic, supported nanoparticles using a DFT-based GA would be computationally prohibitive, so we seek to develop an accurate and inexpensive three-species Pt-Ru-C empirical potential. We found in the literature existing Tersoff-style empirical potentials for the Pt-C\(^{109}\) and Ru-C\(^1\) systems, which we implement mostly unmodified. This leaves the remaining problem of parameterizing the potential for the two-species Pt-Ru interactions and the three-species Pt-Ru-C interactions. This work is still underway, and this chapter contains the progress so far.

Here, I describe my contribution towards the development of a Tersoff-style empirical potential for the ternary Pt-Ru-C system. My interatomic potential is being tested currently by the Ramasubramaniam group and will be used going forward to study structure–property–function relationships of defective-graphene supported PtRu nanoclusters. For the tuning of our Pt-Ru Tersoff potential parameters, we use a reference
set of Pt\(_x\)Ru\(_{1-x}\) alloy nanoparticles reported by Shi \textit{et al.}\textsuperscript{1} who used a GA driven by self-consistent charge density functional tight-binding theory potentials to search for low-energy structures; the Ru-C and Pt-Ru-C interactions are parameterized using a separate data set discussed below.

### 5.2 SUMMARY OF TERSOFF-STYLE INTERATOMIC POTENTIALS

The total energy, \(E\), of a system of atoms is written in Tersoff’s approach\textsuperscript{23,110} as a pairwise sum over atoms

\[
E = \frac{1}{2} \sum_i \sum_{j \neq i} V_{ij} .
\]

(5.1)

The pair-potential, \(V_{ij}\), is in turn given by the expression

\[
V_{ij} = f_c(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})] ,
\]

(5.2)

where

\[
f_c(r) = \begin{cases} 
1 - \frac{1}{2} \sin \left( \frac{\pi r - R}{D} \right) & \text{if } R - D < r < R + D \\
0 & \text{if } r > R - D \\
\end{cases} ,
\]

(5.3)

is a smooth cutoff function, and

\[
f_R(r) = A \exp(-\lambda_1 r) ,
\]

(5.4)

\[
f_A(r) = -B \exp(-\lambda_2 r) ,
\]

(5.5)

are pairwise repulsive and attractive potentials. The parameter

\[
b_{ij} = (1 + \beta^n \zeta_{ij}^{\frac{1}{2n}}) ,
\]

(5.6)

adjusts the strength of the attractive interaction taking into consideration the environment of the bonding atoms (bond order), with

\[
\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^m (r_{ij} - r_{ik})^m] ,
\]

(5.7)

being the effective coordination number of atom \(i\). The three-body term
penalizes deviations from the ideal bond angle \( \theta_0 \), where \( \theta_{ijk} \) is the angle between bond \( ij \) and bond \( ik \). The primary two-body parameters adjusting the attractive and repulsive potentials are \( A, B, \lambda_1, \) and \( \lambda_2 \), (Eqs. 5.4 and 5.5), whereas the three-body parameters are \( c, d, \lambda_3, \) and \( \gamma_{ijk} \) (Eqs. 5.7 and 5.8); for the remaining parameters, we adopt the same simplifications employed by Albe et al.\(^{109} \) by setting \( n = 1 \) (Eq. 5.6), \( m = 1 \) (Eq. 5.7), and \( \cos \theta_0 = -1 \) (Eq. 5.8).

### 5.2 PARAMETER FITTING PROCESS AND RESULTS

We based our attempt to develop a ternary Pt-Ru-C potential upon the premise of combining the Pt-C potential set developed by Albe et al.\(^{109} \) and the Ru-C potential set developed by Förster et al.\(^{111} \) Thus, parameterizing the ternary potential requires producing original Pt-Ru and Pt-Ru-C training sets. As an initial attempt at fitting the Pt-Ru cross-terms, we used Tersoff’s original interspecies mixing rules,\(^{23} \) which define the initial guesses for the two body terms as functions of the parameters of the two singe-species potentials.\(^{23} \) The three-species, three-body parameters are assumed to be identical to the single-species or two-species three-body parameters taken from the potentials already developed by Albe et al. and Förster et al. This means that, for example, a C-Pt-Ru trimer would have a different ground state than a C-Ru-Pt trimer, but the equations governing the Pt-Ru bonds are the same in both cases. Detailed tests revealed serious flaws in the initial mixing strategy as the resulting potential promoted fairly uniform mixing of Pt and Ru to form random alloy clusters (Figure) while is well known that in PtRu clusters of these sizes and compositions, Pt segregates to the surface leaving a Ru-
Further investigation of the root of this problem revealed that the Pt-Ru bonds were too energetically favorable: this is easily visible in Figure 5.1(d, e) wherein the Tersoff potential produces a local minimum in formation energy for clusters with 50-75 at.% Pt while the DFT calculations show a monotonic trend from 0-100 at.% Pt. To remedy this problem, we attempted to disfavor Pt-Ru mixing by reducing the strength of the Pt-Ru bond, which is accomplished most readily by reducing the value of the attractive well-depth, $B_{PtRu}$ (see Eq. 5.5). This approach is consistent with Tersoff’s recommendation for tuning an interspecies bond.\textsuperscript{23}

![Figure 5.1](image)

Figure 5.1: (a–c) Unsupported Pt\textsubscript{0.5}Ru\textsubscript{0.5} nanoparticles of various sizes as generated by the Tersoff-potential driven GA\textsuperscript{10} (Pt: red spheres, Ru: blue spheres; courtesy of Dr. Hongbo Shi). Formation energies of SCC-DFTB-GA generated PtRu clusters of various sizes ($N_{\text{atoms}}$) and compositions (in terms of at.% Pt) as calculated by (d) the naïvely-mixed Tersoff potential and (e) DFT.
Through careful testing, we established an optimal $B_{PtRu}$ value by comparing the DFT formation energy of minimum-energy clusters found by the SCC-DFTB GA to the formation energy of the same clusters calculated by single-point calculations using the PtRu Tersoff potential, which we implemented in LAMMPS.\textsuperscript{11} With the absolute mean error between DFT and Tersoff-potential values for cluster formation energies as the metric of performance (Table 5.1), we found an optimal choice of $B_{PtRu}=57.7$; Figure 5.2 also displays a graphical comparison of the DFT and Tersoff-potential formation energies on a parity plot with excellent agreement between the two sets of data.

Table 5.1: Absolute mean error (AME) in tuned PtRu Tersoff potential prediction of cluster formation energies (eV per atom) compared to DFT at several $B_{PtRu}$ values and the corresponding linear regression slope of the parity plot.

<table>
<thead>
<tr>
<th>$B_{PtRu}$ value</th>
<th>AME (eV)</th>
<th>Best-Fit Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.7</td>
<td>0.176</td>
<td>1.14</td>
</tr>
<tr>
<td>53.7</td>
<td>0.118</td>
<td>1.09</td>
</tr>
<tr>
<td>55.7</td>
<td>0.067</td>
<td>1.05</td>
</tr>
<tr>
<td>57.7</td>
<td>0.058</td>
<td>1.00</td>
</tr>
<tr>
<td>59.7</td>
<td>0.079</td>
<td>0.96</td>
</tr>
<tr>
<td>61.7</td>
<td>0.127</td>
<td>0.91</td>
</tr>
</tbody>
</table>
Figure 5.2: Data cloud and regression for fitting of $B_{\text{PtRu}}=57.7$. The x-axis displays DFT formation energies of 55 atom PtRu nanoparticles and the y-axis displays the tuned Tersoff potential formation energies of same clusters.

In extending the implementation of the Tersoff potential to the PtRuC ternary system for structure prediction of graphene-supported PtRu nanoparticles, we found the RuC potential as taken from Förster et al. to be unsuitable. Specifically, we know from DFT calculations and experimental evidence that Ru should form stronger bonds to graphene than Pt, and that PtRu nanoparticles supported on graphene should be Ru-rich at the nanoparticle-support interface. However, the naively-mixed empirical potential favors Pt-C bonds over Ru-C bonds and thus leads to alloy clusters with Pt at the cluster–graphene interface. The relative strengths of the Pt-C and Ru-C bonds are seen clearly in Table 5.2 where we report the adsorption energies of single atoms of Pt and Ru over pristine and defective graphene as calculated by DFT and the initial Tersoff parameterization. Of key importance is the relative ratio of Pt-C bond strength to Ru-C bond strength: according to DFT, the Ru-C bond should be about 20% stronger than the Pt-C bond. This is clearly not the case in the simply-mixed Pt-Ru-C potential, with the Ru-C bond strength being underestimated by more than half. While this may initially seem surprising, there is clear reason for this discrepancy—the Förster potential was
parameterized for Ru-C interactions implementing an additional dispersion term that is not a normal component of a Tersoff form potential. The LAMMPS package does not as yet have the ability to handle a bond-order potential with dispersion corrections. Therefore, we need to adjust the Ru-C parameter set to compensate for the lost attractive interaction from Förster et al.’s dispersive terms.

Table 5.2: Comparison of Pt\textsubscript{1} and Ru\textsubscript{1} adsorption energies over pristine and defective graphene supports as calculated by DFT and by our PtRuC Tersoff potential before (simple mixing) and after tuning. (All energies are in eV.)

<table>
<thead>
<tr>
<th></th>
<th>DFT</th>
<th>PtRuC before tuning</th>
<th>PtRuC after tuning</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Ru</td>
<td>Pt</td>
</tr>
<tr>
<td>Pristine Graphene</td>
<td>-1.6</td>
<td>-1.5</td>
<td>-1.6</td>
</tr>
<tr>
<td>Vacancy Graphene</td>
<td>-6.5</td>
<td>-7.5</td>
<td>-5.6</td>
</tr>
<tr>
<td>Divacancy Graphene</td>
<td>-7.0</td>
<td>-8.4</td>
<td>-4.4</td>
</tr>
</tbody>
</table>

Tuning the Ru-C potential, however, was less straightforward than tuning the Pt-Ru interaction—simply adjusting the two-body well depth, B\textsubscript{RuC}, was ineffective. Increasing (decreasing) B\textsubscript{RuC} without modifying any three-body terms uniformly increased (decreased) the adsorption energy for all the different graphene supports (with or without defects). On the one hand, low B\textsubscript{RuC} values caused unacceptably large errors for the Ru atom bound at graphene vacancies and divacancies; on the other hand, high B\textsubscript{RuC} values caused unacceptable errors for the Ru atom adsorbed on pristine graphene. To solve this problem, we adjusted B\textsubscript{RuC} as well as the three-body parameters for the RuC interaction, γ\textsubscript{RuC} and c (Eqs. 5.7 & 5.8). All variables were simultaneously tuned using a simple search of the parameter phase space over a wide range for all parameters. At the time of writing this thesis, the search procedure has identified a suitable parameter set which, in initial tests, predicts accurate Ru-C binding energies; the potential is being tested by
coworkers in the Ramasubramaniam group and, once validated, will be employed in future studies of defective-graphene-supported Pt$_x$Ru$_{1-x}$ alloy clusters. This parameter set is shown below in Table 5.3. It should be emphasized that the empirical potential-based GA will only be used to provide reasonable starting guesses for further DFT optimization as was done in previous work from our group.$^{10,11}$ Therefore, some loss of accuracy with the empirical potential is acceptable as long as it furnishes good low-energy initial structures for DFT studies thereby striking a balance between accuracy and computational cost.

Table 5.3: Parameters for tuned Ru-C Tersoff potential, in Lammmps notation. Parameters changed from values in Forster et al.$^1$ during the tuning process are highlighted.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>1.25x10$^6$</td>
</tr>
<tr>
<td>$B$</td>
<td>6</td>
</tr>
<tr>
<td>$R$</td>
<td>2.86</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1</td>
</tr>
<tr>
<td>$n$</td>
<td>1</td>
</tr>
<tr>
<td>$m$</td>
<td>1</td>
</tr>
<tr>
<td>$c$</td>
<td>300</td>
</tr>
<tr>
<td>$\cos \theta_0$</td>
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</tr>
<tr>
<td>$\lambda_1$</td>
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</tr>
<tr>
<td>$\lambda_2$</td>
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</tr>
<tr>
<td>$D$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\zeta_{ij}$</td>
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</tr>
<tr>
<td>$\lambda_3$</td>
<td>0.35614</td>
</tr>
<tr>
<td>$\gamma_{ijk}$</td>
<td>0.01</td>
</tr>
<tr>
<td>d</td>
<td>9.3054</td>
</tr>
</tbody>
</table>
CHAPTER 6
CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

In summarizing the overall progress made in this thesis, we revisit the key questions posed in Section 1.2 and evaluate our progress in addressing these questions.

1) How do we establish accurate representative structures for low-symmetry, supported nanoparticles in computer simulations?

We have shown that genetic algorithm and carefully tuned bond-order potentials can predict realistic low-energy isomers for catalyst nanoparticles supported on defective graphene. Specifically, in this thesis we have developed an appropriate parameter set for the ternary Pt-Ru-C potential, which will be applied by future group members for the understanding of industrially relevant bimetallic, supported, low-symmetry nanoparticles.

2) How do size, composition, and support effects alter the structure–property relationships of nanoscale catalysts?

We have addressed this question in two separate contexts: CO adsorption on Pt nanoclusters and MDR on supported Pt nanoclusters. We showed that realistically structured Pt nanoparticles have intriguing non-monotonic trends with respect to size both for traditional predictors such as the surface $d$-band center and for CO adsorption energy; this is an important finding, as many works in the literature (and our own results) for high-symmetry nanoparticles show monotonic trends for these two quantities. We then showed that the minimum of the surface $d$-band center and the minimum of the CO adsorption energy don’t coincide, and that the origin of this discrepancy is from the interplay of electronic structure, adsorption-site geometry, and fluxionality of the
nanoparticle. This finding is clear evidence that traditional predictors developed for catalysis on crystalline facets must be reexamined, and possibly modified, for nanoclusters. We also showed that by using a machine-learning approach that can handle multiple predictors simultaneously, one may predict the site-specific CO adsorption energy on low-symmetry nanoclusters with near-DFT accuracy. These ideas will be examined for binary Pt-Ru in future work.

We addressed support effects on catalytic activity through the investigation of the methanol decomposition reaction (MDR) over Pt$_{13}$ nanoparticles supported on graphene with various point defects. We showed that the electronic and structural perturbations caused by strong Pt-C bonds at defect sites alter both the thermodynamic and kinetic quantities that determine overall MDR activity and reaction network behavior. We quantified these changes using an in-house MATLAB microkinetic model, which calculates surface coverages, reaction rates, and gas production rates under realistic operating conditions. The microkinetic model predicts that the MDR over Pt$_{13}$ nanoparticles supported on divacancy-graphene exhibits comparable surface-area-normalized reaction rates and hydrogen gas production to the Pt(111) surface, qualitatively agreeing with experiments. The model also shows that the most-active pathway of the reaction network is changed by the support, causing different surface coverage behavior.

3) Are the simple predictors that enable high-throughput calculations on high-symmetry surfaces still valid for low-symmetry nanoparticle surfaces? If not, why do these predictors fail and how can they be improved or supplanted?
We investigated predictor relationships by studying the adsorption of MDR intermediates over the defective-graphene supported Pt$_{13}$ nanoparticles. We found that adsorption energy an MDR intermediate on Pt$_{13}$ nanoparticles (supported or otherwise) is correlated via a simple linear regression to the adsorption energy of the same intermediate on Pt(111). Additionally, we sampled MDR transition states over the unsupported Pt$_{13}$ cluster and showed that they too can be predicted effectively using the initial-state model, which has been used previously to study MDR on the Pt(111) surface.

It should be noted though that while the adsorption energy of a species is correlated across nanoclusters and surfaces, more fundamental descriptors such as the $d$-band center model and coordination number model are less effective for nanoclusters (as in the case of CO adsorption). Here, multivariate machine learning regression approaches might allow us to combine multiple predictors into an effective adsorption energy prediction model for MDR intermediates.

### 6.2 FUTURE WORK

Overall, in this thesis we have made progress towards understanding and facilitating computational catalysis over realistic catalyst structures, as opposed to idealized high-symmetry models. We have developed a multitude of computational tools and a knowledge base that will enable comprehensive and accurate studies of the various effects of catalyst size, morphology, composition, and support on the activity of realistic catalysts. With these capabilities at hand, focusing our efforts in the general direction of catalysis on supported nanoclusters would be a fertile area for future research.
6.2.1 GENERATION AND STRUCTURAL ANALYSIS OF DEFECTIVE-GRAFENEN Supported PTRU NANO Particles

Our newly parameterized PtRuC Tersoff potential enables us to study the role of size, composition, and support effects on the morphological and electronic structure of PtRu nanoparticles, which are among the best catalysts for MDR. My main contribution to this project has been in parameterizing the PtRu and PtRuC interactions. In the immediate future, my coworkers will employ GAs and DFT modeling to study graphene-supported PtRu nanocatalysts. In brief, the GA will be used to generate a database of PtRu nanoparticles of various sizes and compositions over graphene supports. Additional local relaxations with DFT will be performed to fully optimize the cluster morphologies, followed by analyses of the physical and electronic properties of the alloy nanoparticles analogous to Shi et al.’s previous work on Pt nanoparticles.

6.2.2 ANALYSIS OF CATALYTIC PROPERTIES OF DEFECTIVE-GRAFENEN Supported PTRU NANO Particles

Subsequent to studies of the physical properties of PtRu nanoclusters, a promising direction of investigation would be to study the catalytic properties using probe molecules, such as CO, and model reactions, such as MDR. Experiments have shown that the catalytic activity of PtRu nanoclusters is significantly enhanced (more than Pt nanoclusters) by defective-graphene supports,\textsuperscript{19} which we believe could be explained by more facile CO oxidation in the presence of activated water on the Ru sites. With a modest amount of DFT sampling of adsorption energies on the PtRu nanoparticles, scaling relationships and microkinetic modeling could be applied to understand the catalytic behavior of this technologically important catalyst system.
6.2.3 EXTENSION OF THE GENETIC ALGORITHM AND HIGH-THROUGHPUT MDR ANALYSIS

A relatively obvious, but perhaps highly fertile line of research would be to extend the genetic algorithm to additional transition metals. Several different Pt-Metal alloys have been shown to be active for the hydrogen evolution reaction (HER) and MDR, and the application of genetic algorithms in conjunction with DFT modeling would allow for the study of numerous such binary alloy nanoclusters. In the long-term, implementation of the scaling relationships and microkinetic modeling over many different Pt-Metal alloy systems supported over defective graphene would allow for high-throughput analysis of commercially relevant MDR catalysts.

6.2.4 APPLICATION OF MACHINE-LEARNING TOOLS TO TRANSITION STATE PREDICTION

Given the difficulty of high-accuracy transition-state calculations, better techniques for prediction of site-specific transition states for low-symmetry active sites could be a productive direction of research. Application of machine-learning models for prediction of transition states would require a significantly larger training set, which could be built on a large sample of small, unsupported Pt, Ru, or PtRu nanoparticles. By combining accurate, site-specific, machine-learning tools to calculate thermodynamics and kinetics of realistically structured nanoparticles, one could conduct extraordinarily thorough analyses of the effect of nanoparticle support and geometry on simple reactions such as the HER, CO oxidation reaction, and MDR. In the long term, one may envision applying global optimization algorithms to an objective function that combines energetic stability and catalytic activity metrics (predicted via machine-learning tools and simpler kinetic models) for high-throughput rational design of catalysts.
APPENDICES
APPENDIX A

ADSORPTION ENERGIES AND THERMODYNAMICS OF THE MDR ON DEFECTIVE-GRAPHENE SUPPORTED Pt$_{13}$

Density Functional Theory Studies of the Methanol Decomposition Reaction on Graphene-Supported Pt_{13} Nanoclusters

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Supporting Information

ABSTRACT: Defective graphene has been shown experimentally to be an excellent support for transition-metal electrocatalysts in direct methanol fuel cells. Prior computational modeling has revealed that the improved catalytic activity of graphene-supported metal clusters is in part due to increased resistance to catalyst sintering and to CO poisoning, but the increased reaction rate for the methanol decomposition reaction (MDR) is not yet fully explained. Using density functional theory, we investigate the adsorption and reaction thermodynamics of MDR intermediates on defective graphene-supported Pt_{13} nanoclusters with realistic, low-symmetry morphologies. We find that the support-induced shifts in catalyst electronic structure correlate well with an overall change in adsorption behavior of MDR intermediates and that the reaction thermodynamics are modified in a way that suggests the potential of greater catalytic activity. We also show that adsorption energy predictors established for traditional heterogeneous catalysis studies of MDR on macroscopic crystalline facets are equally valid on catalyst nanoclusters (supported or otherwise) with irregular, low-symmetry surface morphologies. Our studies provide theoretical insights into experimental observations of enhanced catalytic activity of graphene-supported Pt nanoclusters for MDR and suggest promising avenues for further tuning of catalytic activity through engineering of catalyst-support interactions.

