



Indian Institute of
Technology Delhi



THE UNIVERSITY
OF QUEENSLAND
AUSTRALIA

**Fine-tuning the microenvironment of the active site on a
heterogeneous catalyst for selective chemical transformation**

Jayendran Iyer

INDIAN INSTITUTE OF TECHNOLOGY DELHI

&

THE UNIVERSITY OF QUEENSLAND

FEBRUARY 2026

© **Indian Institute of Technology Delhi (IITD), New Delhi, 2026**



Indian Institute of
Technology Delhi



THE UNIVERSITY
OF QUEENSLAND
AUSTRALIA

**Fine-tuning the microenvironment of the active site on a
heterogeneous catalyst for selective chemical transformation**

by

Jayendran Iyer

Submitted

in fulfilment of the requirements for the joint degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

&

THE UNIVERSITY OF QUEENSLAND

FEBRUARY 2026

To Ammaiyar and Pattu

Supervisor Certification

This is to certify that the thesis entitled “**Fine-tuning the microenvironment of the active site on a heterogeneous catalyst for selective chemical transformation**” being submitted by **Mr. Jayendran Iyer** to the Indian Institute of Technology Delhi and The University of Queensland for the award of degree of **Doctor of Philosophy** is a record of *bonafide* research work carried out by him. **Mr. Jayendran Iyer** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.



Prof. M. Ali Haider

Department of Chemical Engineering

Indian Institute of Technology Delhi

Hauz Khas New Delhi - 110016



Prof. Debra Bernhardt

Australian Institute for Bioengineering
and Nanotechnology &

School of Chemistry and Molecular
Biosciences

University of Queensland

St. Lucia, Australia - 4076

Abstract

For billions of years, nature has evolved enzymes that can catalyze reactions efficiently to help all the life on earth survive. Today, to meet the global demand of the human population, we need enzyme-like selectivity and efficiency in highly scalable heterogeneous catalysis. This need is particularly critical for challenging transformations, such as converting biomass-derived sugars into fuels and high-value chemicals, addressing pressing sustainability challenges. This thesis envisions a futuristic biorefinery capable of selectively producing desired high-value chemicals with high yield. While simple kinetic or thermodynamic correlations derived from volcano plots have helped accelerate catalyst selection, they have limited the ability to fine-tune product formation rates and yields. To achieve high efficiency in such operations, catalyst designs have developed beyond one-dimensional descriptor-based protocols toward three-dimensional microenvironment perturbations at the active site.

With the help of molecular simulations, this thesis delves into four strategies to fine-tune the local environment around the active site, which are continuously enhancing the performance of heterogeneous catalysts to address the challenges of a futuristic biorefinery. These strategies are: (a) developing multiple active centers, each with a unique role in selective transformations; (b) stabilizing substrates/reactants via a hydrogen-bond network to facilitate proton transfer; (c) enhancing proton-coupled electron transfer (PCET) mechanisms driven by electric field and pH alterations at the electrode–electrolyte interface; and (d) increasing the stability of the active site through confinement.

Chapter 1 discusses a review of these strategies that help fine-tune the catalytic reactivity, selectivity and stability crucial in the biorefinery viewpoint. **Chapter 2** presents all the computational methods used in this thesis to study the potential energy surface for kinetic and thermodynamic analysis using *ab initio* density functional theory, molecular dynamic simulations and machine learning potentials. **Chapter 3** describes the breaking of descriptor-based linear scaling relations on Cu-based single atom alloys showcasing the advantages of multiple active centers. In **Chapter 4**, the stability analysis of dispersed transition metal nanocluster with confinement effect in zeolite is discussed in detail. The structure sensitivity of CO₂ electrochemical hydrogenation reaction on Cu-based alloys is exhibited in **Chapter 5** with the role of solvents,

ions, and coverage. **Chapter 6** highlights the role of electric potential, pH and solvents on Cu catalysts for benzaldehyde hydrogenation. Finally, in summary and outlook (**Chapter 7**), the thesis describes the efforts to undertake rational catalyst design that can yield precise selectivity with each active site playing a unique role using simulations.

