

**CATALYTIC CONVERSION OF BIOMASS-DERIVED
PLATFORM MOLECULES: MECHANISTIC INSIGHTS,
FUNDAMENTAL CHALLENGES AND OPPORTUNITIES FOR
RATIONAL CATALYST DESIGN**

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PLATFORM MOLECULES: MECHANISTIC INSIGHTS,
FUNDAMENTAL CHALLENGES AND OPPORTUNITIES FOR
RATIONAL CATALYST DESIGN**

by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy
to the



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Dedicated to my Grandmother (Dadiji) and Parents.....

Certificate

This is to certify that the thesis entitled “**Catalytic Conversion of Biomass-Derived Platform Molecules: Mechanistic Insights, Fundamental Challenges and Opportunities for Rational Catalyst Design**” being submitted by **Shelaka Gupta** 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 bona-fide 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

Technologies for the processing of lignocellulosic biomass into fuels and chemicals are generally focused on selective chemical transformation of the three different types of constituents; cellulose, hemicellulose and lignin. In this regard, heterogeneous catalytic reactions are employed to defunctionalize and upgrade the platform molecules obtained selectively from these constituents. Herein, systematic studies were performed to deoxygenate and valorize the biomass-derived platform molecules. The selection employed ring-opening, decarboxylation, hydrogenation and hydrodeoxygenation (HDO) reactions carried out on supported metal and oxide catalysts. The platform molecules studied here included an array of cellulose-derived lactones, furans, 2-pyrones and lignin-derived phenolic compounds.

Study on the conversion of lactones (saturated cyclic esters) was focused on understanding the mechanism of ring-opening and decarboxylation reaction. More specifically, oxocarbenium ions were proposed as an intermediate, to play an important role in controlling the rate of ring-opening step. The mechanism of ring-opening and decarboxylation reaction in unsaturated cyclic esters (2-pyrones) formed an interesting case, wherein the reaction in partially saturated 2-pyrones followed a retro-Diels-Alder (rDA) route to selectively yield the desired deoxygenated product. Both solvents and substituents were expected to influence the rDA reaction of partially saturated 2-pyrones, which was studied using density functional theory (DFT) simulations.

An attempt was made to identify a new platform molecule other than the ones listed in the Top-12 list of biobased molecules proposed by the Department of Energy (United States). Towards this, 6-amyl- α -pyrone (6PP) was suggested as a potential platform chemical, which may be obtained directly from the fermentation of waste lignocellulosic biomass. On ring-opening and decarboxylation, 6PP was converted to C₉ linear ketones which are proposed as precursors for jet and diesel range fuels. On hydrogenation, 6PP was converted to δ -decalactone (DDL), which is a food and flavor compound. All of these catalytic transformations of 6PP can be integrated with the upstream fermentation of biomass to form a unique bio- and chemo-catalytic process for providing high value fuels and chemicals.

Towards the development of this integrated fermentation and catalytic process, biogenic impurities (amino acids and protein residues) present in ppm levels (<100 ppm) along with the fermentation-

derived molecules pose a detrimental effect to heterogeneous catalyst stability. Interaction of such impurities with the metal catalyst surface was studied for the first time using DFT simulations. The fundamental knowledge thus developed is expected to open up possibilities of rational design of metal catalyst surface for destabilizing interactions with the biogenic impurities and thereby providing greater stability to the heterogeneous catalyst working in aqueous environment. In this regard a bimetallic alloy of Ni-Au was proposed as a more stable surface for hydrogenation reactions as compared to the bimetallic Pd-Au and monometallic Pd and Ni catalysts.

Catalytic hydrogenation reaction carried out on the Pd catalyst was an interesting case to further explore the influence of catalyst particle size and morphology on the selectivity of a desired product. Phenol hydrogenation reaction on supported and unsupported Pd catalyst was studied as a model reaction, since phenolic compounds are derived from the lignin part of biomass. Detailed mechanistic studies were carried out on Pd (111) and Pd (100) surfaces using DFT calculations to corroborate experimental finding of the collaborating group. Since Pd (111) are the majority (~70% of the surface) sites, high selectivity observed towards the partially hydrogenated product (cyclohexanone) in the experiments is thought to be from the Pd (111) surface. Contrary to this prevalent thought, on using a combined theoretical and experimental approach, Pd (111) surface was demonstrated to selectively produce the completely hydrogenated product, cyclohexanol. Surprisingly, Pd (100), the minority (~25%) sites on the surface, were selectively producing cyclohexanone. These results lead to the development of a comprehensive understanding on facet-dependent selectivity control in phenol hydrogenation on the Pd catalyst.