1. INTRODUCTION

Graphene has been demonstrated to be a very effective support for electrocatalysts for methanol and hydrogen fuel cells. In particular, for direct-methanol fuel cells, graphene-supported platinum clusters have been shown to have high catalytic activity for the methanol decomposition reaction (MDR) and increased resistance to both sintering and CO poisoning. The details of the binding of Pt nanoclusters to defective graphene supports have been studied extensively. Via computational and experimental work, Pt nanoclusters have been shown to adsorb strongly to point-defect sites in the graphene support. Upon binding at point defects, significant charge transfer takes place from the Pt nanoclusters to the graphene support, correspondingly modifying the electronic structure of the nanoclusters. This phenomenon suggests the use of predictors based upon electronic structure, in particular the d-band center model, which have been used to great effect to allow exploration of pure transition metal surfaces and surface alloys for use as catalysts. Other predictors for catalytic activity are based on scaling relationships, which correlate, for example, the adsorption of a molecule on different surfaces to the adsorption energy of a simpler probe molecule on the same surface. These have been demonstrated to be accurate in a wide variety of applications. In previous work, we showed that the d-band center can be used effectively as a predictor for CO adsorption on unsupported or graphene-supported Pt nanoclusters but did not explore any of the MDR intermediates or provide any investigation of adsorption energy scaling relationships. The reduction of CO adsorption energies via support effects offers a possible explanation for the higher tolerance to CO poisoning that supported Pt nanoclusters exhibit, while the strong binding of Pt nanoclusters to defects explains resistance to sintering. However, neither of these observations is sufficient to explain fully the higher catalytic activity for the MDR that is observed in experiments. Thus, the primary goal of this work is to present a detailed density functional theory (DFT) study of the adsorption of MDR intermediates on Pt_{13} nanoclusters with the goal of understanding the role of support effects on reaction thermodynamics. As Pt_{13} nanoclusters (with or without supports) have already been studied in detail, they serve as a model reference system for further exploration of catalytic reactions. We also seek to further extend the use of the d-band center model and adsorption energy scaling relationships from their traditional applications for catalysis at macroscopic crystalline surfaces to more complex supported-cluster reaction networks, thereby expanding the generality of their potential use for rational catalyst design.

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present on high-symmetry surfaces. Due to there being few (if any) symmetry-equivalent adsorption sites on low-symmetry clusters, some form of statistical sampling must be undertaken, which magnifies the effort required to understand a reaction on a single cluster. In addition, clusters adopt different geometries and electronic structures on different supports, requiring separate calculations even for simple quantities such as adsorption energies. The combination of these factors makes exploration of cluster-support systems for their catalytic potential extraordinarily time- and resource-consuming. Therefore, in order to achieve a broad and/or in-depth exploration of supported catalyst design, circumventing these extensive ab initio calculations via robust predictors is highly desirable. In this work, we demonstrate that the d-band center model can be extended for use not only as a predictor for CO adsorption, as we have done before, but more generally as a predictor for the qualitative adsorption behavior of the methanol decomposition reaction across nanoclusters with varying degrees of support interactions.

The MDR has been extensively investigated in part due to its value for understanding and improving catalytic performance for direct methanol fuel cells. Pioneering work in the field was performed by Greetey and Mavrikakis, who investigated the reaction on Pt(111) in extensive detail. They showed via a combination of DFT and microkinetic modeling that the most likely pathway for MDR on a Pt(111) single-crystal surface under ultrahigh vacuum is H2COH → H2COH → H2CO + CO (Path 1), with the first dehydrogenation step being rate-determining. Two other viable, but less favorable, pathways were identified: (i) H2CO + H2CO → H2CO + H2CO → CO + CO (Path 2), with the first step also being the rate-determining step, and (ii) H2CO + H2CO + H2CO → H2CO + H2CO → CO + CO (Path 3), with the first and second steps having approximately the same barriers. In addition to the Pt(111) surface, the MDR pathway has also been fully or partially identified on stepped and defective platinum surfaces, the Cu(111) surface, the Cu(110) surface, and the ZnO(1010) surface, among several others. Kandori et al. showed that the experimental performance of the Pt(111) surface catalyst for the MDR can be predicted qualitatively by a combination of ab initio calculations and microkinetic modeling, along the way reaffirming the dominant pathway established by Greetey and Mavrikakis. In this work, we characterize the adsorption energies and reaction thermodynamics of the three pathways previously identified, considering especially the relationships between the most likely pathways. We believe that the level of understanding in the field, along with the previously identified gap in understanding regarding the effect of supports, makes this reaction-catalyst-support system ideally suited for exploration of predictors for supported catalysis.

Our computational methodology is explained in section 2. Results and discussion on the effect of support binding on the adsorption and reaction thermodynamics of MDR intermediates are presented in section 3. Conclusions and closing remarks are presented in section 4.

2. METHODOLOGY
Spin-polarized DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP). The core and valence electrons were treated using the projector-augmented wave function method. The Perdew–Burke–Ernzerhof generalized-gradient approximation (PBE) was used to describe electron exchange and correlation. From convergence studies, we chose a kinetic energy cutoff of 400 eV and a first-order Methfessel–Paxton smearing of 0.05 eV. All atomic positions were relaxed with a force tolerance of 0.02 eV/Å.

Initial low-energy Pt13 cluster configurations (supported or unsupported) were generated via simulated annealing as reported in ref 11. The supports considered were 8 × 8 single-layer graphene sheets that were either defect free or containing a point defect (vacancy or divacancy) at the cluster adsorption site. Graphene planes were separated in the normal direction by 18 Å of vacuum to prevent spurious interaction with periodic images. The Brillouin zone was sampled by a 2 × 2 × 1 Γ-centered k-point mesh, chosen from convergence studies. Unsupported (isolated) Pt13 clusters were modeled in an 18 Å cube using a single Γ point for reciprocal space sampling. Adsorption energies and reaction energies were sampled on five sites on each cluster. Sampling sites were chosen randomly, with repeated sites or sites hindered by graphene proximity (high steric hindrance) being discarded. Initial configurations for adsorbed molecules were set up to be as close to the Pt(111) adsorption configuration as possible but these eventually relaxed to various local minima as dictated by the local structure of the adsorption sites. Charge transfer analyses were performed using a Bader analysis.

Reference Pt(111) surface calculations were performed on a three-layer, 5 × 5 surface cell with the bottom two layers frozen in their bulk FCC geometry. Slabs of greater thickness with additional five layers were tested and not found to influence the adsorption energies. The slabs were separated by 18 Å of vacuum normal to the surface to prevent spurious interactions. A Γ-centered, 5 × 5 × 1 k-point mesh was used for Brillouin zone sampling. Dipole-moment corrections were applied normal to the surface.

For adsorption energy (Eads) calculations, the following definitions are employed throughout this paper:

- Supported Clusters: Eads = E_{Pt13+support+adsorbate} − E_{Pt13+support} − E_{adsorbate}

- Isolated Cluster: Eads = E_{Pt13+adsorbate} − E_{Pt13} − E_{adsorbate}

- Pt(111) Surface: Eads = E_{Pt(111)+adsorbate} − E_{Pt(111)} − E_{adsorbate}

In eq 1, \(E_{Pt13+support+adsorbate}\) is the total energy of the relaxed Pt13 cluster, graphene support, and adsorbate molecule; \(E_{Pt13+support}\) is the total energy of the Pt13 cluster and graphene support relaxed again after adsorbate removal; and \(E_{adsorbate}\) is the reference energy of the adsorbate isolated in vacuum. In eq 2, for the isolated cluster, \(E_{Pt13+adsorbate}\) is the total energy of the relaxed Pt13 cluster plus adsorbate, \(E_{Pt13}\) is the energy of the isolated Pt13 cluster relaxed after adsorbate removal, and \(E_{adsorbate}\) is the reference energy of the isolated adsorbate; eq 3 is analogous to eq 2 with Pt(111) substituting for the Pt13 cluster. For all molecules considered, the reference state is the molecule in vacuum; for a hydrogen atom, however, the reference state is half the energy of the H2 molecule. Note that as defined, more negative adsorption energies correspond to a stronger bond between the adsorbate and the catalyst.
Figure 1. Relaxed Pt₁₃ clusters that are (a) isolated, (b) on a pristine graphene support, (c) bound at a vacancy defect in graphene, and (d) bound at a divacancy defect in graphene. (C, brown spheres; Pt, gray spheres.)

The thermodynamics of the MDR were calculated using the following definitions of reaction energies:

Supported Clusters:

$$
\Delta E_{\text{tot}} = E_{\text{Pt₁₃-support+product}} + N_{\text{H}} \left( \frac{1}{2} E_{\text{H₂}, p} + \overline{E_{\text{ads}, H}} \right) - E_{\text{Pt₁₃-support+reactant}}
$$

(4)

Isolated Cluster:

$$
\Delta E_{\text{tot}} = E_{\text{Pt₁₃+product}} + N_{\text{H}} \left( \frac{1}{2} E_{\text{H₂}, p} + \overline{E_{\text{ads}, H}} \right) - E_{\text{Pt₁₃-reactant}}
$$

(5)

Pt(111) Surface:

$$
\Delta E_{\text{tot}} = E_{\text{Pt(111)+product}} + N_{\text{H}} \left( \frac{1}{2} E_{\text{H₂}, p} + E_{\text{ads}, H} \right) - E_{\text{Pt(111)-reactant}}
$$

(6)

where $N_{\text{H}}$ is the number of hydrogen atoms being removed from the intermediate in a particular reaction step ($N_{\text{H}} = 1$ in all steps except for the semi-concerted removal of two H atoms from HCOH where $N_{\text{H}} = 2$), $E_{\text{H₂}, p}$ is the DFT energy of an H₂ molecule, and $\overline{E_{\text{ads}, H}}$ is the average adsorption energy of hydrogen on the system being considered [Pt₁₃]. The exact value can be used on Pt(111). By way of benchmarking, this approach was compared with the more conventional approach wherein the products of a reaction step (i.e., the MDR intermediate and the leaving H atom) are coadsorbed on the catalyst surface and the reaction thermodynamics calculated with respect to this configuration. Selected tests on Pt(111) and on the isolated Pt₁₃ cluster (Figure S5) reveal that both approaches provide consistent and reliable estimates of the reaction thermodynamics. On the Pt(111) surface both approaches yield nearly identical results on the isolated Pt₁₃ cluster, the results coincide to within the bounds of statistical error. Thus, employing the average value for hydrogen adsorption energy facilitates reaction thermodynamics analyses at half the computational cost of the coadsorption approach while also minimizing the influence of variations in energy of the relaxed cluster and support, which causes excessive noise in the calculations without lending improved understanding. No entropic contributions or zero-point energies were included in this study.

3. RESULTS AND DISCUSSION

3.1. Supported and Unsupported Reference Pt₁₃ Clusters. The graphene-supported Pt₁₃ clusters used for this study are shown in Figure 1. Initial configurations for the systems used were taken from previous work. The systems chosen for this study are an isolated Pt₁₃ cluster, a pristine-graphene supported Pt₁₃ cluster, a Pt₁₃ cluster supported on a graphene sheet with a single vacancy, and a Pt₁₃ cluster supported on a graphene sheet with an unreconstructed divacancy. These systems were chosen due to previous work indicating that they provided a broad range of support interaction, leading to significant shifts in d-band center and CO adsorption behavior between the systems. The support size was increased relative to our previous work to an 8 × 8 graphene supercell to accommodate larger adsorbed molecules without spurious image interaction.

As discussed in previous work, with the increasing size of point defects in the graphene support, both the binding strength and charge transfer between the Pt cluster and graphene-support increase. This charge transfer induces a change in the electronic structure of the clusters, manifested by a downshift in the d-band center value. The d-band centers of the clusters from Figure S1 are listed in Table 1, and reaffirm these conclusions. The d-band centers of the unsupported cluster and the pristine-graphene-supported cluster (weak cluster-support interactions) are significantly higher than that of the Pt(111) surface; however, sufficiently strong support interaction in the vacancy case lowers the d-band center below the Pt(111) level. The d-band model then suggests that the adsorption energy of molecular adsorbates on these catalysts should be correlated consistently with respect to the d-band shift between the differently supported Pt₁₃ nanoparticles. Indeed, for the case of CO adsorption on graphene-supported or unsupported Pt₁₃ clusters, we have shown previously that trends in adsorbate binding (as well as oxidation barriers) can be rationalized in terms of the d-band shifts. Through this metric we will further unravel the relationship between support effects and adsorption for MDR intermediates below.

3.2. Adsorption of MDR Intermediates. Unlike macroscopic crystal surfaces or faceted nanoparticles, it is impossible to identify a small set of symmetry-equivalent adsorption sites on our low-symmetry, graphene-supported Pt₁₃ nanoclusters. Thus, in order to understand the adsorption behavior, five randomly chosen sites were sampled on each cluster-support system. Sample converged configurations of various adsorbates
on the Pt\(_{13}\) cluster and graphene support are displayed in Figures 2 and 3. Despite variations in local cluster geometry, Pt(111) surface (on-top site), but \(\text{H}_2\text{CO}\) does not; instead, \(\text{H}_2\text{CO}\), which adopts a Pt–C–O–Pt bridge configuration on Pt(111), can adopt either this configuration, an on-top configuration, or a Pt–C–Pt bridge configuration on Pt\(_{13}\) clusters. As another example, CO, which adsorbs most strongly to the fcc site on the Pt(111) surface (as per DFT calculations; the disagreement with experiment is well-known\(^{16-25}\)) adopts on-top, bridge, and hollow low-energy adsorption configurations on Pt\(_{13}\) clusters.

To extend understanding of the MDR on nanoclusters, we sample all intermediates of the favorable pathways for the methanol dehydrogenation reaction under UHV conditions. To do this we consider the following adsorbate molecules: \(\text{H}_2\text{COH}\), \(\text{H}_2\text{CO}\), \(\text{H}_2\text{CO}\), HCO, \(\text{H}_2\text{COH}\), HCOH, CO, and H. This selection is based on the molecules that participate in the most likely UHV reaction pathways identified by Greeley and Mavriliakis.\(^{17}\) Paths 1, 2, and 3 in our current nomenclature (see section 1). In addition, monatomic carbon and oxygen are also studied to establish adsorption energy scaling relationships as was done previously for crystalline surfaces.\(^{16,17,22-24}\) Figure 4 displays the average adsorption energies of each MDR intermediate on all four Pt\(_{13}\) clusters (220 calculations in total) plotted as a function of the corresponding molecular adsorption energy on Pt(111). For each system (i.e., isolated cluster or cluster and support), a linear fit of all adsorption energies (not just average values) versus the respective Pt(111) values was performed, with best-fit parameters listed in Table 2. Despite statistical variation, the adsorption behavior for every system versus Pt(111) shows a very consistent trend: to a very good approximation, all linear fits essentially have the same slope as the dashed line 1:1 line (Figure 4) suggesting that the support induces rigid shifts in the adsorption energies of MDR intermediates on the Pt\(_{13}\) nanoclusters. These rigid shifts can be quantified by the y-intercepts of the best-fit lines and, as shown in the inset of Figure 4, are inversely correlated to the calculated cluster d-band centers. In other words, as the cluster d-band center approaches that of Pt(111) and so do the adsorption energies of MDR intermediates on the cluster (to within statistical variations). This is a noteworthy result as it suggests that, by knowing (a) the adsorption energy of an intermediate on Pt(111) and (b) the d-band center for the cluster of interest (supported or unsupported), one may readily estimate the average adsorption energy for that intermediate on the cluster. Detailed statistical sampling over cluster adsorption

![Figure 3](image-url)  
Figure 3. Adsorption of \(\text{H}_2\text{CO}\) at randomly chosen sites on a vacancy-supported Pt\(_{13}\) cluster. (C, brown spheres; Pt, gray spheres; O, red spheres; H, white spheres.)

![Figure 4](image-url)  
Figure 3. Top row: selected MDR intermediates on Pt(111) surface. Bottom row: same selected MDR intermediates on a single adsorption site of divacancy graphene-supported Pt\(_{13}\). (a) \(\text{H}_2\text{COH}\), (b) \(\text{H}_2\text{CO}\), (c) HCO, (d) \(\text{H}_2\text{CO}\), (e) HCOH. (C, brown spheres; Pt, gray spheres; O, red spheres; H, white spheres.)

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Figure 4. Adsorption energies of MDR intermediates on supported and unsupported Pt_{13} nanoclusters versus adsorption energies on Pt(111). Data points are averages of all sampled adsorption sites on that system and error bars are calculated from Student-T 95% confidence intervals. Lines represent linear fits of all (not just average) molecular adsorption energies for each Pt_{13} cluster. The dashed line is plotted as a guide to the eye. The inset shows the shift (y-intercept) of the adsorption data fits for each system versus their respective d band center; the dashed line is a linear fit that serves as a guide to the eye.

Table 2. Linear Best-Fit Parameters for Adsorption Energies (E_{ads}) of MDR Intermediates on Pt_{13} Nanoclusters to Their Pt(111) Values (Figure 4)

<table>
<thead>
<tr>
<th>system</th>
<th>slope</th>
<th>y intercept (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>isolated cluster</td>
<td>0.97</td>
<td>0.55</td>
</tr>
<tr>
<td>cluster on pristine graphene</td>
<td>1.01</td>
<td>-0.34</td>
</tr>
<tr>
<td>cluster bound at vacancy in graphene</td>
<td>0.97</td>
<td>-0.32</td>
</tr>
<tr>
<td>cluster bound at divacancy in graphene</td>
<td>0.94</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

sites is thus eliminated in favor of a simple scaling relationship. This finding could open up the potential use of support effects as a new control parameter for exploration when conducting high-throughput computational studies of supported catalysts. Systematic exploration of cluster size effects and their interplay with support effects will be reported elsewhere. Bifunctional support effects require special consideration but are not of relevance for our present study. (Consideration of more adsorbate molecules that were not in favorable reaction pathways is provided in the Supporting Information, and the general trends identified here are still applicable.)

For completeness, the adsorption energies and trends in adsorption energy were checked against a multitude of other potential descriptors including charge transfer from the Pt_{13} cluster to the support, charge transfer from the adsorbate to the Pt_{13} cluster, the Fermi level shift of the supported Pt_{13} clusters versus the unsupported case and versus Pt(111), and the d-band center of the Pt_{13} clusters relative to the vacuum level; none of these descriptors proved useful. The excellence of the d-band center position (relative to the Fermi level) as a predictor of average adsorption behavior on catalyst nanoclusters appears to be unique.

3.3. Scaling Relationships on Supported Nanoparticles. Given the successful past use of adsorption energy scaling relationships for heterogeneous catalysis on macroscopic crystalline surfaces, it is natural to inquire whether such relations work on nanoclusters. To the best of our knowledge, beyond a recent series of studies of four-atom unsupported clusters, this question has received scant attention and certainly not for supported, low-symmetry nanoclusters. In Figure 5, we display the adsorption energies of the MDR intermediates on the unsupported and supported Pt_{13} nanoclusters as a function of the adsorption energy of either monatomic carbon or monatomic oxygen; the probe atom (C or O) was chosen depending upon whether the intermediate adsorbed most frequently to the cluster via a C–Pt or an O–Pt bond. In all cases, the most frequently observed cluster–adsorbate bond was the same as that on the Pt(111) surface. For H_2CO, which was seen to bind via C, O, or both simultaneously, O was chosen as the probe molecule due to a superior agreement. As seen from Figure 5, for the most part, the adsorption energy of an intermediate correlates very well with that of the relevant probe molecule leading to a set of robust scaling relationships. The correlation for HCO and H_2COH appears somewhat less robust, but the outlying data for these two cases are contributed by the isolated Pt_{13} clusters. To the extent that the isolated Pt_{13} cluster merely sets the “zero” for probing support interactions and is not relevant as a catalyst, we deem these couple of outliers to be unimportant. The trend of adsorption energies for the C atom on the clusters may initially appear erratic but actually is very similar to the results for carbon-binding molecules on the clusters. Within statistical error, adsorption energies for the isolated, pristine, and vacancy cases are fairly similar; adsorption in the divacancy case is significantly weaker though and in many cases the data even lie above the Pt(111) values. Just as for the d-band center model, the internal variation caused by the low-symmetry cluster sampling does not disrupt the general trends that make adsorption energy scaling relationships an effective predictor.

