UNDERSTANDING THE ROLE OF CATALYST MATERIALS AND PROCESS CONDITIONS IN BIORENEWABLE TRANSFORMATIONS

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by

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DEPARTMENT OF CHEMICAL ENGINEERING

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“Iqra bismi rab bikal lazee khalaq.
Khalaqal insaana min 'alaq.
Iqra wa rab bukal akram.
Al lazee 'allama bil qalam.
'Al lamal insaana ma lam y'alam”

“Read in the name of your Lord who created, created man from a clot. Read, for your Lord is most Generous, Who has taught by means of the pen, has taught man that which he knew not.”

CERTIFICATE

This is to certify that the thesis entitled, ***"Understanding the Role of Catalyst Materials and Process Conditions in Biorenewable Transformations"*** being submitted by **Mr. Ejaz Ahmad** in the fulfilment of requirements for the award of degree of **Doctor of Philosophy** to the Indian Institute of Technology Delhi, (India) is authentic record of work carried out by him. Mr. Ejaz Ahmad has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my 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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EJAZ AHMAD

ABSTRACT

Bio-renewable transformations to produce fuels and chemicals from lignocellulosic biomass are generally carried out at either high temperature (>750 K) or low temperature (<550 K) conditions. At the high temperature, biomass is directly converted into a mixture of valuable products either through a gasification process or through pyrolysis. In contrast, at the low-temperature, biomass is first pretreated to produce a platform chemical (e.g., levulinic acid, ethyl levulinate, 5-hydroxymethylfurfural, etc.), which is further reacted to selectively yield a desired product.

This thesis is focused on understanding and developing both low and high-temperature processes by exploring the role of catalyst materials and process conditions. More specifically, at the low temperature, catalytic transformation of biomass-derived levulinic acid to alkyl levulinates is studied. The catalyst materials explored for this purpose include supported and un-supported heteropolyacids (HPAs) as well as sulfonated carbonaceous materials. The deprotonation energy of the HPAs is theoretically calculated using density functional theory simulations and correlated to the reactivity of the acid catalyst for the synthesis of alkyl levulinates. In addition, reaction mechanisms and kinetics provided insight into the functioning of the catalyst materials. For HPAs, two different types of processes have been developed which include reactions carried out with and without microwave irradiations in a batch reactor. The results obtained showed more than 90%

levulinic acid conversion at 383 K temperature in 90 minutes reaction time in both the reactors.

In addition, heterogenization of Keggin Heteropolyacid has been explored over metal oxide support while preserving the Keggin unit of the parent catalyst. The synthesized catalysts have been characterized using several tools and techniques such as XRD, FT-IR, Raman, HR-TEM which in turn confirmed the intact Keggin unit of the HPW catalyst after heterogenization over TiO_2 support. Furthermore, heterogenized catalysts was found useful for at least 5 cycles without significant loss in its activity and also suitable for synthesis of a wide range of alkyl levulinates by replacing ethanol with other alcohols.

In parallel, the development of the high-temperature process is focused on studying pyrolysis of the lignocellulosic waste biomass (sugarcane bagasse) to gaseous and liquid phase products. In this reaction, biochar produced is observed to act as an in-situ reforming catalyst. Biochar is characterized to understand the role of active metals in producing the deoxygenated bio-oil and hydrogen-rich combustible gases. The process conditions were optimized in order to achieve the maximum yield of reformed products. Under optimum operating conditions, bio-oil obtained contained less than 10 wt.% oxygen which make this process unique. Also, the biochar obtained had a surface area above 90 m^2/g, thereby making it suitable for catalytic applications. Also, nearly 58 wt.% hydrogen-rich combustible gaseous product was obtained under optimum operating conditions.