This dissertation highlights the interplay of geometric, electronic and confinement effects at the active site. The complexity of an active site is just not restricted to which surface, facet, or zeolite it is part to—but also involves the effect due to electronic interactions with adsorbate and the reaction conditions involving pH, solvents, ions and electric field. This makes designing new catalysts and identifying mechanistic routes fascinating in heterogeneous catalysis. The underlying theme of this dissertation is understanding these complex effects through mechanistic insights with model reactions for hydrocarbon valorization in a futuristic biorefinery.

Abstract in Hindi

अरबों वर्षों में प्रकृति ने ऐसे एंजाइम विकसित किए हैं जो पृथ्वी पर जीवन के अस्तित्व को बनाए रखने हेतु अभिक्रियाओं को अत्यंत दक्षता से उत्प्रेरित करते हैं। आज, वैश्विक मानव जनसंख्या की बढ़ती मांगों को पूरा करने के लिए अत्यधिक स्केलेबल विषम उत्प्रेरण में एंजाइम-सदृश चयनात्मकता और दक्षता की आवश्यकता है। यह आवश्यकता विशेष रूप से चुनौतीपूर्ण रूपांतरणों के लिए अत्यंत महत्वपूर्ण है, जैसे कि जैव-द्रव्य से प्राप्त शर्कराओं को ईंधन और उच्च-मूल्य रसायनों में परिवर्तित करना, जो सततता से जुड़ी गंभीर चुनौतियों को संबोधित करता है।

यह शोध-प्रबंध एक भविष्यवादी बायोरिफाइनरी की परिकल्पना करता है, जो उच्च उपज के साथ वांछित उच्च-मूल्य रसायनों का चयनात्मक उत्पादन करने में सक्षम हो। यद्यपि वोल्केनो प्लॉट से प्राप्त सरल गतिकीय या ऊष्मागतिक सहसंबंधों ने उत्प्रेरक चयन को तेज करने में सहायता की है, फिर भी वे उत्पाद निर्माण की दरों और उपज को सूक्ष्म रूप से नियंत्रित करने में सीमित रहे हैं। ऐसी प्रणालियों में उच्च दक्षता प्राप्त करने के लिए, उत्प्रेरक डिज़ाइन अब एक-आयामी वर्णनकर्ता-आधारित प्रोटोकॉल से आगे बढ़कर सक्रिय स्थल पर त्रि-आयामी सूक्ष्म-पर्यावरणीय व्यवधानों की ओर विकसित हो चुके हैं।

आणविक सिमुलेशन की सहायता से, यह शोध-प्रबंध सक्रिय स्थल के आसपास के स्थानीय परिवेश को सूक्ष्म रूप से नियंत्रित करने की चार रणनीतियों का अध्ययन करता है, जो भविष्यवादी बायोरिफाइनरी की चुनौतियों का समाधान करने हेतु विषम उत्प्रेरकों के प्रदर्शन को निरंतर बेहतर बना रही हैं। ये रणनीतियाँ हैं: (क) अनेक सक्रिय केंद्रों का विकास, जहाँ प्रत्येक केंद्र चयनात्मक रूपांतरण में एक विशिष्ट भूमिका निभाता है; (ख) हाइड्रोजन बंध नेटवर्क के माध्यम से सबस्ट्रेट और अभिकारकों को स्थिर करना, जिससे प्रोटॉन स्थानांतरण को सुगम बनाया जा सके; (ग) इलेक्ट्रोड और इलेक्ट्रोलाइट अंतरफलक पर विद्युत क्षेत्र तथा पीएच में परिवर्तनों द्वारा संचालित प्रोटॉन-युग्मित इलेक्ट्रॉन स्थानांतरण तंत्र को सुदृढ़ करना; तथा (घ) परिसीमन के माध्यम से सक्रिय स्थल की स्थिरता को बढ़ाना।

अध्याय 1 में इन रणनीतियों की समीक्षा प्रस्तुत की गई है, जो बायोरिफाइनरी के दृष्टिकोण से उत्प्रेरक की अभिक्रियाशीलता, चयनात्मकता और स्थिरता को नियंत्रित करने में सहायक हैं। अध्याय 2 में इस शोध-प्रबंध में प्रयुक्त सभी संगणकीय विधियों का वर्णन है, जिनमें प्रथम सिद्धांत आधारित घनत्व फलन सिद्धांत, आणविक गतिकी सिमुलेशन तथा मशीन लर्निंग पोटेंशियल के माध्यम से गतिकीय और ऊष्मागतिक