As seen above, the scaling relationships are fairly robust for all adsorbates and cluster–support systems despite local variations in geometry and the corresponding variations in adsorption energies. By substituting the average C and O adsorption energies into the linear fit equations for the various adsorbates (see Figure 5), one can “predict” the average adsorption energies of the MDR intermediates. The predicted adsorption energies for the MDR intermediates can then be compared to the DFT-calculated adsorption energies to assess the overall quality of the correlations. As seen from Figure 6, the scaling relationships based on C and O adsorption energies (Figure 5) function as excellent predictors across the entire spectrum of MDR intermediates and cluster–support systems. The deviation between values predicted by the scaling relationships and calculated from DFT is relatively small throughout the range of adsorption energies being considered. Indeed, the performance of these scaling relationships at predicting the average adsorption energies is surprisingly good given the variation in adsorption geometries and energies between systems, and points to the general robustness of the chosen predictors, inspired from studies on crystalline facets, even for low-symmetry clusters.

3.4. Reaction Thermodynamics. The thermodynamics of the MDR have been explored quite thoroughly in a variety of surfaces and through a variety of methods, as discussed in section 1. Here we perform an initial investigation of the MDR thermodynamics on low-symmetry supported Pt_{13} nanoclusters.

On Pt(111) Gleeley and Mavrikakis identified the pathway H_2COH → H_2COH → HCOH → CO (Path 1) as the
Figure 5. Scaling relationships for adsorption energies of MDR intermediates versus adsorption energies of monatomic carbon or oxygen. Points are average adsorption energies for each system whereas linear fits are to all adsorption data. (The Pt(111) value for HCO overlaps with that for H$_2$COH making the symbols indistinguishable.)

Figure 6. Adsorption energies of MDR intermediates on all systems predicted by fitted scaling relationships based on C and O adsorption energies versus their DFT calculated values. Error bars are Student-t 95% confidence intervals of the DFT-calculated adsorption energies. Equality line is plotted as a guide to the eye.

Two additional pathways, H$_2$COH $\rightarrow$ H$_2$CO $\rightarrow$ HCO $\rightarrow$ CO (Path 2) and H$_2$COH $\rightarrow$ H$_2$COH $\rightarrow$ H$_2$CO $\rightarrow$ HCO $\rightarrow$ CO (Path 3), were identified as possible but relatively noncompetitive as, in comparison to the other two pathways, the rate limiting step of Path 1 has both a significantly lower barrier and higher reverse barrier, yielding an effective rate that is orders of magnitude higher than Paths 2 and 3. COH was shown to be present as a spectator species, with high barriers of formation and decomposition, but also high adsorption energy, leading to a minor poisoning effect on the catalyst surface. Since we used a different exchange-correlation functional (and a different DFT program) than Greeley and Mavrilakis, we revisited their proposed MDR pathways on Pt(111) and obtained essentially the same conclusions. The calculated reaction thermodynamics (eqs 4–6) for the Pt(111) surface as well as for a Pt$_{13}$ cluster.
As for other cluster-support systems are displayed in Figure S4.)

Figure 7. Schematic and thermodynamics of the MDR on Pt(111) and on a Pt$_{13}$ cluster bound at a divacancy in graphene. Brown circles represent carbon atoms, red circles represent oxygen atoms, and the gray bars represent the catalyst surface. All molecules/atoms involved are considered adsorbed until after the decomposition pathway is completed. The adsorbed hydrogens are shown stacked to the right for visual clarity. Blue arrows represent negative reaction energies, while red arrows represent positive reaction energies. The size of each arrow is in exact proportion to the magnitude of the reaction energy, which is indicated beside the arrow. Relaxed structures of all reaction intermediates on a single site for the divacancy-bound cluster can be found in Figure S4.

While we have not calculated actual reaction barriers in this work, we can nevertheless compare the reaction thermodynamics between the Pt(111) surface and the supported/unsupported Pt$_{13}$ clusters and arrive at a preliminary set of conclusions. As predictors for reaction barriers, based on the Bronsted–Evans–Polanyi (BEP) principle, have been shown to be quite robust for Pt(111) among other catalyst surfaces, and even for four-atom metal clusters, we hypothesize the existence of analogous relationships on our graphene-supported Pt$_{13}$ clusters. (Rigorous calculations of BEP relationships for our Pt$_{13}$ systems will be undertaken in future work.) The focus of our comparison for now is between the Pt(111) surface and the divacancy-bound cluster (Figure 7), as the d-band center calculation and adsorption behavior show that the divacancy defect has the strongest effect on the supported Pt$_{13}$ cluster. The thermodynamics of Path 1 are relatively unchanged between the Pt(111) surface and the divacancy-bound Pt$_{13}$ cluster. The statistical nature of our analysis does mean that some reactive sites on the cluster will exhibit reaction energies lower than average, indicating the possibility of outlier sites that contribute significant fractions of the total activity, analogous to the way that step-edges and defects have been shown to contribute significant activity and dominate the overall reaction on larger, faceted nanoparticles. The other two pathways (Paths 2 and 3), however, present interesting differences from the Pt(111) surface. Path 2 ($\text{H}_2\text{COH} \rightarrow \text{H}_2\text{CO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{HCO} \rightarrow \text{CO}$) on Pt(111) is unfavorable due to higher reaction energy and barrier for the first reaction step ($\text{H}_2\text{COH} \rightarrow \text{H}_2\text{CO}$); however, on the divacancy-bound Pt$_{13}$ cluster, this first step is less uphill. Because of these interactions we believe that the second pathway could be more active on the graphene-divacancy-bound Pt$_{13}$ cluster than on the Pt(111) surface. Path 3 ($\text{H}_2\text{COH} \rightarrow \text{H}_2\text{COH} \rightarrow \text{H}_2\text{CO} \rightarrow \text{HCO} \rightarrow \text{CO}$) is less active on Pt(111), once again because of the unfavorable and high barrier for the $\text{H}_2\text{COH} \rightarrow \text{H}_2\text{CO}$. Again, for the divacancy-bound Pt$_{13}$ cluster case this step is significantly less unfavorable, with average reaction energy of essentially zero, and thus Path 3 could become much more active on the graphene-divacancy-bound Pt$_{13}$ cluster than on the Pt(111) surface. Overall, the interaction between the three MDR pathways appears to be significantly changed on the divacancy-bound Pt$_{13}$ cluster with respect to the Pt(111) surface; instead of having one dominant pathway contributing most of the catalytic activity as on the Pt(111) surface, the reaction thermodynamics suggest a millily dominant pathway (that is possibly more active on the divacancy-bound Pt$_{13}$ cluster than on the Pt(111) surface), with two competing pathways also generating significant activity. As all reaction energies are statistical distributions rather than precise values on the low-symmetry supported Pt$_{13}$ clusters, the possibility of contributed activity from extraordinarily active outlier sites on the cluster is also a matter of future interest.

The thermodynamics and adsorption of COH are also of some interest in the graphene-divacancy-bound Pt$_{13}$ case. On Pt(111), COH has a very high adsorption energy, a high barrier of formation, and a very high barrier for decomposition into CO and H. It was found that this combination led to COH being a minor poison to reaction, occupying roughly 10% of available surface sites. However, on the divacancy-bound Pt$_{13}$ cluster, the energetics are very different. COH still has a high adsorption energy, but it is about 1 eV lower than the Pt(111) case (see Table S2 and Figure S1). The reaction energy for forming COH from HCOH is much higher on the divacancy-bound Pt$_{13}$ cluster than on Pt(111), becoming thermodynamically even more unfavorable. This higher reaction energy then suggests the potential of even higher barrier of formation and means that the backward reaction becomes thermodynamically favorable. Finally, the reaction energy for decomposition of COH into CO and H is dramatically more favorable on the divacancy-bound Pt$_{13}$ cluster than on the Pt(111) surface. Considering all of these factors, it seems plausible that less COH would be formed on the divacancy-bound Pt$_{13}$ cluster to begin with, and any COH that is formed could be hydrogenated, dehydrogenated, or adsorbed more easily than on the Pt(111) surface, having the net effect of increasing the availability of reaction sites. The other graphene-supported Pt$_{13}$ clusters also exhibit interesting reaction thermodynamics. More information on their specific details can be found in Figure S3 and Table S5, but a few salient points will be discussed here. First, similarly to the graphene-divacancy-bound Pt$_{13}$ case, it seems likely that on all the Pt$_{13}$ clusters COH either would not be formed in appreciable amounts or would be able to hydrogenate/dehydrogenate to HCOH/CO, and not behave as a minor poison/spectator. Second, in general, most reaction steps have more negative reaction energies on all Pt$_{13}$ clusters relative to Pt(111). Furthermore, the reaction energies are also correlated with the strength of adsorption of the reactants and products on the supported Pt$_{13}$ clusters: weaker/stronger adsorption leads to smaller/larger reaction energies. To the extent that the adsorption energies of intermediates are in turn correlated with the cluster d-band centers, which are sensitive to support effects, the support effect is then manifested on the reaction thermodynamics through this sequence of correlations. This suggests the possibility of different rate-limiting steps for certain pathways on the clusters, and for overall lower barriers assuming that BEP relationships hold for this novel system.
Finally, some of the reaction steps have fairly large uncertainties, which suggests the possibility that the non-uniformity of the clusters could offer a nonzero concentration of sites with much lower barriers, therefore increasing the effective reaction rate of the system in a way that the average values would not indicate; however, it is impossible currently to make any conclusions based on this and more in-depth analysis is surely required.

4. CONCLUSIONS

We investigated the adsorption of MDR intermediates and examined the thermodynamics of several MDR pathways on Pt clusters. The average adsorption energies of the intermediates of the MDR experienced a rigid shift relative to Pt(111) as a result of support interaction, and this shift could be correlated well with the d-band center of the system, which is in turn influenced by the strength of support interaction. In addition, scaling relationships and d-band center correlations established on high-symmetry crystal surfaces appear to be successful for predicting the average adsorption behavior of molecules on supported Pt clusters. A comparison of the MDR thermodynamics between the Pt(111) and vacancy graphene-supported Pt(13) suggest shifts in the interactions between the favorable reaction pathways, and may indicate overall higher activity for graphene-supported Pt clusters compared to the Pt(111) surface. Overall, our studies indicate that defective graphene-supported Pt clusters is a promising MDR catalyst and possesses qualitatively different adsorption and reaction thermodynamics from the Pt(111) surface, which may further explain the high activity seen in defective graphene-supported Pt nanoparticles.

The findings in this work suggest new questions that should be addressed next to move toward the goal of rational design of MDR catalysts. Specifically, it remains to be investigated whether the reaction barriers on the supported clusters are different than those on single-crystal surfaces and if these differences match expectations from experimental work. The validity of BEP-like relationships between the reaction barriers and reaction thermodynamics for these supported-cluster systems remains a significant open question. Confirmation of BEP-like relationships would greatly facilitate computationally inexpensive calculation of the reaction barriers for the full reaction network on the low-symmetry supported Pt clusters, which could enable further investigation into the interplay of multiple support effects under realistic conditions.

This and other questions will be addressed in future work.

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REFERENCES


APPENDIX B

ADSORPTION OF CO ON PT NANOPARTICLES, ENERGY DECOMPOSITION ANALYSIS AND PREDICTION VIA MACHINE-LEARNING


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Supporting Information

ABSTRACT: We present a systematic analysis of CO adsorption on Pt nanoparticles in the 0.2–1.5 nm size range with the aim of unraveling size-dependent trends and developing predictive models for site-specific adsorption behavior. Using an empirical-potential-based genetic algorithm and density functional theory (DFT) modeling, we show that there exists a size window (40–70 atoms) over which Pt nanoparticles bind CO weakly, the binding energies being comparable to those on (111) or (100) facets. The size-dependent adsorption energy trends are, however, distinctly nonmonotonic and are not readily captured using traditional descriptors such as $d$-band energies or (generalized) coordination numbers of the Pt binding sites. Instead, by applying machine-learning algorithms, we show that multiple descriptors, broadly categorized as structural and electronic descriptors, are essential for qualitatively capturing the CO adsorption trends. Nevertheless, attaining quantitative accuracy requires further refinement, and we propose the use of an additional descriptor—the fully frozen adsorption energy—that is a computationally inexpensive probe of CO–Pt bond formation. With these three categories of descriptors, we achieve an absolute mean error in CO adsorption energy prediction of 0.12 eV, which is similar to the underlying error of DFT adsorption calculations. Our approach allows for building quantitatively predictive models of site-specific adsorbate binding on realistic, low-symmetry nanostructures, which is an important step in modeling reaction networks as well as for rational catalyst design in general.

1. INTRODUCTION

Platinum nanoparticles are extensively used as catalysts for electrochemical reactions, in particular having a long history as among the best catalysts for hydrogen and methanol fuel cells. While it is generally desirable to prepare nanoparticles with sizes as small as possible in order to attain high electrocatalytic surface area while optimizing the precious metal, ultrasmall (<1 nm) nanoparticles begin to present significant deviations in properties relative to their larger, bulk-like counterparts. Examples of such behavior have been shown in many cases experimentally and computationally, with the particularly well-known example of gold, which is normally inert, turning into an effective nanocluster catalyst. In addition it has been observed that at the nanometer size range catalytic properties of nanoparticles can become exquisitely sensitive to the particle structure, adding more complexity to the issue. Hence, in this work we seek to understand the properties of sub-nanometer Pt clusters, as they correlate with changing particle size, and attempt to find suitable predictors for adsorbate binding energies that can help circumvent expensive density functional theory (DFT) calculations. Multiple computational groups have also addressed this topic but with a key limitation, namely, focusing only on high-symmetry cluster morphologies. Experimental evidence and computational modeling have shown that real nanoparticles do not adopt high-symmetry structures, and instead adopt somewhat disordered low-symmetry structures. The effects of such morphological variations on the electronic structure are particularly noticeable at small size clusters, as shown in our previous work on supported and unsupported Pt13 nanoparticles. In this work, we present a systematic analysis

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of the influence of cluster size and morphology on adsorbate binding using the well-known catalyst poison, carbon monoxide, as an example.

There have been several investigations into the trends of adsorbate binding energies with size on Pt nanoparticles. Li et al.\(^\text{12}\) studied CO and O adsorption on selected surface sites on Pt nanoclusters and showed that the adsorption energies with respect to cluster size converge to the bulk values rapidly (at ~147 atoms) and monotonically. Toyoda et al.\(^\text{12}\) showed experimentally that the d-band center of Pt nanoparticles tends to shift toward the Fermi level with decreasing size and correlated this shift with a change in electron catalytic activity; unfortunately, their analysis did not extend into the sub-nanometer size range, where we would expect deviations from quantum size effects to arise. Calle-Vallejo et al.\(^\text{14}\) showed on a few truncated octahedral Pt nanoparticles that coordination number is linearly correlated with O, O\(_2\), OOH, H\(_2\)O, and H\(_2\)O adsorption energies across size range but also pointed out that the d-band center model can fail on nanocluster systems. Yudanov et al.\(^\text{15}\) investigated explicitly the relationship of CO adsorption energy with size on various high-symmetry Pd nanoparticles, densely sampling sizes below 116 atoms. They observed a definite minimum in CO adsorption energy around a size of 40 atoms, and a linear dependence of cluster d-band center with size. Han et al.\(^\text{15}\) showed that the d-band center model is accurate for predicting adsorption behavior of O and OH on the facets of cuboctahedral clusters but fails to predict the edge and vertex adsorption behavior accurately. In short, small molecule adsorption on nanoclusters of different geometries have led to contradictory conclusions: monotonic convergence with respect to size versus the existence of local minima and evidence that simple linear prediction models are accurate versus their breakdown.\(^\text{15,14}\) These examples from literature form a contradictory picture, possibly because the properties of nanocluster catalysts can exhibit significant sensitivity to both size and structure. Hence, we seek to investigate in more detail the trends of CO adsorption energy with size of Pt nanoclusters that have realistic, global minimum geometries at all sizes considered: this is necessary in order to fully understand whether the conclusions arrived at are truly due to size effects and not merely due to variations in arbitrarily selected particle geometries. Furthermore, beyond addressing the issue of structure sensitivity, we also explore whether single-predictor models (e.g., based on d-band centers or coordination number) are sufficient to quantify adsorbate binding energies on low-symmetry, low-energy clusters or if multipredator models are essential for quantitative accuracy.

The first key feature of our current work—at variance with previous studies\(^\text{13,14}\)—is that we conduct CO adsorption calculations on low-symmetry, low-energy nanoclusters. These cluster morphologies are obtained by the application of an empirical bond-order potential driven genetic algorithm (GA), described in our previous work.\(^\text{19}\) As shown in that work, the empirical-potential-based GA reliably predicts low-energy, low-symmetry cluster morphologies as confirmed by subsequent verification via DFT calculations across a range of cluster sizes. Hence, this approach both allows us to examine realistic minimum energy structures for any given size of nanoparticle and eliminates having to decide between the fitness of various arbitrary, high-symmetry geometries. Once low-energy cluster morphologies are obtained from the GA at relatively low computational cost, the remainder of the computational effort can be expended in higher-level DFT calculations of adsorbate binding on these clusters. One of the main challenges of investigating adsorbate binding on these low-symmetry structures is that they generally do not possess symmetry-equivalent sites unlike bulk-terminated crystal facets and high-symmetry clusters. Because of this, some form of statistical sampling must be undertaken for calculating even simple adsorption properties, requiring a compromise between accuracy and computational effort spent on repeatedly sampling the same cluster. Thus, it becomes extremely useful to be able to predict both average as well as site-specific adsorption energies on these disordered structures using relatively simple structural metrics and/or limited electronic structure information without having to undertake full-blown DFT adsorption calculations on every available surface site. In order to approach this challenging problem, the second key feature of our work is the application of a machine learning tool\(^\text{53,15}\) to the prediction of CO adsorption energies on sub-nanometer Pt clusters. The use of machine learning techniques in materials science is in its infancy and growing,\(^\text{52,13}\) and a few groups have recently explored using machine learning for predictions of adsorbate binding on transition-metal surfaces, reporting modest errors (<0.1 eV) with respect to DFT.\(^\text{54,55}\) The gradient-boosting algorithm was used recently by Takigawa et al.\(^\text{56}\) to accurately predict the d-band center of bulk alloys and alloy surfaces based on mechanical and structural properties, demonstrating the potential usefulness of machine learning approaches for computational catalysis research. To the best of our knowledge, machine-learning algorithms have yet to be applied to predict adsorbate binding on clusters and our work represents an early example of the promise of this approach to this class of problems.

2. COMPUTATIONAL METHODS

2.1. Genetic Algorithm and Minimum-Energy NanoParticle Morphologies. Realistic structures for Pt\(_{N}\) (N = 4-147) clusters were obtained by sampling the hyper-dimensional energy surface using a GA, the details of which are reported in ref 19. Pt-Pt interactions are described using Albe et al.’s Tersoff-style empirical potential.\(^\text{57}\) As shown previously,\(^\text{19}\) minimum-energy structures found by the GA consistently displayed low symmetry and were confirmed via DFT to be lower in energy than icosahedral and cuboctahedral clusters, indicating the robustness of the GA and the accuracy of Albe et al.’s potential. The GA-optimized clusters are then used as the starting point for subsequent DFT calculations of CO adsorption. The combined empirical-potential-based GA and DFT approach allows us to investigate the coupled effects of morphology and size on the catalytic activity of the clusters.

2.2. Density Functional Theory Calculations. Non-spin-polarized DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP).\(^\text{58-60}\) The core and valence electrons were treated using the projector-augmented wave method. The Perdew–Burke–Ernzerhof (PBE) form of the generalized-gradient approximation was used to describe electron exchange and correlation. From convergence studies, we chose a kinetic energy cutoff of 100 eV and a second-order Methfessel-Paxton smearing of 0.05 eV. All atomic positions were relaxed with a force tolerance of 0.01 eV/Å. The Brillouin zone was sampled using a single Γ point.