Final reaction in this sequence was HDO of biomass-derived furan compounds, wherein the synergistic interaction of Zn with the Pd catalyst was studied using DFT simulations. Zn was shown to participate in C-O bond activation step while Pd surface participated in the hydrogenation step. Overall the study covering an array of platform molecules and catalytic reactions is focused on developing a mechanistic understanding with insights into key fundamental challenges and available opportunities on engineering the catalyst surface.

सार

ईंधन और रसायनों में लिग्नोसेल्यूलोसिक बायोमास के प्रसंस्करण के लिए प्रौद्योगिकी आम तौर पर तीन अलग-अलग प्रकार के घटकों के चयनात्मक रासायनिक परिवर्तन पर केंद्रित है; सेल्युलोज, हेमिसेल्युलोज और लिग्निन। इस संबंध में, विषम उत्प्रेरक प्रतिक्रियाओं को इन घटकों से चुनिंदा रूप से प्राप्त प्लेटफॉर्म अणुओं को हटाने और उन्नयन करने के लिए नियोजित किया जाता है। इसमें, बायोमास-व्युत्पन्न प्लेटफॉर्म अणुओं को डीऑक्सिजेनेट करने और वेलोराइज करने के लिए व्यवस्थित अध्ययन किए गए थे। चयनित रिंग-ओपनिंग, डीकार्बाक्सिलेशन, हाइड्रोजनीकरण और हाइड्रोडीऑक्सीजेशन (एचडीओ) प्रतिक्रियाएं समर्थित धातु और ऑक्साइड उत्प्रेरक पर किए गए हैं। यहां अध्ययन किए गए प्लेटफॉर्म अणुओं में सेल्युलोज-व्युत्पन्न लैक्टोन, फयूरेन्स, 2-पाइरोन और लिग्निन-व्युत्पन्न फेनोलिक यौगिक शामिल हैं।

लैक्टोन (संतृप्त चक्रीय एस्टर) के रूपांतरण पर अध्ययन, रिंग-ओपनिंग और डीकार्बाक्सिलेशन प्रतिक्रिया के तंत्र को समझने पर केंद्रित था। अधिक विशेष रूप से, ऑक्सोकार्बोनेयम आयनों को एक मध्यवर्ती के रूप में प्रस्तावित किया गया था, जो रिंग-ओपनिंग वाले चरण की दर को नियंत्रित करने में महत्वपूर्ण भूमिका निभाते हैं। असंतृप्त चक्रीय एस्टर (2-पाइरोन्स) में रिंग-ओपनिंग और डीकार्बाक्सिलेशन प्रतिक्रिया के तंत्र ने एक रोचक प्रकरण बनाया, जिसमें आंशिक रूप से संतृप्त 2-पाइरोन्स में प्रतिक्रिया ने रेट्रो-डील्स-एल्डर (आरडीए) मार्ग का चयन किया ताकि वांछित डीऑक्सीजेनेटेड उत्पाद का उत्पादन हो सके। आंशिक रूप से संतृप्त 2-पाइरोन्स की आरडीए प्रतिक्रिया पर सॉल्वैंट्स और प्रतिस्थापन के प्रभाव को समझने के लिए डेंसिटी फंक्शनल थ्योरी (डीएफटी) सिमुलेशन का उपयोग किया गया था।

ऊर्जा विभाग (यूनाइटेड स्टेट्स) द्वारा प्रस्तावित बायोबेस्ड अणुओं की शीर्ष-12 सूची में सूचीबद्ध अणुओं के अलावा एक नए प्लेटफॉर्म अणु की पहचान करने का प्रयास किया गया था। इसकी ओर, 6-अमाइल- α -पाइरोन (6PP) को एक संभावित प्लेटफॉर्म रसायन के रूप में सुझाया गया था, जो सीधे अपशिष्ट लिग्नोसेल्यूलोसिक बायोमास के किण्वन से प्राप्त किया जा सकता है। रिंग-ओपनिंग और डीकार्बाक्सिलेशन पर, 6PP को C₉ रेखिक कीटोन्स में बदल दिया गया जो जेट और डीजल रेंज ईंधन के लिए अग्रदूत के रूप में प्रस्तावित हैं। हाइड्रोजनीकरण पर, 6PP को δ -डेकालैक्टोन (DDL) में परिवर्तित किया गया, जो कि एक खाद्य और स्वाद यौगिक है। 6PP के इन सभी उत्प्रेरक परिवर्तनों को बायोमास के अपस्ट्रीम किण्वन के साथ एकीकृत किया जा सकता है ताकि उच्च मूल्य के ईंधन और रसायन प्रदान करने के लिए एक अद्वितीय जैव- और कीमो-उत्प्रेरक प्रक्रिया का निर्माण किया जा सके।