विश्लेषण हेतु संभावित ऊर्जा सतहों का अध्ययन शामिल है। अध्याय 3 में तांबा-आधारित एकल परमाणु मिश्रधातुओं पर वर्णनकर्ता-आधारित रैखिक स्केलिंग संबंधों के विघटन को दर्शाया गया है, जो अनेक सक्रिय केंद्रों के लाभों को उजागर करता है।

अध्याय 4 में ज़ियोलाइट में परिसीमन प्रभाव के साथ विसरित संक्रमण धातु नैनोक्लस्टरों की स्थिरता का विस्तृत विश्लेषण प्रस्तुत किया गया है। अध्याय 5 में तांबा-आधारित मिश्रधातुओं पर कार्बन डाइऑक्साइड के विद्युत-रासायनिक हाइड्रोजनीकरण अभिक्रिया की संरचना-संवेदनशीलता को, विलायकों, आयनों और सतह आवरण की भूमिका के साथ प्रदर्शित किया गया है। अध्याय 6 में बेंज़ाल्डिहाइड हाइड्रोजनीकरण के लिए तांबा उत्प्रेरकों पर विद्युत विभव, पीएच और विलायकों की भूमिका को रेखांकित किया गया है। अंततः, सारांश एवं भविष्य-दृष्टि में, यह शोध-प्रबंध तर्कसंगत उत्प्रेरक डिज़ाइन की दिशा में किए गए उन प्रयासों का वर्णन करता है, जिनका उद्देश्य प्रत्येक सक्रिय स्थल की विशिष्ट भूमिका के साथ सटीक चयनात्मकता प्राप्त करना है।

यह शोध-प्रबंध सक्रिय स्थल पर ज्यामितीय, इलेक्ट्रॉनिक और परिसीमन प्रभावों के पारस्परिक संबंध को रेखांकित करता है। किसी सक्रिय स्थल की जटिलता केवल इस बात तक सीमित नहीं है कि वह किस सतह, किस फेसट या किस ज़ियोलाइट का हिस्सा है, बल्कि इसमें अवशोषित प्रजातियों के साथ इलेक्ट्रॉनिक अंतःक्रियाएँ तथा अभिक्रिया परिस्थितियों से संबंधित प्रभाव, जैसे पीएच, विलायक, आयन और विद्युत क्षेत्र, भी सम्मिलित हैं। यही जटिलता विषम उत्प्रेरण में नए उत्प्रेरकों के डिज़ाइन और यांत्रिक मार्गों की पहचान को अत्यंत रोचक बनाती है। इस शोध-प्रबंध का मूल विषय भविष्यवादी बायोरिफ़ाइनरी के लिए हाइड्रोकार्बन वैलोरीकरण से संबंधित मॉडल अभिक्रियाओं के माध्यम से इन जटिल प्रभावों को यांत्रिक अंतर्दृष्टि के साथ समझना है।

Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of the Graduate School.

I acknowledge that copyright of all material contained in my thesis resides with the copyright holder(s) of that material. Where appropriate I have obtained copyright permission from the copyright holder to reproduce material in this thesis and have sought permission from co-authors for any jointly authored works included in the thesis.

Contributions by others to the thesis

Contributor	Statement of contribution
Prof. M. Ali Haider	Conception and design of the project Analysis and interpretation of research data Drafting and revision Supervision
Prof. Debra Bernhardt	Conception and design of the project Analysis and interpretation of research data Drafting and revision Supervision
Dr. Rachit Khare	Conception and design of the project Analysis and interpretation of research data Drafting and revision
Prof. Johannes Hachmann	Analysis and interpretation of research data
Prof. Johannes Lercher	Analysis and interpretation of research data
Dr. Tuhin S. Khan	Analysis and interpretation of research data
Dr. Fatima Jalid	Non-routine technical work
Prof. Peter Sebastian	Conception and design of the project Drafting and revision
Nitin Murthy	Non-routine technical work
Bharat Venkat Nannapuraju	Non-routine technical work
Prithvi Sunder Manek	Non-routine technical work
Artificial Intelligence	Grammar check

Statement of parts of the thesis submitted to qualify for the award of another degree

No works submitted towards another degree have been included in this thesis.

Research involving human or animal subjects

No animal or human subjects were involved in this research.