Initial structures for the Pt\(_{N}\) clusters were taken from the empirical bond-order potential based GA described above and subjected to an additional conjugate-gradient minimization in VASP to generate the low-energy DFT reference state. While the empirical-potential and DFT potential energy surfaces (PES) are not identical, we have shown previously that the ordering of low-energy structural somers is almost always consistently
preserved between the empirical potential and DFT, which justifies our approach of simply importing the GA structure into DFT without further exhaustive sampling of the PES. High-symmetry icosahedral ($I_h$) and cuboctahedral ($O_h$) clusters were also sampled at discrete “magic-number” sizes (13, 55, and 147 atoms). For the purposes of this study, sampling of CO adsorption was only undertaken at the on-top adsorption sites as this configuration has been found to generally be the most favorable site for CO adsorption on Pt nanoclusters. The CO molecule was placed initially at a distance of 1.88 Å from the selected Pt atom along the radial direction as defined by a vector directed from the nanocluster center-of-mass to the Pt atom. This Pt–C bond distance was chosen from initial test calculations of CO adsorption on clusters that showed this to be the converged Pt–C bond length, on average. CO binding on Pt$_N$ clusters was calculated at numerous on-top sites (between 5 and 20 per cluster) to sample the full range of d-band center positions and coordination numbers available on the cluster. The high-symmetry $I_h$ and $O_h$ clusters were sampled at all the symmetry-equivalent sites and cluster averages were calculated with weights corresponding to the site multiplicity.

The adsorption energy ($E_{ad}$) of a CO molecule on a Pt$_N$ cluster is calculated as

$$E_{ad} = E(\text{Pt}_N + \text{CO}) - E(\text{Pt}_N) - E(\text{CO})$$

where $E(\text{Pt}_N + \text{CO})$ is the total energy of the N atom Pt cluster with one adsorbed CO molecule, $E(\text{Pt}_N)$ is the energy of the isolated N atom Pt cluster, and $E(\text{CO})$ is the energy of the isolated CO molecule. To separate out the contributions from charge redistribution during CO chemisorption from strain relaxation in the molecule and/or the cluster, we employ three distinct definitions adsorption energy. In the first instance, the adsorption energy ($E_{ad}^{FC}$, FC = frozen cluster) now quantifies the ligand effect. Finally, the adsorption energy is calculated by allowing for complete relaxation of the cluster and the molecule, and the resulting quantity ($E_{ad}^{AR}$) accounts for all the underlying processes including the ligand effect as well as strain relaxation in the cluster. The utility of these three definitions in separating out (approximately) the various physical effects upon adsorbate binding as well as their utility as descriptors will be discussed in more detail below.

3. RESULTS AND DISCUSSION

3.1. Cluster-Size-Dependence of d-band Center Energies. The d-band center energy of surface atoms is a widely employed and reliable descriptor for the adsorption energy of small molecules on transition-metal surfaces. In previous work we have also shown that the average d-band center energy of surface atoms on Pt$_N$ nanoclusters can serve as a reasonable descriptor for the adsorption energies of methanol decomposition intermediates and CO. Thus, we first examine the average d-band center energy of the surface atoms ($\varepsilon_d^{s}$) for Pt$_N$ ($N = 4$–147) clusters corresponding to particle diameters of 0.4–1.5 nm, to identify size-dependent trends as well as variations between low-symmetry and high-symmetry ($I_h$ and $O_h$) morphologies.

Figure 1 displays the variation in $\varepsilon_d^{s}$ with cluster size for both GA-optimized, low-energy clusters as well as high-symmetry ones.

For high-symmetry clusters, $\varepsilon_d^{s}$ decreases rapidly with increasing cluster size, converging toward the bulk values for Pt(111) and (100) facets. This behavior can be rationalized by noting that the number of adsorbed CO at the (111) and (100) nanocrystal face increases more rapidly than the number of adsorbed CO at the undercoordinated edge or vertex sites with increasing crystal size, thus driving the average d band position toward the bulk values. While the $I_h$ clusters have only (111) facets and the $O_h$ clusters display both (111) and (100) facets on the surface, $\varepsilon_d^{s}$ does not converge precisely to the bulk Pt(111) values for the former or to a weighted average for Pt(111) and (100) values for the latter, thus reflecting the as-yet non-negligible contributions to the ensemble average from undercoordinated edge or vertex sites that have relatively high d-band centers (Figure S1). The limiting bulk values should be recovered in the thermodynamic limit ($N \rightarrow \infty$).

Irrespective of these details, the main point of note here is the monotonic decrease in $\varepsilon_d^{s}$ toward the limiting bulk values for high-symmetry (magic-number) clusters as a function of size. In contrast, the low-energy, low-symmetry, GA-optimized clusters consistently show lower $\varepsilon_d^{s}$ than the high-symmetry structures over the size range (4–147 atoms) considered here. Moreover, we observe that by the time the cluster is approximately 30 atoms large, $\varepsilon_d^{s}$ drops below the corresponding values for (111) and (100) facets reaching a minimum value around $N = 100$. Beyond $N = 100$, there is a slight upshift in $\varepsilon_d^{s}$ but this remains below the values for (111) and (100) facets. While systematic modeling of clusters larger than 150 atoms was prohibitively expensive, we attempted an additional test calculation (Figure S2) for a larger Pt$_{150}$ cluster and even in that case $\varepsilon_d^{s}$ remains above 0.1 eV below the Pt(111) value. The existence of a local minimum for $\varepsilon_d^{s}$ is particularly interesting as it suggests a preferred cluster size that might bind adsorbates more weakly and, for example, improve the resistance to CO poisoning. It should be noted though that the statistical errors in $\varepsilon_d^{s}$ for our low-symmetry clusters are large enough to suggest that this result is more suggestive of a size range (approximately 30–150 atoms) over which Pt nanoclusters bind adsorbates more weakly than macroscopic crystal facets.
While trends in d-band center energies are suggestive of lower adsorbate binding energies, they do not furnish definitive proof of such behavior. For sub-nanometer clusters, one can expect significant deformation of the cluster upon adsorbate binding and the magnitude of this effect could substantially alter conclusions based on relative d-band positions alone. Hence, we carry out DFT modeling of CO adsorption on Pt nanoclusters next to explicitly calculate CO adsorption energies as a function of cluster size and cluster morphology.

3.2. Cluster-Size-Dependent CO Adsorption Energies and Their Correlation with d-Band Center Energies.

We sampled single-molecule CO adsorption energies across a wide range of GA-optimized Pt$_N$ ($N = 4$–147) clusters considering approximately 200 adsorption sites in total that span the full range of both coordination number and site-specific d-band centers that the surfaces offer. High-symmetry $I_h$ and $O_h$ structures were also studied for comparison against their low-symmetry counterparts as these structures are often used as models for catalyst clusters.

Figure 2 displays the results for average CO adsorption energies, $E_{ads}$, (with full relaxation of the adsorbate and cluster) as a function of cluster size and morphology.

![Figure 2](image)

Figure 2. Average adsorption energy ($E_{ads}^{th}$) of a single CO molecule as a function of cluster size on lower-energy, low-symmetry, GA-optimized Pt clusters, and on high-symmetry icosahedral and cuboctahedral clusters. The CO molecule and Pt clusters are fully relaxed in these calculations. Statistical error bars represent Student-T 95% confidence intervals (except for $Pt_9$ and $Pt_{14}$ for which every adsorption site was sampled and we report the standard deviation) for error bars for the high-symmetry clusters are too small to be visible in this plot. Horizontal dashed lines indicate the reference adsorption energy values on bulk-terminated, FCC Pt(111) and (100) surfaces. The corresponding data for this plot are listed in Table S2.

As a function of cluster size and morphology, while the sample size for high-symmetry $I_h$ and $O_h$ clusters is limited by geometric considerations to $13$, $55$, and $147$ atoms—the Pt$_{55}$ cluster being too large for detailed adsortion studies—it is nevertheless possible to draw some key distinctions relative to the GA-optimized clusters. First, we find that, with increasing cluster size, the CO adsorption energies monotonically approach the values for bulk surfaces although the results are still far from converged to the bulk values at these cluster sizes. In contrast, the GA-optimized Pt clusters show the presence of a local maximum in the CO adsorption energy (less negative implying weaker adsorbate binding) at a cluster size of $N = 55$ for which the CO adsorption energy is almost equal, within statistical error, to that of the Pt(111) surface. As before, taking into account the statistical errors, we see that within a size range of approximately 40–70 atoms, the Pt nanoclusters bind CO molecules as strongly as the Pt(100) or (111) facets. Second, for all sizes considered, the low-symmetry Pt nanoclusters bind CO more weakly than the high symmetry ones. This result can be understood as resulting from the increased stability of the low-symmetry structures relative to the high-symmetry ones, manifested through fewer undercoordinated atoms and lower d-band centers. This gap in adsorption energies becomes smaller as cluster size increases and is expected to eventually close at larger sizes once the cluster surface is dominated by crystalline facets. Nevertheless, in the sub-nanometer range, the differences are certainly non-negligible, ranging from 0.1 to 1.0 eV, thus justifying the need for proper optimization of cluster morphology via global minimization techniques as opposed to ad hoc choices of structures.

To understand more fully the trends of CO adsorption energy with size, and to quantify the relative magnitudes of the ligand and strain effects, we decompose the adsorption process into three distinct steps, as described in section 2.2. Briefly, we calculate adsorption energies for entirely frozen CO molecules and Pt clusters ($E_{ads}^{0}$) when the CO molecule is placed at a typical C–Pt bond length at an on-top site, relaxed CO molecules but frozen Pt clusters ($E_{ads}^{0}$), and fully relaxed CO molecules and Pt clusters ($E_{ads}^{f}$). As the Pt cluster is frozen in the calculation of $E_{ads}^{0}$, this definition of the adsorption energy quantifies the ligand effect. The difference $\Delta E_{ads} = E_{ads}^{f} - E_{ads}^{0}$ is a measure of the contribution from the energy of deformation of the Pt cluster (strain effect) to the total adsorption energy $E_{ads}$. The utility of $\Delta E_{ads}$ will be discussed in detail in section 4. Figure 3 displays

![Figure 3](image)

Figure 3. (a) Average single-molecule CO adsorption energies on Pt clusters calculated with a fully frozen configuration ($E_{ads}^{0}$), relaxed CO but frozen Pt clusters ($E_{ads}^{0}$), and fully relaxed configurations ($E_{ads}^{f}$). (b) The deformation energy $\Delta E_{ads} = E_{ads}^{f} - E_{ads}^{0}$ as a function of cluster size, which accounts approximately for the contribution from cluster deformation (strain effects) to the adsorption energy. Error bars are Student-T 95% confidence intervals with the exception of the four-atom cluster where every site was sampled, and we report standard deviation, only a few representative error bars are shown in (a) for clarity. The exact values with confidence intervals on every data point are reported in Table S2.
these various quantities, averaged over clusters surface sites with the relevant data being summarized in Table S2. As seen from Figure 3a, the trends in average adsorption energies with constrained molecular/cluster configurations (\( E_{ads} \), \( E_{ads}^{0} \)) are quite similar to the fully relaxed adsorption energies (\( E_{ads}^{rel} \)), displaying a local maximum for the Pt55 cluster. As before, we note that the statistical errors are large enough here that the trends are more indicative of a size range for clusters with lower CO binding energy rather than a precise cluster size. We also observe from the relative magnitude of \( \Delta E_{ads} \) to the difference \( \Delta E_{ads} = E_{ads}^{0} - E_{ads}^{rel} \) (Figure 3b) that the ligand effect dominates the CO adsorption process. Interestingly, while the calculated values of \( \Delta E_{ads} \) are rather noisy—exacerbated by being a difference of two noisy quantities—the calculated cluster deformation energies generally lie between 0.2 and 0.5 eV for the range of sub-nanometer Pt clusters studied here.

The existence of a preferred size range, as seen in Figures 2 and 3, over which low-symmetry Pt nanoclusters bind CO more weakly is a noteworthy result of our adsorption calculations as it points to a useful design principle for robust, CO-tolerant Pt nanocatalysts. (Other practical considerations including, for example, support effects can be taken into consideration in the future using similar modeling approaches.) Yet, arriving at this conclusion has required full-blow simulations of CO adsorption, and it is useful to inquire whether simpler descriptors based on cluster geometry and/or electronic structure might be developed to arrive at similar conclusions with much less computational effort. To this end, a quick comparison of Figures 1 and 2 shows that the optimal cluster size for low CO binding, \( N \approx 55 \), does not coincide with the minimum in the average d-band center at \( N = 100 \). The coordination number of surface atoms, another potential descriptor, grows monotonically with size and approaches that for the low energy facets \(^1\) and, hence, cannot by itself capture the local maximum in the adsorption energy curve. These problems in arriving at a single-descriptor based model are magnified even further if one attempts to consider site-specific adsorption energies \(^2\) rather than surface averages. Moreover, the inability of single-descriptor models to capture the adsorption energy trends accurately cannot be attributed to unusual relaxation effects in these sub-nanometer clusters as the adsorption energy trends persist even for the frozen cluster calculations [Figure 3a]. Hence, we turn next to more systematic approaches based on machine-learning algorithms that can help us arrive at robust multidescriptor models.

3.3. Prediction of CO Adsorption Energies via Machine Learning. Having established that single-descriptor models are of limited use in accurately predicting CO adsorption energies, we resort to the application of machine-learning (ML) tools in the search for suitable multidescriptor models. Specifically, we employ the gradient-boosting regression (GBR) algorithm as implemented in the scikit-learn python package.\(^{25,26}\) The GBR model was used recently by Talsiavet al.\(^{27}\) and shown to be accurate in predicting the d-band center energies of crystal surfaces for various bimetallic alloys using readily available mechanical properties of the metals.\(^{28}\) The GBR is superior to a simple linear regression when working with nonlinear data relationships such as are seen between d-band center and CO adsorption energy on the nanoparticles under examination in this work.

To train the ML algorithm and access the accuracy of ML predictions, CO adsorption energies on different surface sites of Pt clusters, including both GA clusters and high symmetry clusters, were used as the target data. A few low but not minimum-energy clusters that were produced by the GA in some of the early generations were also sampled to explore a wider descriptor and target space. In total, 195 sites were sampled for CO adsorption, 75% of which were used for training and the remaining 25% for testing. To reduce bias in data partitioning, we used stratified 5-fold validation, wherein the CO adsorption data for each cluster was randomly split into five different train—test sets, which are constructed to ensure that every data point is in a test set at least once.

Descriptors associated with each adsorption site that are used for the prediction of adsorption energy are broadly grouped into three types:

(i) Type 1 descriptors involve only the electronic structure information calculated from DFT for each adsorption site. One of the most widely used descriptors of this type is the d-band center energy \( e_d \) defined here for a specific adsorption site \( i \). Here, we use a slightly modified version, namely, the generalized d-band center energy \( e_{d}^{\gamma} \) following the concept of generalized coordination number, defined as

\[
e_{d}^{\gamma} = \left( \sum_{j \neq i} e_j / c_{ni} \right) / c_{ni}
\]

which is in essence a local average of the atomic d-band centers. In eq 3, \( c_{ni} \) is the coordination number of atom \( i \) and the sum runs over all nearest neighbors \( j \) of site \( i \). While the usual site-specific d-band center energy or the generalized version can be used with little difference in the quality of the regression analysis for our present purposes (on-top binding), the latter is a more intuitive and convenient definition for further extensions to bridge or hollow binding sites that are not specifically associated with a single atom. Other Type 1 descriptors that were tested in the primary analysis also include e-band and p-band centers, electronic bandwidths, and Bader charges\(^{25} \) of adsorption sites. Several of these were either highly correlated with the d band properties or led to no further improvement in the testing errors. Hence, we work with the generalized d-band center energy as the sole Type 1 descriptor for now.

(ii) Type 2 descriptors involve only structural information on bare clusters, including average nearest-neighbor bond length \( \bar{d}_{i,j} \), generalized coordination number \( c_{ni} \), and cluster radius of gyration \( R_{g} \). The average bond length for a Pt atom \( i \) is calculated as

\[
\bar{d}_{i,j} = \sum_{j \neq i} d_{j} / c_{ni}
\]

where \( d_{j} \) is the distance between an atom \( i \) and its nearest neighbors \( j \) and \( c_{ni} \) is the coordination number of atom \( i \). The generalized coordination number \( c_{ni} \) defined as

\[
c_{ni} = \sum_{j \neq i} c_{nj} / c_{ni}
\]

is generally a better descriptor for adsorption energy than coordination number as has been shown for several small molecules on metal nanoparticle surfaces.\(^{14} \) In eq 4, \( c_{nj} \) is the coordination number of a Pt atom in the bulk FCC phase. The radius of gyration \( R_{g} \) is a cluster property and is the same for all sites on a cluster. These three descriptors thus quantify local, nonlocal, and global structural properties of the cluster and are readily calculated from the optimized cluster structure.
III Type 3 descriptors include now a single descriptor that encapsulates both electronic and structural information on the adsorption site, namely, the fully frozen CO adsorption energy $E^{ads}_{CO}$. As the Pt cluster (that has already been previously relaxed) and the CO molecule do not undergo any further ionic relaxation in this calculation (see section 2), $E^{ads}_{CO}$ can be obtained roughly 2 orders of magnitude faster than $E^{ads}_{Pt}$. It is also clear from Figure 3 that $E^{ads}_{CO}$ closely tracks the size-dependent trends of the target values of $E^{ads}_{Pt}$ thus making it a sensible choice of descriptor.

The descriptors chosen here are by no means unique and other choices are equally reasonable. For now, we proceed with the above three classes and analyze their utility in predicting size-dependent CO adsorption energies.

Figure 4 displays the correlation between DFT-calculated and ML-predicted CO adsorption energies (site-specific and not cluster average) using different combinations of descriptors. When trained by Type 1 descriptors (the generalized d-band center energy) alone, the model shows an absolute mean error (AME) of ~0.22 eV in the test sets [Figure 4a]. It is evident that there are a large number of outliers in even the training set and this is exacerbated for the testing set. Similarly, using purely structural information [Type 2 descriptors; Figure 4b] or only $E^{ads}_{CO}$ [Type 3 descriptors; Figure 4c] both result in AMEs of 0.17.

In short, using just one class of descriptors is rather unsatisfactory in predicting the CO adsorption energies. A combination of electronic structure and structural information results only in a slightly improved AME [Figure 4d]. By combining all descriptor classes though, the AME can be substantially reduced to 0.12 eV [Figure 4e]. This error is of the same order as that reported recently by Xie and co-workers in ML predictions of adsorption of CO on a wide variety of pure transition metal and alloy surfaces.1,25 Importantly, visual inspection of Figure 4e shows that the CO adsorption data is predicted quite accurately across a broad energy window of ~+4 eV. We note in passing that the apparent trend wherein training points are biased below the parity line in this figure is simply a quirk of this particular random split and is not representative of the overall behavior of the GBR model. The inset bar graphs in Figure 4 display the importance of the various descriptors in the final prediction. Focusing on the full descriptor set in Figure 4e, we see that the (generalized) d-band center, average Pt–Pt bond length, and (generalized) coordination number—conventional descriptors based on sound fundamental insights—are still indispensable, as reconfirmed by the ML algorithm. When focusing on sub-nanometer clusters, physical intuition would suggest that size effects (quantified by $N^*$) ought to become relevant for cluster deformation as confirmed by the ML algorithm. Similarly, we expect that the inclusion of $E^{ads}_{CO}$ as a descriptor incorporates some of the fundamental electronic processes during CO chemisorption that are difficult to capture by simple electronic structure information alone (d-band positions and/or widths) thereby significantly improving the predictive capability of the ML algorithm. For completeness, we also tested models with numerous other descriptors (Figure S3) and found little to no improvement over the smaller, physically motivated subset of descriptors employed here. Overall, the model suggests that the CO adsorption process on Pt nanoclusters is a particularly complex one to capture, requiring consideration of multiple factors including site-specific electronic structure and coordination, cluster size effects, and at least an approximate consideration of adsorbate–metal bond formation. It remains to be seen whether these considerations carry over more broadly to adsorbate binding on metal nanoclusters and to what extent model simplification is possible as cluster sizes begin to approach submonolayer regimes where one might expect size effects to be less significant. Nevertheless, for sub-nanometer clusters we are now able to implement accurate, inexpensive, and robust predictive models by combining modern computational tools with traditional physical insights, which can help push the frontier of rational catalyst design. Beyond macroscopic crystal surfaces to low-symmetry nanoscale catalysts.

