

**UNDERSTANDING THE ROLE OF IMPURITIES, SOLVENTS, AND
CATALYTIC ACTIVE SITES IN THE VALORISATION OF
BIORENEWABLE PLATFORM CHEMICALS**

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BIORENEWABLE PLATFORM CHEMICALS**

by

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to the**



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Dedicated to my beloved children,

Mr. Adam Khaldoon, Ms. Emine Maryam

and my lovely family.....

Certificate

This is to certify that the thesis entitled "**Understanding the Role of Impurities, Solvents, and Catalytic Active Sites in the Valorisation of Biorenewable Platform Chemicals**" being submitted by **Haseena K. V** to the Indian Institute of Technology Delhi for fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering is a record of bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which, to my knowledge, has reached the requisite standard for the submission of the thesis. The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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Abstract

Biomass-based technologies are recently gaining popularity as a prospective substitute for petroleum-based chemicals and fuel production. Current research and technologies based on biomass mainly focus on utilizing non-edible lignocellulosic biomass to produce platform molecules. Towards this, thoughtful integration of chemo and biocatalysis is expected to open up many novel processes and routes for the sustainable production of high-value chemicals and fuels. Importantly, in such processes, the reaction environment is often complex, comprising solvents, catalyst material, and impurities from the fermentation media. In the present study, an attempt was made to understand the interactions of impurities, solvents, and catalytic active sites via hydrogenation and hydrodeoxygenation reactions of selected platform molecules.

Firstly, the interaction of fermentation impurities with the metal catalyst was examined. The platform molecules produced from the biomass often carry trace amounts (<100 ppm) of biogenic impurities from the fermentation media. These impurities are generally amino acids, protein residues, and vitamins which are used as nitrogen sources for microbial growth. It has been observed that these impurities interact with the catalyst particles, causing deactivation. Catalytic transfer hydrogenation (CTH) of 6-*amyl*- α -pyrone (6PP) to δ -decalactone (DDL) is chosen as a probe reaction, and trace quantity (100 ppm) of model impurities was introduced to examine its effect on the catalyst performance. Strong inhibition of the catalyst activity was observed in the presence of sulfur-containing amino acids, whereas other amino acids were not found to cause a significant change in the reactivity. A mechanistic understanding of the interaction of sulfur-bearing amino acids with the Pd catalyst is developed using density functional theory (DFT) calculations, which is fundamental for the development of stable catalysts suitable for complex reaction environments.

Secondly, the role of solvents in the CTH reaction of *trans, trans*-muconic acid (ttMA) to adipic acid is studied. Muconic acid is a platform molecule produced from both glucose and lignin fractions of biomass. The CTH of ttMA using formic acid as a hydrogen source is studied in different solvents. Interestingly, the reaction proceeded to 100% conversion and high product yield (89%) in polar protic solvents such as water, methanol, and ethanol. In comparison, negligible conversion (7%) is observed in the case of nonpolar solvents like hexane and cyclohexane. In order to develop a mechanistic understanding of the promotional effect of water in ttMA hydrogenation, DFT simulations are performed.

Finally, the dependence of particle morphology on product selectivity was studied in the hydrogenation and hydrodeoxygenation reactions of platform molecules (cinnamaldehyde, and guaiacol) using Pd nanostructures of different shapes and sizes. DFT simulations were employed to unravel mechanistic insights into the experimental observations of the collaborating group. Pd nanostructures of octahedra and cubic shapes used in the reaction were modelled using Pd (111) and Pd (100) surfaces, respectively. Consistent with the experimental observation, CAL hydrogenation hydrocinnamaldehyde (HCAL) is observed to be energetically favoured on Pd (111) sites. However, an alternate route involving cinnamyl alcohol (COL) is observed to be predominant on the Pd (100) surface. Thus, the overall selectivity to the final hydro cinnamyl alcohol (HCOL) formation is expected to be catalysed by the Pd (100) facets via the COL intermediate. In contrast, in the HDO reaction of guaiacol, both the Pd octahedra and cubes predominantly produce the hydrogenated product, which is aligned with the DFT calculated energetics of the hydrogenation and HDO reactions of guaiacol on Pd (111) and Pd (100) surfaces. However, the deoxygenated product formation is observed to be energetically more feasible on the cube particles, the Pd (100) surface.