Acknowledgements

First and foremost, my sincere gratitude goes to my supervisors, Prof. M. Ali Haider and Prof. Debra Bernhardt. They gave me the freedom to explore, steered me back in the right direction whenever I drifted away, and exercised great patience when I made blunders. They have instilled in me research ethics and life lessons that will remain my most valuable takeaways from this journey.

Throughout this journey, I had the great opportunity to learn from my collaborators — Prof. Johannes Lercher, Prof. Peter Sebastian, Prof. Johannes Hachmann, Prof. Andrew Whittaker, Dr. Rachit Khare, Dr. Tuhin S. Khan, Dr. Fatima Jalid, Dr. Debabrata Bagchi, and Dr. Qiaoyun Wang. Each project offered a new perspective and challenged me to think more broadly.

This journey was made lively through moments of laughter, conversations, tears, and occasional disagreements shared with members of the REC Lab and the Bernhardt Group. My heartfelt thanks go to all the present and past group members who made my stay in Delhi and Brisbane truly memorable. I am also indebted to my family for their patience, trust, and unwavering support throughout this journey.

Financial support

This research was supported by research scholarships provided by the Indian Institute of Technology Delhi, The University of Queensland, and the Prime Minister’s Research Fellowship (PMRF). Additional financial support was received through research grants from the UQ–IITD Academy of Research (UQIDAR), the PMRF, Department of Science and Technology (DST) Matrix grant and the Scheme for Promotion of Academic and Research Collaboration (SPARC).

Keywords

density functional theory, molecular dynamics, heterogeneous catalysis, microenvironment, machine learning

Australian and New Zealand standard research classifications (ANZSRC)

ANZSRC code: 030703, Reaction Kinetics and Dynamics, 60%

ANZSRC code: 090402, Catalytic Process Engineering, 20%

ANZSRC code: 090401, Carbon Capture Engineering (excl. Sequestration), 20%

Fields of research classification

FoR code: 0307, Theoretical and Computational Chemistry, 60%

FoR code: 0904, Chemical Engineering, 40%]

Table of Contents

Chapter 1. Fine-tuning the microenvironment of catalytic active site for selective chemical transformation.....	1
1.1 Introduction	1
1.1.1 Challenging transformations for sustainability	3
1.1.2 Principles of computational catalyst design.....	6
1.2 Alloying effects	8
1.2.1 Selective hydrogenation and dehydrogenation reactions.....	9
1.2.2 Coupling reactions	13
1.3 Confinement effect.....	14
1.4 Solvent effects	19
1.4.1 Effect of solvents on the stability of surface species	19
1.4.2 Solvents as proton shuttling agent and/or proton donor	22
1.5 Effects of electrochemical environment.....	23
1.5.1 Potential and pH effect on electrochemical CO ₂ reduction reaction	26
1.5.2 Alkali metal cation effect on electrochemical CO ₂ reduction reaction.....	27
1.6 Thesis objectives	30
Chapter 2. Methodology	32
2.1 Overview	32
2.2 Density functional theory	32
2.3 Molecular dynamics simulations.....	34
2.4 Machine learning potentials	39
2.5 Understanding potential energy surface in catalytic systems.....	42
2.6 Energy corrections due to electrode potentials.....	45
2.7 Systems studied in this thesis	47
Chapter 3. Breaking linear scaling relationships in the reactivity of Cu-based single atom alloys for alcohol dehydrogenation	48
3.1 Overview	48

3.2 Introduction	49
3.3 Methodology	52
3.4 Results	56
3.5 Discussion	68
3.6 Summary	71
Chapter 4. Conceptualizing a bio-inspired confined active site microenvironment to tailor the reactivity of transition metal nanoclusters	73
4.1 Overview	73
4.2 Introduction	73
4.3 Methodology	75
4.4 Results and Discussion	78
4.5 Summary	85
Chapter 5. Machine learning potentials to guide reaction mechanisms at the metal-water interface	86
5.1 Overview	86
5.2 Introduction	86
5.3 Methods	89
5.3.1 Density functional theory calculations	89
5.3.2 Machine Learning Potentials	91
5.4 Results	93
5.4.1 C–C coupling step as a case study	93
5.4.2 Development of machine learning potentials	94
5.4.3 MLP as a guide to transition state search	96
5.4.4 Effects due to Pd active sites, solvent, surface coverage and cation	100
5.5 Discussion	101
5.6 Summary	103
Chapter 6. Influence of the metal-solvent microenvironment in electrochemical hydrogenation of aldehydes on Cu	104