4. CONCLUSIONS

We studied Pt nanoclusters, ranging from 0.2–1.5 nm in diameter, to understand size-dependent trends in the energetics of CO binding and to correlate these with morphological and electronic descriptors. An important aspect of our approach was to employ a genetic algorithm to determine unambiguously the low-energy morphologies of the Pt nanoclusters, which uniformly adopt low-symmetry structures for the sizes considered here. GA-optimized clusters show a nonmonotonic trend of surface d-band centers with respect to size, going from very high values at small sizes to a minimum around Pt10 before slowly asymptoting toward the Pt(111) surface value. This is in clear contrast to the essentially monotonic behavior of high-symmetry, cubiccrystallographic and icosahedral morphologies, which are not true low-energy structures for sub-nanometer Pt clusters. The CO adsorption behavior on GA-optimized clusters also presents similar nonmonotonic behavior with a global maximum at around Pt10.
By employing machine learning algorithms, we showed that the nonmonotonic trends in CO adsorption energies are not accurately captured by traditional single descriptor models based on d-band center energies or coordination number. Multidescrictor models based on d-band centers and structural information (coordination number, bond lengths, and cluster size) do not perform much better either. By adding a new descriptor to our models, namely, the "all-frozen" adsorption energy \( E_{\text{ads}} \), which partially incorporates some of the features of CO-Pt bond formation, we were able to achieve significant improvement in the machine learning model. We suggest that this descriptor, \( E_{\text{ads}} \), which can be calculated at minimal computational overhead, might be broadly applied across other systems to predict site-specific adsorption energies with higher accuracy; studies along these lines will be pursued elsewhere.

Overall, our work demonstrates the potential for developing accurate, predictive models of adsorbate binding on realistic nanocluster morphologies by integrating robust structural optimization methods with machine learning algorithms. Progress along these lines can significantly aid rational design of nanoscale catalysts, particularly in the sub-nanometer range where both structural and electronic properties differ fundamentally from those at larger length scales.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jchem.6b00128.

Additional figures and tables of the trends of surface d-band center with size, detailed of the d-band center and coordination number distribution of cuboctahedral Pr_{400}, trends of CO adsorption with size, and results of machine learning with additional descriptors. (PDF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


APPENDIX C

PROTECTIVE MOLECULAR PASSIVATION OF BLACK PHOSPHORUS

ARTICLE OPEN

Protective molecular passivation of black phosphorus

Vladia Artel1, Qiushi Guo2, Hagai Cohen3, Raymond Gasper2, Ashwin Ramasubramaniam2, Fengnian Xia2* and Doron Naveh1

Black phosphorus is a fascinating layered material, with extraordinary anisotropic mechanical, optical and electronic properties. However, the sensitivity of black phosphorus to oxygen and moisture poses significant challenges for technological applications of this unique material. Here, we report a viable solution that overcomes degradation of few-layer black phosphorus by passivating the surface with self-assembled monolayers of octadecyltrimchlorosilane that provide long-term stability in ambient conditions. Importantly, we show that this treatment does not cause any undesired carrier doping of the bulk channel material, thanks to the emergent hierarchical interface structure. Our approach is compatible with conventional electronic materials processing technologies thus providing an immediate route toward practical applications in black phosphorus devices.

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INTRODUCTION

Black phosphorus (BP) is one of the most interesting layered materials, holding promise for emerging electronic and optoelectronic device technologies.1-4 The crystalline structure of BP displays in-plane anisotropy in addition to the out-of-plane anisotropy characteristic to layered materials.5-9 Therefore, BP supports anisotropic optical and transport responses that can enable unique device architectures.7 Its thickness-dependent direct bandgap varies in the range of 0.3–2.0 eV (from single-layer to bulk, respectively), making BP suitable to optoelectronics in a broad spectral range.8,10 With high room-temperature mobility, exceeding 1000 cm² V⁻¹ s⁻¹ in thin films, BP is also a very promising material for electronics. However, BP is sensitive to oxygen and humidity11 due to its orthorhombic crystalline structure. The surface electron lone pairs are reactive and can lead to structural degradation upon exposure to air, which in turn leads to significant deterioration in device performance in ambient conditions.12-14

The unique and desirable optoelectronic properties of BP1-4 have motivated much recent work to ameliorate its problematic air and moisture instability. Promising strategies to address this problem include the formation of a protective capping layer or a controlled stable native oxide15 at the surface. Capping of BP with two-dimensional layered materials such as graphene and BN16 have provided stability for a period of 18 days. Alternatively, a 25 nm thick layer of alumina17 formed by atomic layer deposition was also found to be efficient, especially with the addition of a hydrophilic fluoropolymer layer that improved the stability over several weeks.17 More recently, organic functionalization of BP layers of allyl diazonium has been shown to provide effective chemical passivation although this is accompanied by p-doping of the channel material.17 Here, we passivate BP with self-assembled monolayers (SAMs) of octadecyltrimchlorosilane (OTS), thus gaining important advantages in terms of stability, oxidation resistance, and elimination of electronic devices degradation.

RESULTS AND DISCUSSION

SAMs are known for their effective surface passivation capabilities, particularly in semiconductor nanostructures.18,19 OTS molecules, comprised of an eighteen carbon chain backbone, a trichlorosilane head group and a methyl (CH₃) functional group, can form smooth and uniform SAMs on oxidized substrates; these crystalline-like, close-packed SAMs20 can substantially reduce oxygen penetration toward the underlying reactive substrate. A scheme of our device structure is shown in Fig. 1a, where a thin native phosphorus oxide (PO) layer bridges between OTS molecules and a BP crystal that forms the channel of a field-effect transistor (FET). The source and drain electrodes were defined by electron beam lithography on exfoliated BP flakes (8–10 nm thick) followed by metallization (Ti/Au). After lift-off, devices were cleaned with acetone and isopropanol and then immersed in hexane solution of OTS (see methods for details) for 1 h to obtain OTS coating on BP. X-ray photoelectron spectroscopy (XPS) characterization, applied on bulk BP samples, clearly differentiates between the OTS-coated and uncoated BP, both exposed to air for the same period of time. Normalized P 2p core level spectra of coated (blue) and uncoated (red) BP are presented in Fig. 1b, from which two pronounced differences are observed. First, in coated samples, the relative intensity of the broad peak around 134 eV, associated with BP oxide (BPO), is significantly smaller than in uncoated samples, indicating a thinner P-oxide layer as compared to bare BP. Because OTS coating of BP was performed in ambient conditions, a very thin layer of BPO still exists at the surface. Second, a pronounced spectral broadening of the low binding energy line (at ~130 eV) toward higher binding energies is imposed upon the OTS coating. A secondary, smaller broadening of the highly oxidized regime (at ~134 eV) toward lower binding energies is also seen. These spectral signatures of OTS-coated BP are further analyzed in detail and provide a possible mechanism for the surface reaction, as elaborated upon below.

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The efficiency of OTS passivation in preventing the typically rapid degradation of uncoated BP, is further confirmed by Raman spectroscopy, where the intensity of the A\textsubscript{1g} peak of BP (normalized to the intensity of Si substrate peak at 520 cm\textsuperscript{-1}) provides a measure of sample's structural stability. In uncoated BP (Fig. 1c) a rapid decrease of the A\textsubscript{1g} signal is observed, associated with the loss of long-range order,\textsuperscript{12} due to oxidation and subsequent amorphization of the BP. In contrast, the spectra of OTS-coated samples (Fig. 1d) are stable to the level of fluctuations arising from variations between measurements. Complementary to the Raman analysis, optical microscopy of OTS-coated devices (Figs 2e–f) also shows no visible signs of degradation that are typical to BP.\textsuperscript{11}

The electronic properties probed by transport measurements of FET devices also show clear degradation of uncoated BP devices, with the current response decaying to negligible levels after 14 days (Fig. 2a; also see SI for additional data). Conversely, coated devices maintain their field-effect behavior over a period of 28 days, as shown in Fig. 2b. To ascertain whether the molecular layer dopes the BP, we measured the transport properties of the devices right before and immediately after coating, and found negligible variations in their transport characteristics. In particular, the negligible effect of OTS on threshold voltage (Fig. 2c and Fig. S4) precludes Fermi level shifts or charge transfer between BP and the molecular layer. Furthermore, the on/off current ratios (Fig. 2b and Fig. S3) prove that BP maintains its original electronic properties while stabilized with OTS. These results are significant and, notably, in contrast with other molecular layers such as aryl diazonium on BP,\textsuperscript{15} showing that BP preserves its original properties under the OTS coating. Figure 2d further demonstrates that the transconductance (and hence, the hole mobility) is retained during the process of OTS self-assembly. Contrary to the decay of transport with time in bare BP (Fig. 2a) the stability of OTS-coated BP is remarkably persistent, suggesting that a robust corrosion-resistant molecular film is formed on the BP surface.

The success of OTS coatings in stabilizing BP and preserving its original electronic properties was studied in further detail by inspecting the SAM quality and its interaction with BP. Based on XPS (see SI for additional details) we conclude that a nearly vertically-aligned, ordered SAM is formed on the BPO (see Fig. 1a). We find a CSI atomic ratio (extracted after elimination of background signals) of \(\approx 24\), which is in excellent quantitative agreement with the value expected after correcting for the standard signal attenuation across the \((\text{CH}_2)_{\text{N}}\text{CH}_2\) backbone of the molecules. More precisely, the theoretical CSI ratio for a perfect vertical orientation of the molecules is \(\approx 26.4\); hence, on average, slightly tilted molecules (\(\approx 25^\circ\) to the surface normal) better fit the experimentally extracted value.

Beneath the OTS layer, a thin (\(\approx 2\) nm) BPO layer is detected, consisting of low O:P stoichiometry, with a significant amount of partially oxidized P components, as shown in Fig. 3c. Importantly, the total signal of oxidized P-2p components (including those components of intermediate oxidation that appear in the coated sample only, as in Fig. 3c) normalized to the bulk BP signal, is roughly conserved in the coated samples with respect to uncoated ones. This fact suggests that limited reduction of preformed BPO takes place; a process involving removal of oxygen atoms, while the number of corresponding phosphorus atoms remains unaffected. In fact, the chemical reaction with OTS
Fig. 2  Current transfer curves of uncoated (a) and OTS-coated (b) devices sampled over a period of 28 days in room atmosphere. I-V curves of as-fabricated (uncoated, solid line) and right after OTS-coating (dotted curves), showing negligible effect of the passivation treatment on device transfer curves (c), and device transconductance (d). Optical micrographs of the FET devices before OTS coating (e) and 28 days after OTS-coating (f).

involves the release of Cl atoms that are expected to cause mild reduction of the top BPO layer, analogous to surface oxide reduction and corrosion of AI contacts in electronic devices. Remarkably, the amount of oxygen depleted from the BPO layer is comparable to the amount of oxygen required for the Si-Ox interface between BPO and OTS (see SI for details). We, therefore, infer that the binding process of OTS is self-supported by the pre-existing BPO layer, which enables the success and robustness of our treatment.

Our proposed mechanistic interpretation is supported by multiple independent results. Firstly, based on our electrical measurements, we infer that no dopant ions of the BPO bulk takes place, which suggests that the bulk BP is indeed unaffected directly by the OTS. In other words, the thin oxide layer that is formed spontaneously, prior to OTS binding, seems to provide efficient protection against BP doping by any of the applied chemical agents. Also, no apparent traces of Cl atoms were observed on the BP surface, indicating that the hydrolysis reaction of OTS was complete. Secondly, controlled surface charging (CSC) data (Fig. S1) shows that BP remains highly conductive. The recorded line-shifts as the electron flood gun (EFG) was switched on and off were about 250 meV for the oxidized P, whereas the BP shifts were as small as 20 meV (see SI for details). As a reference, surrounding regimes of the adhesive tape shift by ~600 meV under the very same conditions. This analysis suggests that the top BPO layer is slightly reduced during the exposure to OTS, such that the local stoichiometry changes from about POx to about P2O5 on the average. Finally, computed binding energy shifts indicate (as discussed hereafter) a range of intermediate oxidation states at the BPO/OTS interface that fit well our measured intermediate P signals in Fig. 3d, signals that are missing from the corresponding P 2p spectrum of uncoated BP.

Ab initio density functional theory (DFT) calculations were applied as an independent probe of the OTS binding to BP. The structural models considered consist of a unit cell of BPO in a low oxidation state, analogously to an OTS SAM on either a polymerized or a non-polymerized configuration (Fig. 3a, b). From DFT calculations, medium-binding-energy states (between 130-133 eV) were obtained, which is in line with the measured spectrum of the OTS-coated BP (Fig. 3c), where signals from partially oxidized states were resolved, as shown in Fig. 3d and further elaborated upon in the SI tables. The calculated chemical shifts (Tables S1 and S4) roughly fall into two categories: one set of states that are ~0.3-0.6 eV above the bulk P 2p level and a second set at ~1.8-1.9 eV above the lowest P 2p levels. While the actual structure of the surface oxide is most likely amorphous and hence, significantly more complex, the observed agreement between core level energies for the surface-functionalized theoretical model and the XPS data supports the picture of chemical bonding, rather than mere physisorption, between the OTS molecules and the BPO.

To conclude, we have demonstrated a simple and effective strategy to stabilize water-scale black phosphorus thin films in the future. In the process of attachment to BP, OTS partially reduces the pre-existing surface oxide, a process quantitatively evaluated by XPS. The stabilization of BP is independently confirmed by transport measurements, Raman spectroscopy, and DFT calculations. We have shown that the native oxide layer of BP plays
multiple critical roles in the surface functionalization process. Firstly, the BPO layer enables the binding of ordered, close-packed OTS layers by providing the oxygen for the hydrolysis process and presenting a flexible template for assembly. Secondly, the remaining thin oxide layer provides the necessary screening against undesired doping effects associated with inter-diffusion and charge transfer between BP and OTS. Finally, the oxide layer itself is stabilized by OTS and is part of the overall protective capping over the BP channel (see SI for more detail). Overall, this study provides an inexpensive, reliable, and scalable solution to the vexing stability problems of BP thus paving the way for future technological applications.

METHODS

OTS coating
OTS encapsulation was achieved by immersion of devices in 3 ml dry hexane solution containing 30 μl of OTS for 1 h in a sealed tube to minimize air and moisture exposure. The samples were then washed in cold hexane and soaked for 10 min in hot hexane to remove OTS residues. Finally, samples were blow dried with nitrogen.

For coating bulk BP samples (V2O, Graphene, 7803-51-2), the same anchoring procedure was performed, following immersion of BP for 1 min in 5% acetic acid solution (in acetone) and blow dried with nitrogen prior to soaking in OTS solution.

Raman spectroscopy
Raman spectra were collected on a Horiba Labram HR spectrometer with exciting laser line at 532 nm.

Device fabrication
BP flakes were mechanically exfoliated on a clean surface of 90 nm SiO2/Si wafer. Electrodes were patterned by electron beam lithography and metalized with 350 nm Ti/Au.

XPS measurements
XPS measurements were carried out on a Kratos Axis Ultra DLD spectrometer, using monochromatic Al kα source at a relatively low power, in the range of 15-75 W. Samples were kept under inert atmosphere prior to their insertion into the vacuum, such that their exposure to air was limited to less than 1 min. The base pressure in the analysis chamber was kept below 10⁻⁷ Tor. The SCS' data further provides information on the electrical properties of the resolved domains. Complementary measurements were performed on BP flakes deposited on Ti and exposed to OTS at various conditions (not shown). Curve fitting was done using the Vision software, referring to control measurements on the bare adhesive tape and on samples dominated by polymerized OTS.
DFT calculations
Spin-polarized DFT calculations were performed using the Vienna ab initio Simulation Packages. The core and valence electrons were treated using the projector-augmented wave method. The Perdew-Burke-Ernzerhof generalised-gradient approximation was used to describe electron exchange and correlation. From convergence studies, a kinetic energy cut-off of 400 eV was chosen. Electronic convergence was accelerated with a Gaussian smearing of 0.05 eV for relaxation calculations; the Blöchl tetrahedron method was used thereafter for single-point electronic structure calculations. Dipole corrections were applied along the vacuum direction of the supercell (normal to the hPQ layer). Core-level shifts were calculated in the initial-state approximation.

CHANGE HISTORY
A correction to this article has been published and is linked from the HTML version of this article.

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AUTHOR CONTRIBUTIONS
D.N. and O.G. fabricated the devices and performed Raman and electrical measurements. H.C. and O.G. performed XPS measurements and analysis. H.C. and A.R. performed theoretical calculations and analysis. D.N. and P.X. conceived the idea, designed the experiments and analyzed the data. All authors discussed the results and commented on the manuscript.

COMPETING INTERESTS
The authors declare no competing interests.

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Molecular passivation of black phosphorus
Vladia Antel et al.

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APPENDIX D

LITHOGRAPHICALLY PATTERNED FUNCTIONAL POLYMER–GRAPHENE HYBRIDS FOR NANOSCALE ELECTRONICS

Lithographically Patterned Functional Polymer–Graphene Hybrids for Nanoscale Electronics

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Supporting Information

ABSTRACT: Two-dimensional (2D) materials are believed to hold significant promise in nanoscale optoelectronics. While significant progress has been made in this field over the past decade, the ability to control charge carrier density with high spatial precision remains an outstanding challenge in 2D devices. We present an approach that simultaneously addresses the dual issues of charge-carrier doping and spatial precision based on a functional lithographic resist that employs methacrylate polymers containing zwitterionic sulfonate pendant groups for noncovalent surface doping of 2D materials. We demonstrate scalable approaches for patterning these polymer films via electron-beam lithography, achieving precise spatial control over carrier doping for fabrication of high-quality, all-2D, lateral p–n junctions in graphene. Our approach preserves all of the desirable structural and electronic properties of graphene while exclusively modifying its surface potential. The functional polymer resist platform and concept offers a facile route toward lithographic doping of graphene- and other 2D material-based optoelectronic devices.

KEYWORDS: graphene, doping, p–n junction, polystyrene, interface, zwitterion

Two-dimensional (2D) materials exhibit important physical and electronic properties and are poised to benefit optoelectronic technologies and emerging electronic device paradigms. Due to their relatively high carrier mobilities and long-term environmental stability, 2D electronic materials are promising alternatives to organic semiconductors in the fields of printable and flexible electronics.1 While much progress has been made in the fabrication of 2D materials based devices, the ability to exercise precise spatial control over majority carrier type and concentration remains an outstanding challenge that must be overcome for engineering integrated circuits and systems. In this work, we design a hybrid polymer–graphene platform for carrier doping of graphene via noncovalent adsorption of functional polymer thin films. We demonstrate scalable approaches for patterning these polymer films via electron-beam lithography, achieving precise spatial control over carrier doping for fabrication of lateral homojunctions. Our approach preserves all of the desirable structural and electronic properties of graphene, while exclusively modifying its surface potential, and offers a facile route toward lithographic doping of graphene-based devices.

Graphene is a special case of a zero-bandgap 2D semiconductor that poses challenges for nanoscale electronics while simultaneously affording scientific and technological opportunities. Numerous modern electronic devices utilize semiconductors as their basic building blocks and cannot be fabricated with gapless graphene. Nonetheless, the unique electronic properties of graphene allow for emerging device architectures beyond traditional semiconductor electronics.7 For example, analogous to wave-guiding in ray optics, p–n junctions in graphene can guide ballistic carrier currents8; this functionality exploits the unusual angle-dependent conductance of graphene junctions to achieve phenomena such as electron focusing and collimation.9 In some cases, ballistic graphene devices operate in a manner similar to analog electronic multipliers.8,9 Graphene p–n junctions also display unusual light-matter interactions including the photo-thermoelectric...
Figure 1. Chemical structure of poly(sulfobetaine-co-methyl)methacrylate used in this work (a), and its patterning process with electron beam and the resulting shift in chemical potential (b). Dose and resolution calibration charts optimized to 100 nm features (c) and atomic force micrograph of lines defined on PSBMA-co-PMMa resist with 30 keV electron beam (d) with its cross-section along the white line shown in topographic map (e).

effect\(^6\) and self-driven, bias-free photocurrents.\(^7\) Thus, there is significant interest in developing precise and scalable methods for area-selective carrier doping of graphene for realizing novel 2D optoelectronic devices.