इस एकीकृत किण्वन और उत्प्रेरक प्रक्रिया के विकास के लिए, किण्वन-व्युत्पन्न अणु के साथ-साथ पीपीएम के स्तर (<100 पीपीएम) में मौजूद बायोजेनिक अशुद्धियां (एमिनो एसिड और प्रोटीन अवशेष) विषम उत्प्रेरक स्थिरता के लिए हानिकारक प्रभाव

पैदा करती हैं। धातु उत्प्रेरक सतह के साथ इस तरह की अशुद्धियों की सहभागिता का पहली बार डीएफटी सिमुलेशन का उपयोग करके अध्ययन किया गया था। इस प्रकार विकसित मौलिक ज्ञान से उम्मीद है कि बायोजेनिक अशुद्धियों के परस्पर प्रभाव को अस्थिर करने के लिए धातु उत्प्रेरक सतह के तर्कसंगत डिजाइन की संभावनाओं को खोला जा सकता है और इस तरह जलीय वातावरण में काम करने वाले विषम उत्प्रेरक को अधिक स्थिरता प्रदान की जा सकती है। इस संबंध में NiAu के एक द्विधात्विक मिश्र धातु को हाइड्रोजनीकरण प्रतिक्रियाओं के लिए प्रस्तावित किया गया था, जो कि द्विधात्विक PdAu और मोनोमेटैलिक Pd और Ni उत्प्रेरक के मुकाबले अधिक स्थिर सतह था।

वांछित उत्पाद की चयनात्मकता पर उत्प्रेरक कण आकार और आकृति विज्ञान के प्रभाव का पता लगाने के लिए Pd उत्प्रेरक पर किए गए हाइड्रोजनीकरण प्रतिक्रिया एक रोचक प्रकरण था। फिनोल हाइड्रोजनीकरण प्रतिक्रिया समर्थित और असमर्थित Pd उत्प्रेरक पर एक मॉडल प्रतिक्रिया के रूप में अध्ययन की गयी थी, क्योंकि फिनोलिक यौगिक बायोमास के लिग्निन भाग से प्राप्त होते हैं। सहयोगी समूह के प्रायोगिक खोज को पुष्ट करने के लिए डीएफटी गणना का उपयोग करते हुए Pd (111) और Pd (100) सतहों पर विस्तृत यंत्रवत अध्ययन किए गए। चूंकि Pd (111) बहुसंख्यक हैं (सतह का ~70%) स्थल, प्रयोगों में आंशिक रूप से हाइड्रोजनीकृत उत्पाद (साइक्लोहेक्सानोन) के प्रति देखी गई उच्च चयनात्मकता को Pd (111) सतह से माना जाता है। इस प्रचलित विचार के विपरीत, एक संयुक्त सैद्धांतिक और प्रायोगिक दृष्टिकोण का उपयोग करने पर, Pd (111) सतह को चुनिंदा रूप से पूरी तरह से हाइड्रोजनीकृत उत्पाद, साइक्लोहेक्सानॉल का उत्पादन करने के लिए प्रदर्शित किया गया था। आश्चर्यजनक रूप से, Pd (100), अल्पसंख्यक (~ 25%) सतह पर, चुनिंदा रूप से साइक्लोहेक्सनोन का उत्पादन हुआ। ये परिणाम Pd उत्प्रेरक पर फिनोल हाइड्रोजनीकरण में पहलू-निर्भरता नियंत्रण पर एक व्यापक समझ के विकास की ओर ले जाते हैं।

इस क्रम में अंतिम प्रतिक्रिया बायोमास-व्युत्पन्न फ्यूरेन यौगिकों का एचडीओ था, जिसमें Pd उत्प्रेरक के साथ Zn का सहक्रियात्मक परस्पर प्रभाव समझने के लिए डीएफटी सिमुलेशन का उपयोग किया गया था। Zn को C-O बॉन्ड सक्रियण चरण में भाग लेने के लिए दिखाया गया जबकि Pd सतह ने हाइड्रोजनीकरण चरण में भाग लिया था। कुल मिलाकर यह अध्ययन प्लेटफॉर्म अणुओं और उत्प्रेरक प्रतिक्रियाओं की एक सरणी को कवर करने के साथ साथ महत्वपूर्ण मूलभूत चुनौतियों में अंतर्दृष्टि के साथ एक यंत्रवत समझ विकसित करने और उत्प्रेरक सतह पर इंजीनियरिंग के उपलब्ध अवसरों पर केंद्रित है।

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