6.1 Overview	104
6.2 Introduction	105
6.3 Methodology	106
6.4 Results and Discussion	109
6.4.1 Benzaldehyde hydrogenation on Cu (111): acidic conditions	109
6.4.2 Benzaldehyde hydrogenation on Cu (111): alkaline condition.....	112
6.4.3 Overall mechanism on Cu (111): acidic versus alkaline.....	114
6.5 Summary	116
Chapter 7. Summary and outlook	117
References	120
Appendix A	136
Appendix B	148
Appendix C	154
Appendix D	157
Publication details and CV	159

Table of Figures

Figure 1.1. Selective chemical transformations on a heterogeneous catalyst via selective hydrogenation, dehydrogenation and C–C coupling with particular focus on the role of microenvironment of the active site.....	3
Figure 1.2. Schematic representation of key processes in a futuristic biorefinery that involves fermentation, selective hydrogenation, oxygen removal and C–C coupling to obtain high grade fuel and fine chemicals.	5
Figure 1.3. Strategies to tune the microenvironment of the active sites in heterogeneous catalysis.	7
Figure 1.4. Potential energy diagram of Pd _d Cu SAA. Ease of H ₂ dissociation at Pd sites and spillover to Cu host help in selective hydrogenation of hydrocarbons on these SAAs.(Reproduced with permission from ref 37. Copyright, American Chemical Society).	11
Figure 1.5. Partial hydrogenation or partial oxidation of multifunctional hydrocarbons. I. Adsorption configuration and projected density of states (pDOS) of crotonaldehyde on (a) monometallic Fe, Au and Pt (111) surfaces and (b) Fe _d Au and Pt _d Au SAAs. pDOS in blue, red, solid black and dashed black represent HOMO, HOMO-1, host metal and guest metal, respectively (Reproduced with permission from ref 42. Copyright, American Chemical Society). II. Product distribution for HMF hydrogenolysis over (a) Pt _d Co SAA and (b) Co nanoparticles. (c) Proposed pathway for HMF to DMF (Reproduced with permission from ref 43. Copyright, American Chemical Society).	12
Figure 1.6. I. Effect of Pd on Au in oxidative ethanol coupling. Conversion and EtOAc selectivity are represented in solid bars and reaction rate for oxidation and coupling are presented in dotted lines (Reproduced with permission from ref 48. Copyright, Elsevier). II. (a) Water dissociation barrier on Cu, Ag _d Cu SAA, AgCu NW. (b) Free energy difference of *CO hydrogenation (Reproduced from ref 49).	14
Figure 1.7. Effect of metal species encapsulated in zeolites. I. Change in selectivity with Pd encapsulation for ethyne hydrogenation (Reproduced with permission from ref 56. Copyright, Wiley-VCH Verlag GmbH & Co. KGaA). II. Influence of microenvironment over phenol hydrogenation in (a) Pd@KL, (b) Pd@NaKL and (c) Pd@HKL (KL=potassium form of Linde	