In this work, we present a hybrid graphene–functional polymer (hard–soft materials) platform that simultaneously addresses the dual issues of carrier doping and scalable device processing. Specifically, we exploit the extreme sensitivity of graphene to its immediate environment and engineer suitable zwitterionic polymers that induce appreciable surface potential shifts in graphene via adsorbed interfacial dipoles. A key feature of these polymers is that the zwitterionic moieties are incorporated as pendant groups attached to poly(methyl methacrylate) (PMMA) backbones, rendering them amenable to patterning via electron-beam lithography. We note that other molecules\(^8\) and polymers (e.g., poly(4-vinylpyridine) and poly(vinyl chloride))\(^9\) have been utilized in the past for doping graphene, with complementary doping achieved via rubber-stamping of bis(2fluoromethanesulfonyl) and poly(ethylene imine).\(^10\) The key innovation in our work is the development of lithographically processed polymer dopant that can be directly patterned on the target undoped material for achieving carrier density control at high spatial resolution.

RESULTS AND DISCUSSION

Noncovalent adsorption of dopant moieties is an attractive approach for modulating the electronic properties of 2D materials while preserving their overall structural integrity and purity and therefore provide significant advantages over ion implantation methods.\(^11\) Here, we employ methacrylate polymers containing zwitterionic sulfobetaine (SB) pendant groups for contact with graphene. The SB moiety incorporates a sulfonate anion and ammonium cation with a net dipole moment of 15.2 D, as estimated from density functional theory (DFT) calculations. Prior studies by Emrick and co-workers showed that PSBMA thin films significantly reduced the work function of ITO, Au, Al and graphene (by 1.09, 1.52, 0.36, and 1.64 eV, respectively),\(^12\) which motivates the use of these polymers to design functional lithographic resists. Moreover, the zwitterionic concentration is an important knob for adjusting the PSBMA-induced work-function shift and therefore is a strong motivator for applying our copolymer method of doping.\(^13\) Briefly, the zwitterionic PSBMA-co-MMA was synthesized by conventional (zero-alkane initiated) free radical polymerization in trifluoroethane (TFE), as shown in Figure 1. Monomer conversion, monitored by $^1$H NMR spectroscopy, after 6 h at 70 °C approached 60–70% matched the targeted feed ratio. The molecular weight of the polymer was 54 kDa, as estimated by gel permeation chromatography (GPC) in TFE, and the polydispersity value was ~1.4. The solution processibility of the polymer is pertinent to the design and implementation of resists for lithographic patterning. Sulfobetaine imparts solubility to the PMMA copolymer in salt water, TFE, and polar aprotic solvents such as N-methyl pyrrolidone (NMP). This advantageous solubility, coupled with high molecular weight, makes this polymer an excellent candidate for lithographic processing on substrates.

The synthesized copolymer with a 1:1 ratio of SMMA/MMA ratio was optimized as a solution-processable positive tone resist with respect to exposure dosage (30 keV e-beam) and development conditions to achieve patterned functional films of 80 nm thickness and 200 nm line width and pitch (Figure 1b). Figure 1c displays an atomic force micrograph of a patterned resist showing sharp topography maps of 10 nm long lines of 200–300 nm width and pitch. The level of spatial resolution achieved with our resist is comparable to that of commercial PMMA resists when processed with the same beam energy and resist thickness; the key difference is that our PSBMA-co-MMA) photoreist is a functional resist that can n-dope graphene.

The doping effect of the PSBMA-co-PMMa photoreist on graphene was studied by Raman spectroscopy. Figure 2a
Figure 2. Optical micrograph of a graphene–PSBMA hybrid (a); Raman mapping of the G peak (b) scanned over marked area in (a) and representative spectra from the bare (blue) and PSBMA-covered areas (red).

 displays an example of the polymer photosresist applied by spin coating to a 40 μm × 10 μm monolayer of CVD-grown graphene (on Si/SiO₂), patterned by e-beam writing, then developed with solvent only the right half of the flake. Thereafter, local chemical potential shifts of graphene in the polymer-coated and bare regions were inferred by mapping the optical phonon (G-mode) energy via Raman spectroscopy. The Raman G peak of graphene arises from bond stretching of all pairs of sp² atoms and is a signature of the number and quality of layers, doping level, and confinement.¹⁵-¹⁶ Parts b and c of Figure 2 display a Raman map of the entire graphene monolayer as well as individual line scans taken along the length of the monolayer from which we observe a clear shift in the G-peak frequency from 1589 cm⁻¹ in the uncoated region to 1593 cm⁻¹ in the polymer-coated part; the frequency shift clearly results from the resist pattern. This shift in the optical phonon energy indicates a change in carrier concentration with respect to the neutrality point. However, these doping-induced shifts do not shed light on the carrier type; to glean this information, we turn to transport measurements.

Measurements of gate-resolved conductivity of graphene field-effect transistors (FETs) provide precise values of the average carrier density induced by the functional polymer in the graphene monolayer. Specifically, the average carrier density, n, is given by $n = \frac{C_g \times (V_g - V_{th})}{e}$, where $C_g$ is the gate capacitance and $V_g$ and $V_{th}$ are the gate and neutrality point voltages, respectively. We prepared a series of five FETs on a single-monolayer of CVD graphene (Figure 3a), two devices were unexposed by lithography and therefore remained coated with the functional polymer dopant, two devices were exposed and developed to measure transport in the bare graphene region, and one device spanned the functionalized and bare graphene regions effectively measuring transport across a homojunction. Control experiments were also performed on bare- and PMMA-coated graphene devices to confirm the absence of unintentional, process-related doping effects from PMMA (see the SI for details). In comparing the charge-neutrality voltage (Figure 3), we observe a shift of ~20 V (over 285 nm of Si/SiO₂) between the coated and uncoated devices. This shift in the charge neutrality point of graphene induced by the P(SBMA-co-MMA) resist corresponds to a doping level of $1.35 \times 10^{11}$ cm⁻² and a Fermi-level shift determined by $\phi = \frac{\Delta V}{\Delta n} = \frac{V_{th}}{n_{th}}$ where $\phi = 10^3$ m/s is the Fermi velocity of carriers in graphene and $n_{th}$ is the effective doping level.¹⁷ Furthermore, comparing the device characteristics of the bare FETs versus the polymer-coated ones (see Figures S2 and S3) reveals two important conclusions: (i) our surface functionalization method produces uniform carrier doping over the polymer-coated regions and (ii) the field-effect mobility of charge carriers is barely affected upon surface functionalization, which indicates negligible introduction of charged impurities from the polymer film.

The ability of P(SBMA-co-MMA) to produce lateral graphene heterojunctions is seen in the device characteristics in Figure 3d that show the distinct I–V signature of a p–n junction. We attribute the formation of this p–n homojunction to the potential shift induced within the polymer-coated graphene region by the SI molecular dipole moment. From

Figure 3. (a) Optical micrograph of hybrid graphene–PSBMA device consisting of monolayer graphene partially covered with PSBMA (green region). (b) Gate-resolved I–V curves taken from the PSBMA-covered and bare regions of the device (yellow and blue lines, respectively). (c–d) I–V curves of the three control devices shown in the optical micrograph namely, the PSBMA-covered device (C1), the p–n junction (C2), and the bare device (C3).
basic electrostatics, the shift in surface potential of polymer-coated graphene is \( \Delta \Phi = - \frac{D}{\varepsilon_{si}} \), where \( D = \rho \mu \) is the dipole moment per unit area of polymer–graphene interface, \( \rho \) is the area density of dipoles at the polymer–graphene interface, \( \mu \) is the component of the zwitterionic molecular dipole moment normal to the graphene sheet, and \( \varepsilon_{si} \) is the effective dielectric constant of the embedding medium (SiO\(_2\) and polymer) defined by \( \varepsilon_{si} = (\varepsilon_{SiO2} + \varepsilon_{polymer})/2 \). Specific to our case, the functional resist contains 0.16 M units of zwitterions corresponding to an area density of \( \rho \approx 2.1 \times 10^{13} \text{cm}^{-2} \) at the polymer–graphene interface. With the measured Fermi level shift of \( \Delta \Phi \approx 0.2 \text{eV} \) and an effective dielectric constant of \( \varepsilon_{si} \approx 4 \), we arrive at an estimate of \( \mu \approx 103 \) D for the molecular dipole moment of adsorbed SB moieties.

To further understand the physical and electronic interactions between the polymer thin film and graphene, we performed first-principles density functional theory (DFT) calculations using the Vienna Ab Initio Simulation Package (VASP). While it is impractical to model the adsorbed polymer chains in their entirety, important insights can be gained by considering the key components of the system, namely, the SB pendant group and the graphene sheet. Our computational model thus consists of a 6 × 6 graphene supercell on which we adsorb the SB pendant groups. As seen from Figure 4a, the SB moiety adsorbs in a flat configuration—interacting with the graphene sheet via the terminal sulfate and methyl groups—with a calculated binding energy of 0.92 eV, indicative of a stable polymer–graphene interface. Figure 4a displays the transfer of charge from the SB pendant group and the graphene sheet; as expected, the oppositely charged ends of the zwitterionic moiety induce corresponding regions of electron accumulation and depletion within the graphene monolayer. The charge redistribution within the graphene monolayer is fairly localized, extending but a few unit cells beyond the adsorbed SB group, and is clearly not long-ranged. On average though, the induced positive and negative charges within the graphene sheet cancel each other, and unlike our previous work on TTF pendant groups adsorbed on MoS\(_2\), there is no net charge transfer between graphene and SB. The bonding mechanism between the SB pendant group and the graphene sheet is thus primarily via nonsolvated and localized charge-transfer interactions.

We further observe from Figure 4b that the S and N atoms are at slightly different heights from the graphene sheet in the adsorbed configuration. This surface dipole may be further decomposed into components transverse and normal to the graphene sheet. The transverse components of the dipoles of randomly adsorbed SB pendant groups will, on average, cancel out and contribute only to short-range scattering mechanisms; the normal components are, however, additive leading to a net dipole moment normal to the graphene sheet (\( \mu = 4.7 \text{D} \)). This surface dipole induces a shift in the charge-neutrality point of the graphene sheet toward the vacuum level as seen from the density of states plot in Figure 4c. Correspondingly, the planar-averaged DFT local potential in Figure 4d shows a reduced work function of the graphene sheet on the side with the adsorbed SB moiety (\( \phi = 3.32 \text{ eV} \)) relative to the side without the surface dipole (equivalently, the bare graphene sheet; \( \phi = 4.24 \text{ eV} \)). While the DFT calculation does not take into account dielectric screening from the substrate and polymer film, as a first approximation the work function shift, \( \Delta \phi_{\text{predicted}} \approx 0.92 \text{ eV} \), may be renormalized simply by the effective dielectric constant of the embedding medium, \( \varepsilon_{si} \approx 4 \), which leads to a predicted work function shift of \( \Delta \phi_{\text{predicted}} \approx 0.23 \text{ eV} \). This excellent...
quantitative agreement between theory and experiment bolsters the view of purely noncovalent electrostatic interactions between the functional polymer and graphene. An immediate consequence of this electrostatic picture of polymer–graphene interactions is that the zwitterion concentration can be tuned a priori to induce desired Fermi level shifts in graphene, which will be studied elsewhere.

CONCLUSIONS

In conclusion, we have demonstrated a scalable and precise approach for fabricating hybrid polymer–graphene nanoscale devices. Beyond graphene, the ability to dope other 2D materials—including semiconductors such as transition-metal dichalcogenides and phosphorene, among others—in a controlled manner can be pivotal for the development of nanoscale optoelectronic devices. The patterning and synthetic methods developed in this work can be extended more generally to other 2D materials and, in conjunction with polymer dielectric substrates, could offer a path towards low-power, flexible 2D-materials-based electronics.

METHODS

Graphene Synthesis and Device Fabrication. Graphene was transferred to CVD synthesized by others with some adaptations (ref 23). For graphene transfer, the copper was etched by ammonium persulfate (Merck, >99%). The graphene layer was formed into the desired shapes using AZ nLOP 2020 negative tone resist followed by oxygen plasma etch. On the top of the graphene bar, six electrodes (Ti/Pt 5/55 nm) were patterned by electron-beam lithography using PMMA and metallized by electron-beam evaporation followed by lift off.

PSBMA–PMMA Copolymer Synthesis and Characterization. Sulfobetaine methacrylate, methyl methacrylate, 2,2-azobisobutyrylactylite, and methanol were purchased from Aldrich. Trithlo trimethanol was purchased from TCI chemicals. ABIIBN was recrystallized from toluene and MMA was run through a plug of basic alumina to remove the inhibitor before use. All other reagents were used as received.

Polymer Synthesis. Into a 25 mL round-bottom flask were added SBMA 1.0 g, 3.6 mmol), MMA (0.36 g, 3.6 mmol), and ABIIBN (7.0 mg, 0.045 mmol) and toluene (30 mL) in TFE (34 mL). The solution was degassed under nitrogen atmosphere for 30 min and then heated to 70 °C in an oil bath. The mixture stirred at 70 °C for 6 h and then quenched by exposure to ambient atmosphere. The resulting solution was precipitated into methanol, and the solid was collected by centrifugation and then washed several times with methanol. The solid was then dried under vacuum and lyophilized to remove excess water. Yield 0.75 g 55%. The molecular weight of the polymer was 54 kDa, measured by gel permeation chromatography (GPC) in TFE, with polymer dispersity of 1.4. Spectroscopic data are given in the SI.

Patterning of PSBMA–PMMA copolymer. A solution of 10 mg PSBMA–PMMA copolymer was dissolved in 1 mL of TFE. The solution was stirred for 72 h at room temperature. The sample was spin-coated with the solution (500 rpm/s, 3000 rpm/45 s) and baked for 2 min at 120 °C on a hot plate. The polymer was exposed to a 30 kV e-beam (VEGA3, Tescan) with a dosage of 1200 μC/cm2 and developed in preheated NMP (100 °C) for 3 min (for a silicon substrate) or 1 min (for a silicon/graphene substrate) followed by 50 s in air (allowing the sample to cool down gradually). The sample was then washed with isopropanol for 30 s, followed by light nitrogen flow.

AFM Measurement. Data were collected using a Bio FastScan AFM (Bruker, AXS, Santa Barbara, CA).

Raman Characterization. Silicon wafers containing graphene or patterned graphene (10 μm window of the PSBMA–PMMA copolymer) were placed in a vacuum chamber (HFS600E/PB4, Linkam Scientific Instruments). Raman spectra were measured using a Raman microscope (LabRAM HR Evolution, HORIBA Scientific) with a 532 nm laser. Mapping data were fit to Lorentzian functions using a custom Matlab script.

Electrical Measurement. Samples were wire bonded to a ceramic leadless chip carrier and then placed and measured in a vacuum chamber (Montana Instruments) for measurements using a Keithley 2540 or Keysight B1500A. All presented data were collected at room temperature.

Computational Data. Non-spin-polarized, planewave DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP). The core and valence electrons were treated using the projector-augmented wave method. The Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation was used to describe exchange and correlation. van der Waals interactions were approximated via the zero-damping DFT D3 method of Grimme et al. From convergence studies, a kinetic energy cutoff of 400 eV was chosen. Electronic convergence was accelerated with a Gaussian smearing of 0.01 eV for relaxation calculations; the Blöchl tetrahedron method was used thereafter for calculating density of states and the local potential. All systems had between 12 and 15 Å of vacuum normal to the graphene layer to prevent spurious interactions between images. Dipole connections were applied normal to the graphene monolayer along the vacuum direction. Atomic positions and in-plane cell dimensions were relaxed with a force tolerance of 0.02 eV/Å. For relaxation calculations, the Brillouin zone was sampled with a 3 × 3 × 1 Γ-centered k-point mesh, determined to be sufficient from convergence studies. For single-point electronic structure calculations, after relaxation, the Brillouin zone was sampled with a 13 × 13 × 1 Γ-centered k-point mesh.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.7b08844.

Synthetic methods and characterization of the polymer; electrical measurements and control experiments of devices covered with pure PMMA; electrical resistance and conductivity of p−n junction (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. H.A., O.S., and M.W. developed the protocol for the resist processing with electron-beam lithography. H.A. fabricated and characterized devices, M.K. and O.S. assisted in electrical measurements and Raman data processing. C.S. synthesized graphene and prepared samples. R.S. and T.E. synthesized and characterized PSBMA copolymer. R.G. and A.R. conducted the computational analysis. D.N. conceived and supervised the study.

Notes

The authors declare no competing financial interest.

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APPENDIX E

MATLAB MICROKINETIC MODEL CODE FOR PREDICTION OF MDR KINETICS

%%% Batch reactor
% Model of the methanol decomposition reaction over a platinum catalyst
% surface. Run this file to run the model and plot the results. Uses
% chemical thermodynamics and kinetics to calculate realistic reaction
% constants, then integrates a unitless set of ODEs.
% Chemical data from:
% My work, to be published
% Equations from:
% My work, to be published
% Statistical Thermodynamics
% Harmonic Transition State Theory
% ODES and reaction network from:
% My work, to be published

% Run this file

% Full Complexity Reaction Network
% (1) H3COH + S* <=> H3COH*
% (2) H3COH* + S* <=> H3CO* + H*
% (3) H3CO* + S* <=> H2CO* + H*
% (4) H2CO* + S* <=> HCO* + H*
% (5) HCO* + S* <=> CO* + H*
% (6) 2H* <=> H2(g) + 2S*
% (7) CO* <=> CO(g) + S*
% (8) H3COH* + S* <=> H2COH* + H*
% (9) H2COH* + S* <=> HCOH* + H*
% (10) HCOH* + S* <=> COH* + H*
% (11) COH* + S* <=> CO* + H*
% (12) HCOH* + 2S* <=> CO* + 2H*
% (13) H2COH* + S* <=> CH2O* + H*
% (14) HCOH* + S* <=> HCO* + H*

% overall H3COH(g) <=> CO(g) + 2H2(g) catalyzed by S

clear all
close all
%Realistic conditions range from ~400-600 K and 1-5 atm

global T P
T = 498; %Temperature in kelvin
P = 1*(101325); %Pressure in Pa a.k.a. J/m3

% alpha = (CtotS) / (Cmax * V), where CtotS (mol) total surface sites,
% Cmax (mol/m3) max fluid conc, V (m3) volume fluid
alpha = 0.1; % dimensionless, surface-to-gas capacity ratio
Cmax = 122/5; % (mol/m3), max fluid-phase conc- 100% MeOH at 498K 5atm

% set params array to send to user-written function in ode45 calls
params = [alpha, Cmax];

%% integrate
% y(1) = psi-H3COH  y(2) = psi-H2   y(3) = psi-CO
% y(4) = theta-H3COH y(5) = theta-H   y(6) = theta-CO
% y(7) = theta-H3CO y(8) = theta-H2CO y(9) = theta-HCO
% y(10) = theta-H2COH y(11) = theta-HCOH y(12) = theta-COH

y0 = [1 0 0 ...
       0 0 0 ...
       0 0 0 ...]; % initial conditions
%appropriate time span is a bit different for each system
% Check in odes.m to see which system is being modeled
% For Slab: 2e8
% For Unsupported: coverage -> 0, results not useful
% For Pristine: 1e9 looks okay
% For Vacancy: coverage -> 0, results not useful
% For Divacancy: 2e8 looks okay
tspan = [0 2e9]; % time span
[t,y] = ode15s('odes',tspan,y0,[],params);

%% Get equilibrium time
%this is used for easier plotting and consistent quantification of results
%define equilibrium as when the surface species stop changing much
%not worrying about the gas equilibrating, as it doesn't affect the
%surface much
% [c_i, epsilon] = find_equilibrium(y(:,4:12), 1e-5);
sz = size(t);
c_i = sz(1);