Overall, this study provides mechanistic insights into the key reactions driving the catalytic valorisation of platform chemicals. It specifically examines the influence of reaction environments such as biogenic impurities, solvents, and catalyst facets on the catalyst activity and product selectivity. The fundamental insights gained from these investigations are anticipated to pave the way for the rational design of stable catalyst materials capable of resisting deactivation. These findings will also aid in predicting optimised reaction environments for desired chemical transformation and in developing catalyst materials with tailored morphologies for specific chemical transformations. Collectively, these advancements are critical in optimizing catalytic processes toward sustainable production of chemicals and fuels.

सार

बायोमास और बायोमास-आधारित प्रौद्योगिकियाँ हाल ही में पेट्रोलियम-आधारित रसायनों और ईंधन उत्पादन के संभावित विकल्प के रूप में लोकप्रियता प्राप्त कर रही हैं। बायोमास पर आधारित वर्तमान शोध और प्रौद्योगिकियाँ मुख्य रूप से प्लेटफॉर्म अणुओं का उत्पादन करने के लिए गैर-खाद्य लिग्नोसेल्यूलोसिक बायोमास का उपयोग करने पर ध्यान केंद्रित करती हैं। इस दिशा में, कीमो और बायोकैटेलिसिस के विचारशील एकीकरण से उच्च-मूल्य वाले रसायनों और ईंधनों के स्थायी उत्पादन के लिए कई नई प्रक्रियाएँ और मार्ग खुलने की उम्मीद है। महत्वपूर्ण रूप से, ऐसी प्रक्रियाओं में, प्रतिक्रिया वातावरण अक्सर जटिल होता है, जिसमें विलायक, उत्प्रेरक सामग्री और किण्वन माध्यम से अशुद्धियाँ शामिल होती हैं। वर्तमान अध्ययन में, चयनित प्लेटफॉर्म अणुओं की हाइड्रोजनीकरण और हाइड्रोडीऑक्सीजनेशन प्रतिक्रियाओं के माध्यम से अशुद्धियों, विलायकों और उत्प्रेरक सक्रिय साइटों की परस्पर क्रियाओं को समझने का प्रयास किया गया है।

सबसे पहले, धातु उत्प्रेरक के साथ किण्वन अशुद्धियों की अंतःक्रिया की जांच की जाती है। बायोमास से उत्पादित प्लेटफॉर्म अणु अक्सर किण्वन माध्यम से बायोजेनिक अशुद्धियों की ट्रेस मात्रा (<100 पीपीएम) ले जाते हैं। ये अशुद्धियाँ आम तौर पर अमीनो एसिड, प्रोटीन अवशेष और विटामिन हैं जिनका उपयोग माइक्रोबियल विकास के लिए नाइट्रोजन स्रोतों के रूप में किया जाता है। यह देखा गया है कि ये अशुद्धियाँ उत्प्रेरक कणों के साथ अंतःक्रिया करती हैं, जिससे निष्क्रियता होती है। 6-एमाइल- α -पाइरोन (6PP) से δ -डेकैलेक्टोन (DDL) के CTH को जांच प्रतिक्रिया के रूप में चुना जाता है, जिसमें मॉडल अशुद्धता की ट्रेस मात्रा (100 पीपीएम) पेश की जाती है। सल्फर युक्त अमीनो एसिड (Cys और Met) की उपस्थिति में उत्प्रेरक गतिविधि का मजबूत अवरोध देखा जाता है, जबकि अन्य अमीनो एसिड (Ala, Arg) प्रतिक्रियाशीलता में महत्वपूर्ण परिवर्तन का कारण नहीं पाए गए। DFT गणनाओं का उपयोग करके सल्फर युक्त अमीनो एसिड, Cys और Met की Pd उत्प्रेरक के साथ अंतःक्रिया की एक यांत्रिक समझ विकसित की गई है।