type zeolite) (Reproduced with permission from ref 58, Copyright, Elsevier). III. The effect of Fe structures on methane oxidation (Reproduced with permission from ref 60)	16
Figure 1.8. I. Furfural hydrogenation over Pd@S-1 (a) and Pd@Na-ZSM-5 (b) with products involving furfural alcohol (FAL), 2-methylfuran (2-MF), furan, 1,5-pentanediol (PDO) and others (Reproduced with permission from ref 71. Copyright, American Chemical Society). II. Furfural (FFL) hydrogenation over Cu@TS-1 modulated by Na ⁺ for furfural alcohol (FAL) production (Reproduced with permission from ref 73. Copyright, American Chemical Society).	18
Figure 1.9. Schematic representation showing the effect of hydrogen bond network to tune ground state (GS) and transition state (TS) energy states for hydrogenation of A*.	20
Figure 1.10. Effect of solvents on free energy of reactants (ground states (GS)) and transition states (TS). Excess free energy barrier as a function of excess chemical potential for (a) adsorbed H and (b) adsorbed benzaldehyde, respectively, in various solvents (Adapted with permission from ref 78. Copyright, Springer Nature).	21
Figure 1.11. Phenol heat of adsorption in implicit solvent, gas phase, aqueous phase using bond additivity model with respect to experimentally derived values over Pt (111) and Rh (111) (Reproduced with permission from ref 25. Copyright, American Chemical Society).	22
Figure 1.12. Influence of electrode potential and pH on reaction kinetics. The representation shows a proton-coupled electron transfer to A* species on the cathode surface. I. Effect of potential. The black, orange and blue states in for reactant (R) depict the energy levels at 0, U_{eq} , U potentials (V vs SHE). η is the overpotential. The transition state (TS) is affected by potentials above U_{eq} due to partial electron transfer (denoted by transfer coefficient α). II. Effect of pH. The black energy states show energy levels of reactant (R), transition state (TS) and product (P) at high acidic (A) and high alkaline (B) conditions, respectively. The orange states represent the change in pH. Proton is the hydrogen source in highly acidic conditions (pH=0), while water is the hydrogen source in highly alkaline conditions (pH=14). This representation is plotted assuming a constant potential, i.e. on SHE scale.	25
Figure 1.13. Effect of pH on CO ₂ RR. Schematic representation of CO ₂ reduction on Cu electrodes. Here, OH adlayer on Cu represents the alkaline environment (a) formation of C ₁ products in the absence of OH adlayer (b) formation of C ₂₊ products in the presence of OH adlayer (Reproduced with permission from ref ¹⁰⁴)	27

Figure 1.14. Effect of cation on hydrogenation rates and interfacial water structure. I. on C_1 product formation (Reproduced with permission from ref ¹¹⁰ . Copyright, American Chemical Society) II. on C_{2+} product formation (Reproduced with permission from ref ¹¹¹ . Copyright, American Chemical Society)	29
Figure 2.1. General workflow in GNNs to train feature vectors. Here, it is represented with a molecular system with 3 water molecules in the box.	40
Figure 2.2. Procedure to estimate minimum energy structure using DFT and MLPs.	44
Figure 2.3. Sella's saddle point optimization algorithm.	45
Figure 3.1. Possible mechanistic routes for ethanol reaction on catalyst surfaces via O–H, α -C–H, β -C–H, C–C and C–O bond activation in ethanol. Only α -C–H and O–H activation is considered here in constructing the <i>ab initio</i> MKMs for the formation of acetaldehyde via reaction routes 1 and 2. The orange slab represents the catalyst surface.	56
Figure 3.2. Volcano plot for ethanol conversion over the terrace (111) sites of transition metal catalysts and SAAs at 450 K and 1 bar calculated from (a) scaling MKM, (b) schematic representation of GBR algorithm, (c) trend in the TOFs calculated for Cu based SAAs plotted on the scaling <i>ab initio</i> MKM using the ML predicted binding energies. Error bar = 0.2 eV. Note that the turnover frequencies (TOFs) shown here are reported on a decimal logarithmic scale.	58
Figure 3.3. TOFs calculated for the initial (a) O–H and (b) α -C–H bond activation of ethanol over the terrace (111) sites of transition metal catalysts and SAAs at 450 K and 1 bar using the scaling MKM. Error bar = 0.2 eV. Note that the turnover frequencies (TOFs) shown here are reported on a decimal logarithmic scale.....	59
Figure 3.4. Reaction diagram for the NODH reaction on Cu (111) via reaction route 1 (black) and route 2 (red). Images in the inset show the structures of the initial (IS), transition (TS) and final (FS) state of the elementary reaction steps. The maxima mark the TS point with the activation energy of the intrinsic step highlighted on the slope. Species represented with the * are adsorbed on the surface. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Cu and C–Cu bond distances. All the bond distances are in Å.	59
Figure 3.5. Reaction diagram for the NODH reaction on Ni ₄ Cu (111) via reaction route 1 (black) and route 2 (red). Images in the inset show the structures of the initial (IS), transition (TS) and final (FS) state of the elementary reaction steps. The maxima mark the TS point with the activation	

energy of the intrinsic step highlighted on the slope. Species represented with the * are adsorbed on the surface. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow, blue and green represent C–H, O–H, C–O, O–Ni, C–Ni and O–Cu bond distances. All the bond distances are in Å. 61