%% Plot Reactor Progress

t = t(1:c_i);
y = y(1:c_i,:);
\( p_{h3coh} = y(:,1); \)
\( p_{h2} = y(:,2); \)
\( p_{co} = y(:,3); \)
\( t_{h3coh} = y(:,4); \)
\( t_{h} = y(:,5); \)
\( t_{co} = y(:,6); \)
\( t_{h3co} = y(:,7); \)
\( t_{h2co} = y(:,8); \)
\( t_{hco} = y(:,9); \)
\( t_{h2coh} = y(:,10); \)
\( t_{hcoh} = y(:,11); \)
\( t_{coh} = y(:,12); \)

figure(1)
plot(t,p_{h3coh}, t,p_{h2}, t,p_{co})
tt = 'Reactor Detail, Gas Phase';
title(tt)
xlabel('t')
ylabel('Concentrations (Unitless)')
ylim([0 1])
xlim([0 t(end)])
legend('\Psi_{H3COH}', '\Psi_{H_2}', '\Psi_{CO}', 'location', 'northEast')

\[ t_s = 1 - t_{h3coh} - t_{h3co} - t_{h2co} - t_{hco} - t_{h} - t_{co} -... \]
\[ t_{h2coh} - t_{hcoh} - t_{coh}; \]

\[ \text{total moles} = p_{h3coh} + p_{co} + p_{h2} +... \]
\[ \alpha*(t_{h3coh} + t_{co} + t_{h} +... \]
\[ t_{h3co} + t_{h2co} + t_{hco} +... \]
\[ t_{h2coh} + t_{hcoh} + t_{coh}; \]

figure(2)
plot(t,t_{h3coh}*100, t,t_{h}*100, t,t_{co}*100, t,t_s*100,'k--',... \[ t_{h3co}*100, t_{h2co}*100, t_{hco}*100,... \]
\[ t_{h2coh}*100, t_{hcoh}*100, t_{coh}*100) \]
tt = 'Reactor Detail, Surface Species';
title(tt)
xlabel('t')
ylabel('Surface Coverage (%)')
ylim([0 100])
xlim([0 t(end)])
legend('\Theta_{H_{3}COH}', '\Theta_{H}', '\Theta_{CO}', '\Theta_{s}',... \[ '\Theta_{H_{3}CO}', '\Theta_{H_{2}CO}', '\Theta_{HCO}',... \]
\[ '\Theta_{H_{2}COH}', '\Theta_{HCoh}', '\Theta_{COH}',... \]
'location', 'northEast')
% figure(3)
% plot(t,t_h3co*100, t,t_h2co*100, t,t_hco*100,...
%   t,t_h2coh*100, t,t_hcoh*100, t,t_coh*100)
% tt = 'Reactor Detail, Intermediate Surface Species';
% title(tt)
% xlabel('t')
% ylabel('Surface Coverage (%)')
% ylim([0 1*100])
% xlim([0 t(end)])
% legend('{\Theta_{H_{3}CO}','{\Theta_{H_{2}CO}',...
%        '{\Theta_{HCO}',...
%        'location','northEast')
%
% figure(4)
% plot(t,t_h3coh*alpha+p_h3coh, t,t_h*alpha+p_h2, t,t_co*alpha+p_co, ...
%       t,total_moles)
% tt = 'Reactor Detail, Total Stoich';
% title(tt)
% xlabel('t')
% ylabel('Concentrations (Unitless)')
% ylim([0 2])
% xlim([0 t(end)])
% legend('H_{3}COH','H','CO','Total',...
%     'location','northEast')
%
% Turn over frequency calculations
% Get effective rates at equilibrium
% [dydt, rvec] = odes(t(end),y(end,:),[],params);
% rfs = rvec(:,1); rbs = rvec(:,2);
% for n=1:49
%     [a,b] = odes(t(end-n),y(end-n,:),[],params);
%     dydt = [dydt,a];
%     rfs = [rfs,b(:,1)]; rbs = [rbs,b(:,2)];
% end
% dydt_avg = mean(dydt,2);
% rf_avg = mean(rfs,2); rb_avg = mean(rbs,2);
% dydt = dydt_avg;
% rvec = [rf_avg, rb_avg];

%%%% printing H2 production for my own self
y(end,2)

function ks = calc_ks_slab(t_co)
% calculates the parameters (alpha, ks) for the methanol decomposition
%reaction over a Pt(111) surface. For other surfaces only the adsorption energies and barriers are changed. Has a lot of thermodynamic and kinetic setup information

%only input currently is the binding energy of CO

% Setup
% using my enthalpy information, but all vibration frequencies and ZPE
% are still from G&M 2006

% Full Complexity
% (1) H3COH + S* <=> H3COH*
% (2) H3COH* + S* <=> H3CO* + H*
% (3) H3CO* + S* <=> H2CO* + H*
% (4) H2CO* + S* <=> HCO* + H*
% (5) HCO* + S* <=> CO* + H*
% (6) 2H* <=> H2(g) + 2S*
% (7) CO* <=> CO(g) + S*
% (8) H3COH* + S* <=> H2COH* + H*
% (9) H2COH* + S* <=> HCOH* + H*
% (10) HCOH* + S* <=> COH* + H*
% (11) COH* + S* <=> CO* + H*
% (12) HCOH* + 2S* <=> CO* + 2H*
% (13) H2COH* + S* <=> CH2O* + H*
% (14) HCOH* + S* <=> HCO* + H*

%fundamental constants

global T P
N_A = 6.022E+23; %avogadro's number, #/mol
kB = 1.38064852E-23; %boltzmann constant, in J/Kelvin
h = 6.626070040E-34; %planck constant, in J*second
R = 8.3144698; %universal gas constant, in J/K/mol
Tref = 0; %273.15 is 0 C- can use 0K?
Rmod = R * (6.242e+18) * (N_A)^(-1); %R in eV/K /molecule, same as kB in eV

%c = 2.9979e10; %speed of light in cm/s

%Molecular masses in Kg
masses = [5.3207E-26
5.1533e-26
4.9859e-26
4.8186e-26
4.6512e-26
3.3474e-27
5.1533e-26
4.9859e-26
4.8186e-26];
Desorption reactions defined as "forward" for equilibrium constants calculations

Species identification

1) H₃COH*  2) H₃CO*  3) H₂CO*
4) HCO*  5) CO*  6) H*
7) H₂COH*  8) HCOH*  9) COH*
10) _s
11) H₃COH(g) 12) CO(g) 13) H₂(g)

Stoich = [-1 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0 0 0 1 1 0 0 0 0 0 0 0 0 0]

Zero point corrected barriers, in eV
from Kandoi 2006
% 0.47 for step 2 is a constructed from G&M 2004, with avg. delta-ZPE
% 0.60 for step 14 is made using initial-state approximation
Ebar = [0.00 0.47 0.11 0.05 0.12 0.00 0.00 0.51 0.43 0.59 0.80 0.24 0.29 0.60];

ModesGas = [...
3859 3086 3007 2954 1452 1442 1420 1315 1129 1051 1005 285 2942 2883 2800 1425 1283 1262 1115 869 631 0 0 0 2942 2895 2883 1425 1283 1262 1115 869 631 0 0 0 2640 1926 1031 0 0 0 0 0 0 0 0 0 2640 1926 1031 0 0 0 0 0 0 0 0 0 2210 0 0 0 0 0 0 0 0 0 0 0 554 0 0 0 0 0 0 0 0 0 0 0 3855 3253 3106 1426 1305 1181 1008 478 384 0 0 0 3707 2801 1449 1308 1154 1065 0 0 0 0 0 0 3072 1373 1049 0 0 0 0 0 0 0 0 0]

ModesAds = [...
3674 3110 3045 2970 1438 1427 1416 1294 1130 1043 976 507 2986 2895 2818 1403 1380 1367 1090 1086 1021 431 256 0 3001 2922 1422 1194 1125 944 580 494 325 0 0 0 2692 1785 959 804 491 265 0 0 0 0 0 0 1822 356 324 313 0 0 0 0 0 0 0 0 0 1099 565 543 0 0 0 0 0 0 0 0 0]
% G&M claim they couldn't confirm the existence of a Transition state
% Rxn 13 & 14 are copies of rxns 9 and 12
ModesTrans = [...
0 0 0 0 0 0 0 0 0 0 0
3009 2961 2841 1899 1413 1386 1380 1104 1092 1000 508 404 270 230
2996 2913 1949 1516 1409 1173 989 609 359 251 242 0 0 0
0 0 0 0 0 0 0 0 0 0 0
1792 1688 924 621 261 254 244 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0 0 0 0
3623 3087 3001 1760 1419 1338 1188 1108 1078 757 533 476 218 0
]

ModesRctnts = [...
0 0 0 0 0 0 0 0 0 0 0
3674 3110 3045 2970 1438 1427 1416 1294 1130 1043 976 507
2986 2895 2818 1403 1380 1367 1090 1086 1021 431 256 0
0 0 0 0 0 0 0 0 0 0 0
2692 1785 959 804 491 265 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
0 0 0 0 0 0 0 0 0 0 0
3674 3110 3045 2970 1438 1427 1416 1294 1130 1043 976 507
3688 3117 2988 1415 1327 1171 1081 1014 735 490 418 261
3280 2994 1329 1168 1122 856 472 453 323 307 0 0
3704 1292 1100 523 503 385 0 0 0 0 0 0
3280 2994 1329 1168 1122 856 472 453 323 307 0 0
3688 3117 2988 1415 1327 1171 1081 1014 735 490 418 261
3280 2994 1329 1168 1122 856 472 453 323 307 0 0
]

% Reference state for enthalpies is H2(g)&CO(g) at 0 Kelvin
% H3COH H3CO H2CO HCO CO H(2) H2COH HCOH COH
HGas = [-1.92 0.46 -0.59 1.08 0.00 0.00 0.30 1.71 2.92];
Eads = [-0.28 -1.66 -0.58 -2.48 -1.89 -0.49 -2.32 -3.46 -4.88*1.025];
% COH binding energy adjusted to better match literature results?
% Coverage-dependent CO binding energy
% fitting to match percent drop from Fampiou (2015)
Eads(5) = -1.89 + 0.0065*exp(4.79*t_co); %G&M 2006, slight adjustment

ZPEads = [ 0.00  0.10  0.04  0.09  0.04  0.14  0.11  0.05  0.15];
HGas = HGas.'; Eads = Eads.'; ZPEads = ZPEads.'; % just doing some housecleaning
HSurf = HGas + Eads + ZPEads + cPIG(ModesAds)*(T-Tref);
HGas = HGas + cPIG(ModesGas)*(T-Tref);
SGas = EntropyIG(ModesGas);

% Fudge factor to make entropy closer to experimental values, checked using CH3OH and CH2O and CO
SGas = SGas.*1.1;

% Surface Entropy from Campbell 2013
% more accurate than traditional Stat Mech approach
% some silly business because H* reference is 1/2 H2(g)
SGas_H2 = SGas(6);
SGas(6) = SGas(6)/2;

% Calc SSurf with corrected 1/2H2 gas
SSurf = SGas.*0.70 - 3.3*Rmod;

% Restore H2 gas
SGas(6) = SGas_H2;

%% generate values & Return
kfs = SolveKf();
Keqs = SolveKeq();
kbs = kfs./Keqs;

% Some cleaning up of KF and KB
h3coh_desorb = kfs(1);
Keqs(1) = 1/Keqs(1); % flip the Keq
% K = kf/kr
% K*kr = kf
h3coh_adsorb = Keqs(1)*h3coh_desorb;
kfs(1) = h3coh_adsorb; kbs(1) = h3coh_desorb;

% normalize by kb*T/h, and return
kfs = kfs./(kB*T/h);
kbs = kbs./(kB*T/h);

ks= [kfs(1),kbs(1),...;
kfs(2),kbs(2),...;
kfs(3),kbs(3),...;
kfs(4),kbs(4),...;
kfs(5),kbs(5),...;
kfs(6),kbs(6),...;
kfs(7),kbs(7),...;]
kfs(8),kbs(8),...
kfs(9),kbs(9),...
kfs(10),kbs(10),...
kfs(11),kbs(11),...
kfs(12),kbs(12),...
kfs(13),kbs(13),...
kfs(14),kbs(14)];

%%% Function for Forward Rate Constants
function Kfs = SolveKf()
%Solves for forward rate constants using pure transition state theory for
%surface-surface reactions and a modified TST eqn. from Campbell, 2013
%Species identification
% 1) H3COH*    2) H3CO*    3) H2CO*
% 4) HCO*      5) CO*      6) H*
% 7) H2COH*    8) HCOH*    9) COH*
% 10) *_s
% 11) H3COH(g) 12) CO(g)   13) H2(g)

As=zeros(14,1);
Kfs=zeros(14,1);

%surface reactions 2-5, 8-14
%Get prefactors
%Straight-up TST
for i=2:5
    As(i) = ((kB*T)/h)*exp( ( SVib(ModesTrans(i,:)) - SVib(ModesRctnts(i,:)) )/ Rmod );
end
for i=8:14
    As(i) = ((kB*T)/h)*exp( ( SVib(ModesTrans(i,:)) - SVib(ModesRctnts(i,:)) )/ Rmod );
end

%Adsorption-Desorption Reactions 1,6,7
%From Campbell, 2013- desorption prefactors, modified TST
function s_t = strans1d(m)
%Function for Calculation of 1D translational entropy
%assume is just 1/3rd the 3-D translational entropy
%Sacker-Tetrode Equation
s_t = (1/3)*Rmod*(log( ((2*pi*m*kB*T)^(3/2)) / (h^3) ) + log(kB*T/P) + 5/2);
end

As(1) = (kB*T/h) * exp((SGas(1)-strans1d(masses(1))-SSurf(1))/Rmod);
As(6) = (kB*T/h) * exp((SGas(6)-strans1d(masses(6))-SSurf(6)*2)/Rmod);
As(7) = (kB*T/h) * exp((SGas(5)-strans1d(masses(5))-SSurf(5))/Rmod);

%Get kfs
for i=1:14
    Kfs(i) = As(i)*exp(-Ebar(i)/(Rmod*T));
end
end

%%% Function for Equilibrium Constants
function Keqs = SolveKeq()
%Solves for equilibrium constants based on temperature and pressure
%(implicit in the enthalpy and entropy, which have been calculated at a
%given T and P)
%Species identification
% 1) H3COH*  2) H3CO*  3) H2CO*
% 4) HCO*     5) CO*    6) H*
% 7) H2COH*   8) HCOH*  9) COH*
% 10) *_s
% 11) H3COH(g) 12) CO(g)  13) H2(g)

Hs = [HSurf; 0.0; HGas(1); HGas(5); HGas(6)];
Ss = [SSurf; 0.0; SGas(1); SGas(5); SGas(6)];

%Grab enthalpy and entropy for the reactions
HRxn=zeros(14,1);
SRxn=zeros(14,1);
GRxn=zeros(14,1);
%Surface Reactions 2-5, 8-14
%Adsorption Reactions 1, 6, 7
for i=1:14 %14 reactions
    for j=1:13 %13 possible reactants
        %Sum up the reaction step contributions
        HRxn(i)=Stoich(i,j)*Hs(j) + HRxn(i);  
        SRxn(i)=Stoich(i,j)*Ss(j) + SRxn(i); 
        GRxn(i)=HRxn(i) - T*SRxn(i);  
    end
end

%Calculate the Ks
Keqs=zeros(14,1);
for i=1:14
    Keqs(i)=exp(-GRxn(i)/(Rmod*T));
end
end

%%% Function for Entropy Calculations
function entropy = EntropyIG(Modes)
%Calculates the entropy of a gas molecule assuming Ideal Gas
%Partition Functions:
%Simple Translation (Sacker-Tetrode Equation)
%Rigid Rotor Rotation
%Harmoic Oscillator Vibration

%Moments of Inertia for the gas phase molecules in amu angstrom^2
MomIs = [
    14.7589 2.4821 1.8294
    15.6791 3.2511 3.2511
    13.1462 1 1
    11.1952 0.8319 1
    8.9159 1 1
    0.138 1 1
    19.7630 2.5918 0.3804
    22.6555 1.8421 1
    12.2000 0.7726 1
];
MomIs = MomIs * 1.66054e-27 * (1E-10)^2;  % Moments of Inertia in kg m^2

% Rotational Symmetry Numbers- I'm a bit unsure about these but the contribution
% to total entropy is quite low
% and the entropy values agree quite well with experiment
Sym = [2;4;3;1;1;1;2;2;1];

Modes = Modes * c;  %conversion to s^-1
sz = size(Modes);
entropy = zeros(sz(1),1);

% Function for calculation of Translational Entropy
function strans = STrans(m)
    %Sacker-Tetrode Equation
    strans = Rmod*(log( ((2*pi*m*kB*T)^(3/2)) / (h^3) ) + log(kB*T/P) + 5/2);
end

% Function for calculation of Rotational entropy
function srot = SRot(I1,I2,I3,sigmaRot)
    srot = Rmod*( log( (8*(pi^2)*sqrt(8*(pi^3)*I1*I2*I3)*((kB*T)^(3/2))) / (sigmaRot*(h^3)) ) + 3/2);
    if isinf(srot)
        srot=0;
    end
end

% Vibrational entropy calculation handled externally
for i=1:sz(1)
    % Return Values
    entropy(i) = STrans(masses(i)) + SRot(MomIs(i,1),MomIs(i,2),MomIs(i,3),Sym(i)) + SVib(Modes(i,:));
%% Function for Heat Capacity Calculations
function cP = cPIG(Modes)
sz = size(Modes);
cP = zeros(sz(1),1);
for i= 1:sz(1)
  %Translations
  cP_trans = (3/2)*Rmod;
  %Rotations
  cP_rot = (3/2)*Rmod;
  %Vibrations handled by external cPVib function
  %Return
  cP(i) = cP_trans + cP_rot + cPVib(Modes(i,:));
end
end

%% Function for Vibrational entropy partition
function svib = SVib(modes)
%Calculates vibrational entropy for a set of vibrational modes
%Using Harmonic Oscillator approximation
svib = 0;
modes = modes.*c; %conversion to 1/s
for freq = modes
  x = h*freq/(kB*T);
  vib = Rmod * ( x/(exp(x)-1) - log(1-exp(-1*x)) );
  if isnan(vib)
    vib = 0;
  end
  svib = svib + vib;
end
end

%% Function for Vibrational Heat Capacity partition
function cP = cPVib(modes)
%Calculates vibrational c_P for a set of vibrational modes
%Using Harmonic Oscillator approximation
C_P = 0;
modes = modes.*c; %conversion to 1/s
for freq = modes
  x = h*freq/(kB*T);
  vib = Rmod * ( exp(x)*((x/(exp(x)-1))^2) );
  if isnan(vib)
    vib = 0;
  end
  cP = cP + vib;
end
function [dydt, rvec] = odes(t,y,flags,params)

alpha = params(1); Cmax = params(2);
% y(1) = psi-H3COH  y(2) = psi-H2  y(3) = psi-CO
% y(4) = theta-H3COH  y(5) = theta-H  y(6) = theta-CO
% y(7) = theta-H3CO  y(8) = theta-H2CO  y(9) = theta-HCO
% y(10) = theta-H2COH  y(11) = theta-HCOH  y(12) = theta-COH
% reassign 'y's to new names I can check more easily
p_h3coh = y(1);  p_h2 = y(2);    p_co = y(3);
t_h3coh = y(4);  t_h = y(5) ;    t_co = y(6);
t_h3co  = y(7);  t_h2co = y(8);  t_hco = y(9);
t_h2coh = y(10); t_hcoh = y(11); t_coh = y(12);

%% Grab Ks
% Note: all the thermodynamics and kinetics parameters are
% stored inside the calc_ks function
% get unit-inconsistent k values
ks = calc_ks_vcy(t_co);

k1=ks(1); km1=ks(2);
k2=ks(3); km2=ks(4);
k3=ks(5); km3=ks(6);
k4=ks(7); km4=ks(8);
k5=ks(9); km5=ks(10);
k6=ks(11); km6=ks(12);
k7=ks(13); km7=ks(14);
k8=ks(15); km8=ks(16);
k9=ks(17); km9=ks(18);
k10=ks(19); km10=ks(20);
k11=ks(21); km11=ks(22);
k12=ks(23); km12=ks(24);
k13=ks(25); km13=ks(26);
k14=ks(27); km14=ks(28);

%% Convert 'ks' into unitless/s ready for odes
% Adsorption/Desorption Reactions
k1p = k1*Cmax; %H3COH
\[ \text{km7p} = \text{km7}\ast\text{Cmax}; \%\text{CO} \]
\[ \text{k6p} = \text{k6}\ast\text{alpha}\ast\text{Cmax}; \%\text{H2} \]
\[ \text{km6p} = \text{km6}\ast\text{Cmax}\ast\text{alpha}\ast\text{Cmax}; \]

**%Surface Reactions**
\[ \text{k2p} = \text{k2}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km2p} = \text{km2}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k3p} = \text{k3}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km3p} = \text{km3}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k4p} = \text{k4}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km4p} = \text{km4}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k5p} = \text{k5}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km5p} = \text{km5}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k8p} = \text{k8}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km8p} = \text{km8}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k9p} = \text{k9}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km9p} = \text{km9}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k10p} = \text{k10}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km10p} = \text{km10}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k11p} = \text{k11}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km11p} = \text{km11}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k12p} = \text{k12}\ast(\text{alpha}\ast\text{Cmax})\wedge2; \]
\[ \text{km12p} = \text{km12}\ast(\text{alpha}\ast\text{Cmax})\wedge2; \]
\[ \text{k13p} = \text{k13}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km13p} = \text{km13}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{k14p} = \text{k14}\ast(\text{alpha}\ast\text{Cmax}); \]
\[ \text{km14p} = \text{km14}\ast(\text{alpha}\ast\text{Cmax}); \]