दूसरे, ट्रांस, ट्रांस-म्यूकोनिक एसिड (टीटीएमए) से एडिपिक एसिड तक उत्प्रेरक स्थानांतरण हाइड्रोजनीकरण (सीटीएच) प्रतिक्रिया में सॉल्वैंट्स की भूमिका का अध्ययन किया जाता है। म्यूकोनिक एसिड बायोमास के ग्लूकोज और लिग्निन अंश दोनों से निर्मित एक प्लेटफॉर्म अणु है। हाइड्रोजन स्रोत के रूप में फॉर्मिक एसिड का उपयोग करके टीटीएमए के सीटीएच का अध्ययन विभिन्न सॉल्वैंट्स में किया जाता है। पानी और मेथनॉल और इथेनॉल जैसे ध्रुवीय प्रोटिक सॉल्वैंट्स का उपयोग करके 120 मिनट में 70 डिग्री सेल्सियस पर पूर्ण रूपांतरण (100%) और उच्च उत्पाद उपज (89%) देखी जाती है। इसकी तुलना में, हेक्सेन और साइक्लोहेक्सेन जैसे गैर-ध्रुवीय सॉल्वैंट्स के मामले में नगण्य रूपांतरण (7%) देखा जाता है। सॉल्वैंट्स की भूमिका की यांत्रिक समझ विकसित करने के लिए, घनत्व कार्यात्मक सिद्धांत (डीएफटी) सिमुलेशन किए जाते हैं।

अंत में, विभिन्न आकृतियों और आकारों के Pd नैनोस्ट्रक्चर का उपयोग करके प्लेटफॉर्म अणुओं (सिनामेल्लिहाइड, और गुआयाकोल) के हाइड्रोजनीकरण और हाइड्रोडीऑक्सीजनीकरण प्रतिक्रियाओं में उत्पाद चयनात्मकता पर कण आकृति विज्ञान की निर्भरता का अध्ययन किया जाता है। फोकस में प्रतिक्रिया की यांत्रिक अंतर्दृष्टि को उजागर करने के लिए DFT सिमुलेशन का उपयोग किया जाता है।

प्रतिक्रिया में उपयोग किए गए अष्टफलक और घन आकार के Pd नैनोस्ट्रक्चर को क्रमशः Pd (111) और Pd (100) सतहों का उपयोग करके मॉडल किया जाता है। प्रायोगिक अवलोकन के अनुरूप, CAL हाइड्रोजनीकरण हाइड्रोसिनामेलिहाइड (HCAL) को Pd (111) साइटों पर ऊर्जावान रूप से पसंद किया जाता है। हालांकि, सिनामाइल अल्कोहल (COL) को शामिल करने वाला एक वैकल्पिक मार्ग Pd (100) सतह पर प्रमुख पाया जाता है। इस प्रकार, अंतिम हाइड्रो सिनामाइल अल्कोहल (HCOL) गठन के लिए समग्र चयनात्मकता को COL मध्यवर्ती के माध्यम से Pd (100) पहलुओं द्वारा उत्प्रेरित किए जाने की उम्मीद है। इसके विपरीत, ग्वाइयाकोल की एचडीओ प्रतिक्रिया में, पीडी ऑक्टाहेड्रा और क्यूब्स दोनों मुख्य रूप से हाइड्रोजनीकृत उत्पाद का उत्पादन करते हैं, जो कि पीडी (111) और पीडी (100) सतहों पर ग्वाइयाकोल के हाइड्रोजनीकरण और एचडीओ प्रतिक्रिया के डीएफटी गणना ऊर्जा के साथ संरेखित है। हालांकि, डीऑक्सीजनेटेड उत्पाद गठन को क्यूब कणों, पीडी (100) सतह पर ऊर्जावान रूप से अधिक व्यवहार्य पाया गया है। कुल मिलाकर, यह अध्ययन प्लेटफॉर्म रसायनों के उत्प्रेरक मूल्यांकन को संचालित करने वाली प्रमुख प्रतिक्रियाओं में यंत्रवत अंतर्दृष्टि प्रदान करता है। यह विशेष रूप से उत्प्रेरक गतिविधि और उत्पाद चयनात्मकता पर सॉल्वेंट्स, बायोजेनिक अशुद्धियों और उत्प्रेरक पहलुओं जैसे प्रतिक्रिया वातावरण के प्रभाव की जांच करता है। ये अंतर्दृष्टि रसायनों और ईंधन के स्थायी उत्पादन की दिशा में उत्प्रेरक प्रक्रियाओं को अनुकूलित करने के लिए महत्वपूर्ण हैं।

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