Figure 3.6. Reaction diagram for the NODH reaction on Au (111) via reaction route **1** (black) and route **2** (red). Images in the inset show the structures of the initial (IS), transition (TS) and final (FS) state of the elementary reaction steps. The maxima mark the TS point with the activation energy of the intrinsic step highlighted on the slope. Species represented with the * are adsorbed on the surface. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Au and C–Au bond distances. All the bond distances are in Å. 63

Figure 3.7. Reaction diagram for the NODH reaction on Ni_dAu (111) via reaction route **1** (black) and route **2** (red). Images in the inset show the structures of the initial (IS), transition (TS) and final (FS) state of the elementary reaction steps. The maxima mark the TS point with the activation energy of the intrinsic step highlighted on the slope. Species represented with the * are adsorbed on the surface. All the energies are calculated with respect to the vapor phase energy of ethanol. The numbers in white, black, red, yellow and blue represent C–H, O–H, C–O, O–Ni and C–Ni bond distances. All the bond distances are in Å. 64

Figure 3.8. TOFs calculated for ethanol conversion over the terrace (111) sites of (a) Cu and Cu based SAAs in 350 – 450 K range, (b) Au and Ni_dAu SAA in 400 – 500 K range, using the *ab initio* non-scaling MKM at 1 bar. 65

Figure 3.9. TOFs calculated for the initial O–H and α-C–H bond activation of ethanol over the terrace (111) sites of (a) Cu, (b) Ni_dCu, (c) Pt_dCu, (d) Pd_dCu, (e) Au, and (f) Ni_dAu catalyst surfaces using the *ab initio* non-scaling MKM at 1 bar. 67

Figure 3.10. Transition state (TS) energy scaling with respect to the final state (FS) energy of the product for (a) O–H activation via route **1** (b) α-C–H activation via route **2**. 68

Figure 4.1. (a) Mo₂S₄ structure. (b) Faujasite (NaY) zeolite with extra framework Na⁺ cations. The blue spheres show the cation positions marked as sites S_I, S_{I'}, S_{II} and S_{III}. 77

Figure 4.2. Cluster adsorption with extra-framework Na⁺ in NaY zeolite. The change in binding energy of Mo₂S₄ cluster in NaY supercage is calculated with respect to the lowest energy configuration. Due to displaced Na_{III}⁺, the cation position in NaY (III) model zeolite is referred

also referred as Na^+ in the supercage in text, while due to the absence of direct Na^+ - Mo_2S_4 interaction in NaY (I') model zeolite, it is referred as Na^+ away from the supercage. The double and single anchored Mo_2S_4 in (a, b) NaY (III) and (c, d) NaY (I') models are the most stable configurations with $\Delta\text{B.E.}$ highlighted in kJ/mol, among the configurations tested. The spheres in cyan, yellow and blue denote molybdenum, sulfur and sodium atoms, respectively. For clarity purpose, only a section of supercage is shown in the ring format. The atom-atom distance in each configuration is in Å. 79

Figure 4.3. Cluster transition from Al1 to Al3 in the presence (a) and absence (b) of Na_{III}^+ . The numbers in the reaction diagram denote the energy difference in kJ/mol. The spheres in cyan, yellow and blue denote molybdenum, sulfur and sodium atoms, respectively. For clarity purpose, only a section of supercage is shown in the ring format. The atom-atom distance in each configuration is in Å. Only Na^+ ions at a distance of less than 3.6 Å from sulfur or molybdenum is depicted in (b). 82

Figure 4.4. Ethene hydrogenation on Mo_2S_4 . R-A and R-B indicate two pathways for 1st hydrogenation of ethene at the Mo active site viz through first H_2 adsorption and first ethene adsorption, respectively. The 2nd hydrogenation follows a common intermediate (I-AB) to produce ethane (P-AB). The spheres in cyan, yellow and blue denote molybdenum, sulfur and sodium atoms, respectively. For clarity purpose, only a section of supercage is shown in the ring format. Only Na atoms at a distance on less than 3.6 Å from the sulfur or molybdenum is depicted in the figures above. The atom-atom distance in each configuration is in Å..... 83

Figure 4.5. Effect of extraframework cations in supercage on ethene hydrogenation. The green and red plots represent ethene hydrogenation in NaY (III) and NaY (I') models, respectively. R-A indicates 1st hydrogenation of ethene at the Mo active site through first H_2 adsorption. The 2nd hydrogenation follows an ethoxy intermediate (I-AB) to produce ethane (P-AB)..... 85