**%free sites concentration**
\[ \text{t}_s = 1 - \text{t}_\text{h3coh} - \text{t}_\text{h3co} - \text{t}_\text{h2co} ... \]
\[ \quad - \text{t}_\text{hco} - \text{t}_\text{co} - \text{t}_\text{h} ... \]
\[ \quad - \text{t}_\text{h2coh} - \text{t}_\text{hcoh} - \text{t}_\text{coh}; \]

**% Reaction Network**
\% (1) \text{H3COH} + \text{S} \leftrightarrow \text{H3COH}\ast \\
\% (2) \text{H3COH}\ast + \text{S} \leftrightarrow \text{H3CO}\ast + \text{H}\ast \\
\% (3) \text{H3CO}\ast + \text{S} \leftrightarrow \text{H2CO}\ast + \text{H}\ast \\
\% (4) \text{H2CO}\ast + \text{S} \leftrightarrow \text{HCO}\ast + \text{H}\ast \\
\% (5) \text{HCO}\ast + \text{S} \leftrightarrow \text{CO}\ast + \text{H}\ast \\
\% (6) 2\text{H}\ast \leftrightarrow \text{H2(g)} + 2\text{S}\ast \\
\% (7) \text{CO}\ast \leftrightarrow \text{CO(g)} + \text{S}\ast \\
\% (8) \text{H3COH}\ast + \text{S} \leftrightarrow \text{H2COH}\ast + \text{H}\ast \\
\% (9) \text{H2COH}\ast + \text{S} \leftrightarrow \text{HCOH}\ast + \text{H}\ast \\
\% (10) \text{HCOH}\ast + \text{S} \leftrightarrow \text{COH}\ast + \text{H}\ast \\
\% (11) \text{COH}\ast + \text{S} \leftrightarrow \text{CO}\ast + \text{H}\ast
% (12) HCOH* + 2S* <=> CO* + 2H*
% (13) H2COH* + S* <=> CH2O* + H*
% (14) HCOH* + S* <=> HCO* + H*

%% defining reaction rates
r1 = k1p* p_h3coh* t_s;         rm1 = km1* t_h3coh;
r2 = k2p* t_h3coh* t_s;         rm2 = km2p* t_h3co* t_h;
r3 = k3p* t_h3co* t_s;         rm3 = km3p* t_h2co* t_h;
r4 = k4p* t_h2co* t_s;         rm4 = km4p* t_hco* t_h;
r5 = k5p* t_hco* t_s;         rm5 = km5p* t_co* t_h;
r6 = k6p* (t_h^2);              rm6 = km6p* p_h2* (t_s^2);
r7 = k7* t_co;                   rm7 = km7p* p_co* t_s;
r8 = k8p* t_h3coh* t_s;         rm8 = km8p* t_h2coh* t_h;
r9 = k9p* t_h2coh* t_s;         rm9 = km9p* t_hco* t_h;
r10 = k10p* t_hco* t_s;         rm10 = km10p* t_co* t_h;
r11 = k11p* t_co* t_s;          rm11 = km11p* t_co* t_h;
r12 = k12p* t_hco* (t_s^2);    rm12 = km12p* t_co* (t_h^2);
r13 = k13p* t_h2co* t_s;         rm13 = km13p* t_h2co* t_h;
r14 = k14p* t_hco* t_s;          rm14 = km14p* t_hco* t_h;

%% odes
dy1dt =  alpha*( -r1 + rm1 );   %balance for p_h3coh
dy2dt =  alpha*( r6 - rm6 );    %balance for p_h2
dy3dt =  alpha*( r7 - rm7 );    %balance for p_co
dy4dt =  r1 - rm1 - r2 + rm2 - r8 + rm8;  %balance for t_h3coh
dy5dt =  2*(-r6 + rm6) +...
   r2 + r3 + r4 + r5 + r8 + r9 + r10 + r11 ...
   + 2*r12 + r13 + r14 ...
   - rm2 - rm3 - rm4 - rm5 - rm8 - rm9 - rm10 - rm11 ...
   - 2*rm12 - rm13 - rm14;       %balance for t_h
dy6dt =  r5 - rm5 + r12 - rm12 ...
   - r7 + rm7;                   %balance for t_co
dy7dt =  r2 - rm2 - r3 + rm3;    %balance for t_h3co
dy8dt =  r3 - rm3 - r4 + rm4 + r13 - rm13;  %balance for t_h2co
dy9dt =  r4 - rm3 - r5 + rm5 + r14 - rm14;  %balance for t_hco
dy10dt =  r8 - rm8 - r9 + rm9 - r13 + rm13;  %balance for t_h2coh
dy11dt =  r9 - rm9 ...
   - r10 + rm10 - r12 + rm12 ...
   - r14 + rm14;                 %balance for t_hco
dy12dt =  r10 - rm10 - r11 + rm11;  %balance for t_coh

%% return
dydt = [dy1dt ; dy2dt ; dy3dt ; dy4dt ; dy5dt ; dy6dt;...
dy7dt ; dy8dt ; dy9dt ; dy10dt; dy11dt; dy12dt];
rvec = [r1  rm1]
r2  rm2
r3  rm3
r4  rm4
r5  rm5
r6  rm6
r7  rm7
r8  rm8
r9  rm9
r10 rm10
r11 rm11
r12 rm12
r13 rm13
r14 rm14};
APPENDIX F

SUPPORTING INFORMATION FOR CHAPTER 3: KINETICS OF THE METHANOL DECOMPOSITION REACTION OVER DEFECTIVE-GRAPHENE SUPPORTED Pt NANOPARTICLES: A MULTI-SCALE COMPUTATIONAL STUDY

Table F.1: DFT-sampled barriers for the MDR over the unsupported 13-atom Pt nanoparticles. Values in eV. No barriers reported for steps one, six, and seven as these are adsorption/desorption reactions and assumed to have zero-barrier, as is consistent with the MDR literature.4,17

<table>
<thead>
<tr>
<th>Barriers</th>
<th>Unsupported Pt\textsubscript{13}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step/Site</td>
<td>A</td>
</tr>
<tr>
<td>s1</td>
<td></td>
</tr>
<tr>
<td>s2</td>
<td></td>
</tr>
<tr>
<td>s3</td>
<td></td>
</tr>
<tr>
<td>s4</td>
<td></td>
</tr>
<tr>
<td>s5</td>
<td></td>
</tr>
<tr>
<td>s6</td>
<td></td>
</tr>
<tr>
<td>s7</td>
<td></td>
</tr>
<tr>
<td>s8</td>
<td>1.08</td>
</tr>
<tr>
<td>s9</td>
<td>1.14</td>
</tr>
<tr>
<td>s10</td>
<td>0.64</td>
</tr>
<tr>
<td>s11</td>
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</tr>
<tr>
<td>s12</td>
<td>0.96</td>
</tr>
<tr>
<td>s13</td>
<td></td>
</tr>
<tr>
<td>s14</td>
<td></td>
</tr>
</tbody>
</table>

Table F.2: DFT-sampled adsorption energies averaged over all sites sampled on each system, values used in the microkinetic model.

<table>
<thead>
<tr>
<th>Pt(111)</th>
<th>Divacancy-Graphene Pt\textsubscript{13}</th>
<th>Vacancy-Graphene Pt\textsubscript{13}</th>
<th>Pristine-Graphene Pt\textsubscript{13}</th>
<th>Unsupported Pt\textsubscript{13}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{3}COH</td>
<td>-0.28</td>
<td>-0.3</td>
<td>-0.54</td>
<td>-0.46</td>
</tr>
<tr>
<td>H\textsubscript{3}CO</td>
<td>-1.66</td>
<td>-1.9</td>
<td>-2.31</td>
<td>-2.17</td>
</tr>
<tr>
<td>H\textsubscript{2}CO</td>
<td>-0.58</td>
<td>-0.85</td>
<td>-0.69</td>
<td>-0.91</td>
</tr>
<tr>
<td>HCO</td>
<td>-2.48</td>
<td>-2.52</td>
<td>-2.81</td>
<td>-2.89</td>
</tr>
<tr>
<td>H\textsubscript{2}COH</td>
<td>-2.32</td>
<td>-2.23</td>
<td>-2.45</td>
<td>-2.55</td>
</tr>
<tr>
<td>HCOH</td>
<td>-3.46</td>
<td>-3.38</td>
<td>-3.44</td>
<td>-3.66</td>
</tr>
<tr>
<td>COH</td>
<td>-4.88</td>
<td>-3.77</td>
<td>-3.74</td>
<td>-3.91</td>
</tr>
<tr>
<td>CO</td>
<td>-1.89</td>
<td>-1.74</td>
<td>-2.45</td>
<td>-2.6</td>
</tr>
</tbody>
</table>
Table F.3: Gas and Surface formation energies for all MDR molecules, Carbon, and Oxygen. All energies in eV.

<table>
<thead>
<tr>
<th></th>
<th>DFT Energy</th>
<th>Gas Formation Energy</th>
<th>Pt(111)</th>
<th>Divacancy-Graphene Pt13</th>
</tr>
</thead>
<tbody>
<tr>
<td>H3COH</td>
<td>-30.22</td>
<td>-1.90</td>
<td>-2.18</td>
<td>-2.20</td>
</tr>
<tr>
<td>H3CO</td>
<td>-24.48</td>
<td>0.46</td>
<td>-1.10</td>
<td>-1.44</td>
</tr>
<tr>
<td>H2CO</td>
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<tr>
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<td>-1.67</td>
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<tr>
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<tr>
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<tr>
<td>O</td>
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<td>5.84</td>
<td>1.75</td>
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<th>Unsupported Pt13</th>
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<td>-1.81</td>
<td>-1.85</td>
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<td>-0.99</td>
<td>-1.52</td>
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<td>CO</td>
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<td>C</td>
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<td>-1.26</td>
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<td>-0.99</td>
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<tr>
<td>O</td>
<td>-1.56</td>
<td>1.03</td>
<td>0.86</td>
<td>0.55</td>
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Figure G.1 displays the adsorption energies of MDR intermediates sampled at random adsorption site on all the systems considered in this study. Presented in this manner, one can clearly see that there is a general trend of all molecules adsorbing more weakly on Pt$_{13}$ clusters that interact more strongly with the support, although individual results can deviate from the general trend.

Figure G.1: Adsorption energies of all MDR intermediates as well as atomic C, O, H on all systems. Error bars are student-T 95% confidence intervals.

Unlike all other MDR intermediates, COH has a higher adsorption energy on Pt(111) than on any of the supported Pt$_{13}$ nanoclusters, causing the slope of linear fits in Fig. 2.4 of the paper to deviate from the Pt(111) case leading to the result in Fig. G.2.
Nevertheless, COH adsorption energies fit with the trend that the increased support effect reduces adsorption energy, so the best-fit lines are still more or less rigidly shifted between the Pt$_{13}$ cluster cases. The intercepts are also correlated well with the $d$-band centers of the Pt$_{13}$ clusters, which can be seen in the inset of Fig. G.2. The slope and intercept of the adsorption energy linear fits vs. their Pt(111) values are shown in Table G.1 and the raw data for Fig. G.1 are displayed in Table G.2.

Figure G.2: Adsorption energy of all MDR intermediate molecules on the four Pt$_{13}$ clusters displayed versus their Pt(111) adsorption energy. Points are averages, linear fits are against all data (not only averages). Error bars are student-T 95% confidence intervals. Pt(111) adsorption values (1:1) are plotted as the gray dashed line. Inset: $y$-axis offset of linear fits versus $d$-band center. Gray dashed line is a linear fit that serves as a guide to the eye.
Table G.1: Adsorption energies of MDR intermediates and probe molecules on Pt(111) as well as supported and unsupported Pt$_{13}$ clusters. Errors are obtained from Student-T 95% confidence intervals.

<table>
<thead>
<tr>
<th>Pt(111)</th>
<th>Isolated</th>
<th>Pristine</th>
<th>Vacancy</th>
<th>Divacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_3COH$</td>
<td>-0.28</td>
<td>-0.69±0.26</td>
<td>-0.46±0.20</td>
<td>-0.54±0.14</td>
</tr>
<tr>
<td>$H_3CO$</td>
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<td>-2.93±0.38</td>
<td>-2.54±0.40</td>
<td>-2.68±0.35</td>
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<tr>
<td>$H_2CO$</td>
<td>-0.59</td>
<td>-1.17±0.44</td>
<td>-0.92±0.36</td>
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<tr>
<td>$HCO$</td>
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<td>$H_2COH$</td>
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<tr>
<td>$HCOH$</td>
<td>-3.47</td>
<td>-3.79±0.30</td>
<td>-3.67±0.28</td>
<td>-3.45±0.12</td>
</tr>
<tr>
<td>CO</td>
<td>-5.38</td>
<td>-4.94±0.61</td>
<td>-4.41±0.41</td>
<td>-4.25±0.25</td>
</tr>
<tr>
<td>COH</td>
<td>-1.91</td>
<td>-2.46±0.18</td>
<td>-2.62±0.32</td>
<td>-2.47±0.25</td>
</tr>
<tr>
<td>C</td>
<td>-6.94</td>
<td>-7.10±0.20</td>
<td>-7.31±0.48</td>
<td>-7.37±0.66</td>
</tr>
<tr>
<td>O</td>
<td>-4.09</td>
<td>-5.29±0.29</td>
<td>-4.98±0.20</td>
<td>-4.81±0.26</td>
</tr>
<tr>
<td>H</td>
<td>-1.61</td>
<td>-1.89±0.16</td>
<td>-1.84±0.20</td>
<td>-1.71±0.14</td>
</tr>
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</table>
The details for the reaction energies on Pt$_{13}$ and all Pt$_{13}$–graphene systems are shown in Fig. G.3 while Table G.3 lists the raw data. Figure S4 displays an example of the relaxed structures of all reaction intermediates on a single site for the divacancy-bound cluster. It is difficult to identify an obvious trend between the overall reaction behavior and the strength of the support effect, although, as noted in Section 2.3.2, Paths 2 and 3 become competitive with Path 1 on Pt$_{13}$ clusters relative to the Pt(111) surface. Future calculations of reaction barriers will allow for clearer correlations between support effects and reaction kinetics.

Figure G.5 presents a comparison of the conventional co-adsorption approach for reaction thermodynamics with the average H-adsorption energy approach adopted in this work (see Eqs. 4-6 in Chapter 2). As seen, both approaches deliver results that are comparable to within statistical error. The average H-adsorption approach thus has the benefit of providing the same quality of information as the co-adsorption approach at approximately half the computational cost.

**Table G.2**: Reaction energies for MDR on Pt(111) as well as supported and unsupported Pt$_{13}$ clusters. Errors are calculated using Student-T 95% confidence intervals.

<table>
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<tr>
<th>Reaction Step</th>
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<th>Pristine</th>
<th>Vacancy</th>
<th>Divacancy</th>
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<td>-0.19±0.28</td>
<td>0.23±0.43</td>
</tr>
<tr>
<td>$H_3COH \rightarrow H_2COH + H$</td>
<td>-0.34</td>
<td>-0.58±0.16</td>
<td>-0.81±0.43</td>
<td>-0.56±0.18</td>
<td>-0.33±0.23</td>
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<tr>
<td>$H_3CO \rightarrow H_2CO + H$</td>
<td>-0.37</td>
<td>-0.38±0.41</td>
<td>-0.52±1.01</td>
<td>0.15±0.37</td>
<td>-0.53±0.58</td>
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<tr>
<td>$H_2COH \rightarrow H_2CO + H$</td>
<td>0.45</td>
<td>-0.03±0.38</td>
<td>0.25±0.72</td>
<td>0.54±0.27</td>
<td>0.04±0.36</td>
</tr>
<tr>
<td>$H_2COH \rightarrow HCOH + H$</td>
<td>-0.20</td>
<td>-0.32±0.22</td>
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<td>-0.04±0.44</td>
<td>-0.22±0.13</td>
</tr>
<tr>
<td>$H_2CO \rightarrow CHO + H$</td>
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<td>-0.96±0.43</td>
<td>-1.15±0.95</td>
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<td>-0.64±0.49</td>
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<tr>
<td>$HCOH \rightarrow CHO + H$</td>
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<td>-0.67±0.22</td>
<td>-0.51±0.48</td>
<td>-0.65±0.30</td>
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<tr>
<td>$HCOH \rightarrow COH + H$</td>
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<td>0.31±0.45</td>
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<td>0.20±0.59</td>
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<tr>
<td>$HCO \rightarrow CO + H$</td>
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<td>-0.85±0.37</td>
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<tr>
<td>$COH \rightarrow CO + H$</td>
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<td>$HCOH \rightarrow CO + 2H$</td>
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<td>-1.50±0.57</td>
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Figure G.3: Thermodynamics of supported and unsupported Pt13 systems. Blue arrows represent downhill reaction steps, red arrows represent uphill reaction steps, and the arrows are in exact proportion with the average reaction energy for that step on that system. Brown circles - C; Red circles - O; Grey circles - H; Grey bar - catalyst surface. Hydrogens are considered adsorbed on the surface for energy calculation and shown stacked to the right for visual clarity.
Figure G.4: All reaction intermediates on a single site on the divacancy graphene supported Pt$_{13}$. 
**Figure G.5:** Benchmarking of reaction energies calculated using true co-adsorption ("Co-Ads") and the average H-adsorption ("Avg H") assumption for two MDR reaction pathways on Pt(111) and an isolated Pt$_{13}$ cluster. Error bars are student-T 95% confidence intervals. The “Co-Ads” and “Avg H” lines have been slightly offset horizontally for clarity.
Figure H.1: Distribution of coordination numbers (blue bars) as well as $d$-band center energies of atoms on the surface (black “+” symbols) and in the bulk (red “+” symbols) for the cuboctahedral Pt$_{309}$ cluster. Surface $d$-band centers of FCC Pt(111) and Pt(100) surfaces are shown for reference.
Figure H.2: Average $d$-band center energy of the surface atoms, $\overline{\epsilon_d^{\text{surf}}}$, as a function of cluster size, $N$. The solid curve passing through data for GA-optimized structures is merely a guide to the eye. Error bars are standard deviations; representative error bars are shown only for certain sizes to maintain legibility. The exact values of $d$-band center energy with confidence intervals for every data point can be found in Table S1. Horizontal dashed lines indicate the reference $d$-band center energies on bulk-terminated, FCC Pt(111) and (100) surfaces.
Table H.1: Average $d$-band center energy of surface atoms, $\bar{\epsilon}_{d}^{\text{sur}}$, and standard deviations, $\sigma$, as a function of cluster size, $N$.

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<td>$\sigma$</td>
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Table H.2: Average all-relaxed ($\overline{E}_{ads}^{AR}$), frozen cluster ($\overline{E}_{ads}^{FC}$), and all-frozen ($\overline{E}_{ads}^{AF}$) CO adsorption energies and Student-T 95% confidence intervals as a function of cluster size on Pt$_N$ clusters; for the 4-atom cluster the reported errors are standard deviations.

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Figure H.3: DFT-calculated CO adsorption energies on the surface sites of Pt clusters versus the prediction from GBR model with all descriptors. Below is a list of the descriptors used for this figure:

q  valence electrons associated with each atom (from Bader analysis)
$\overline{w}_d$ general $d$-band width
$\overline{w}_p$ general $p$-band width
$\overline{w}_s$ general $s$-band width
$w_d$ $d$-band width
$w_p$ $p$-band width
$w_s$ $s$-band width
$\overline{\varepsilon}_d$ general $d$-band center energy with respect to the Fermi level
$\overline{\varepsilon}_p$ general $p$-band center energy with respect to the Fermi level
$\overline{\varepsilon}_s$ general $s$-band center energy with respect to the Fermi level
$\varepsilon_d$ $d$-band center energy with respect to the Fermi level
$\varepsilon_p$ $p$-band center energy with respect to the Fermi level
$\varepsilon_s$ $s$-band center energy with respect to the Fermi level

The remaining descriptors are explained in Section 3.3 of the publication (Appendix B).


