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

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&

THE UNIVERSITY OF QUEENSLAND

FEBRUARY 2026

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by

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Submitted

in fulfilment of the requirements for the joint degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

&

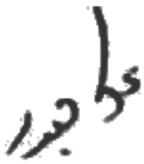
THE UNIVERSITY OF QUEENSLAND

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.



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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 CO_2 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 एंज़ाइम 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 एंज़ाइम-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 सब्सट्रेट 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 बायोरिफाइनरी 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.

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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%]

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