Figure 5.1. Metal water-interface on PdCu_3 intermetallic alloys. (a) Four models of PdCu_3 intermetallic alloys represented with random CO^* coverage, water and ion orientations. (b) Workflow followed in this work. Here GS is the geometry optimized structure, TS is the transition state structure. Spheres in orange, blue, magenta, red, grey and white represent copper, palladium, potassium, oxygen, carbon, and hydrogen atoms, respectively. 91

Figure 5.2. Performance of MLPs with varying train size. The mean absolute error (MAE) in activation energy (E_{act}) is calculated with reference to DFT-derived E_{act} . The computational cost

presented here is the cost for generating training data from DFT and does not include the training cost. The connecting lines are just guide to the eyes. 96

Figure 5.3. OCCOH* formation barrier (a) and reaction energy (b) on 9 unseen test cases using DFT and MLP. MLP I, II, III and IV denote potentials trained from Dataset I, II, III and IV. The TS search from DFT is obtained by converging NEB. MLP-derived TS structures are derived from TS search using ML-NEB followed by its optimization in Sella. 97

Figure 5.4. Sella TS as a guide to locate alternate high energy structures. For test case 3, the nature of TS differs in DFT-NEB TS (a) and Sella TS (b). We used Sella TS as an intermediate image in the initial guess to run new DFT-NEB between the same R and P states. The TS, thus, obtained from corrected DFT-NEB is in (c). E_{act} represents the activation energy for OCCOH* formation. Distances in Å. Some of the water and CO* molecules are removed for better visualization. Spheres in orange, blue, magenta, red, grey and white represent copper, palladium, potassium, oxygen, carbon, and hydrogen atoms, respectively. 99

Figure 5.5. OC...CO vs OC...CO...H type TS. The activation barriers from MLP are derived after TS optimization in Sella. $O_{CO}-H$ distance of 1.4 Å is noted as a threshold between OC...CO and OC...CO...H type TS. A horizontal dashed line at the activation barrier of 0.75 eV is taken as a threshold. 99

Figure 5.6. Role of Pd active sites in PdCu₃. The activation and reaction energies for 58 successful TS optimization using MLP IV is plotted here. The configurations used here are unseen and generated by randomly orienting CO* on PdCu₃ (100) models. The CO* coverage range used in these configurations are between 50-70 %. A horizontal dashed line at the activation barrier of 0.75 eV is taken as a threshold. 101

Figure 6.1. Electrochemical hydrogenation of benzaldehyde (BZ) to benzyl alcohol (BA, C=O hydrogenation product) and hydrobenzoin (HB, C–C coupling product). 106

Figure 6.2. Initial (IS), transition ($TS^\ddagger$), and final states (FS) of (a) first H addition via PCET and (b) second H addition via PCET, for BA* formation, and (c) C–C coupling accompanied by PCET, for HB* formation on the Cu (111) surface. The estimated charges on the Cu surface (q_{Cu}), determined using Bader charge analysis, and the corresponding work functions (ϕ) are also shown. The reported number are interatomic distances in Å. Cu: gray, C: orange, O: red, H: white/purple. Some H₂O molecules have been removed for clarity. 111

Figure 6.3. Initial (IS), transition ($TS^\ddagger$), and final (FS) states for H addition to adsorbed BZ molecule via the Langmuir-Hinshelwood type surface reaction between BZ^* and H^* on Cu (111) surface.....	112
Figure 6.4. Initial states (IS), transition states ($TS^\ddagger$), and final states (FS) of (a) the first H addition to adsorbed BZ to form the hydroxy intermediate, (b) the second H addition to the hydroxy intermediate to form BA^* , and (c) the C–C bond formation between surface hydroxy intermediate and physisorbed BZ molecular to form HB^* in alkaline conditions. The simulations were performed on a Cu (111) surface with net charge = -1 . The reported number are interatomic distances in Å. Cu: grey, C: orange, O: red, H: white. Some H_2O molecules have been removed for clarity.....	115
Figure 6.5. Proposed mechanism for BA and HB formation during BZ ECH on Cu/C in (a) acidic and (b) alkaline media.....	116