सारांश

लिग्नोसेल्यूलोसिक बायोमास से ईंधन और रसायनों का उत्पादन करने के लिए जैव-अक्षय परिवर्तन आमतौर पर या तो उच्च तापमान (> 750 K) या कम तापमान (<550 K) की स्थिति में किया जाता है। उच्च तापमान पर, बायोमास को सीधे मूल्यवान उत्पादों के मिश्रण में या तो गैसीकरण प्रक्रिया के माध्यम से या पायरोलिसिस के माध्यम से परिवर्तित किया जाता है। इसके विपरीत, कम तापमान पर, बायोमास को पहले एक मंच रसायन (जैसे, लेविलेनिक एसिड, एथिल लेवुलेट, 5-हाइड्रॉक्सीमेथाइलफ्यूरफ्यूरल, आदि) का उत्पादन करने के लिए किया जाता है, जो कि एक वांछित उत्पाद का चयन करने के लिए आगे प्रतिक्रिया करता है।

यह थीसिस उत्प्रेरक सामग्री और प्रक्रिया स्थितियों की भूमिका का पता लगाकर कम और ऊँची दोनों प्रक्रियाओं को समझने और विकसित करने पर केंद्रित है। अधिक विशेष रूप से, कम तापमान पर, बायोमास-व्युत्पन्न लेविलेनिक एसिड के क्षारीय लेविलिनेट्स के उत्प्रेरक परिवर्तन का अध्ययन किया जाता है। इस उद्देश्य के लिए खोजी गई उत्प्रेरक सामग्रियों में समर्थित और बिना समर्थित हेटरोपॉलेकस (एचपीएएस) और साथ ही साथ सल्फोनेटेड कार्बोनसियस सामग्री शामिल हैं। HPAs के अवक्षेपण ऊर्जा को सैद्धांतिक रूप से घनत्व कार्यात्मक सिद्धांत सिमुलेशन का उपयोग करके गणना की जाती है और एल्काइल लेवुलिनेट्स के संश्लेषण के लिए एसिड उत्प्रेरक की प्रतिक्रियाशीलता से संबंधित है। इसके अलावा, प्रतिक्रिया तंत्र और कैनेटीक्स ने उत्प्रेरक सामग्री के कामकाज में अंतर्दृष्टि प्रदान करने पर केंद्रित है। एचपीएएस के लिए, दो अलग-अलग प्रकार की प्रक्रियाओं को विकसित किया गया है जिसमें एक बैच रिएक्टर में माइक्रोवेव विकिरण के साथ और बिना प्रतिक्रिया किए गए प्रतिक्रियाएं शामिल हैं। प्राप्त किए गए परिणामों ने दोनों रिएक्टरों में 90 मिनट की प्रतिक्रिया समय में 383 K तापमान पर 90% से अधिक लेविलेनिक एसिड रूपांतरण दिखाया।

इसके अलावा, उत्प्रेरक की केगिन इकाई के संरक्षण के दौरान केगिन हेटेरोपायसीड के विषमकरण का धातु ऑक्साइड समर्थन पर लगाया गया है। संश्लेषित उत्प्रेरकों को कई उपकरण और तकनीकों का उपयोग करते हुए दिखाया गया है जैसे कि XRD, FT-IR, Raman, HR-TEM, जो बदले में TiO_2 समर्थन पर विषमजनन के बाद HPW उत्प्रेरक की अक्षुण्ण कीगिन इकाई की पुष्टि करते हैं। इसके अलावा, हेटेरोजेनाइज्ड उत्प्रेरक को कम से कम 5 चक्रों के लिए उपयोगी पाया गया था, जो इसकी गतिविधि में महत्वपूर्ण नुकसान के बिना और अन्य अल्कोहल के साथ इथेनॉल की जगह से एल्काइल लेविनालेट्स की एक विस्तृत श्रृंखला के संश्लेषण के लिए उपयुक्त है।

समानांतर में, उच्च तापमान प्रक्रिया का विकास गैसीय और तरल चरण उत्पादों के लिए लिग्नोसेल्युलोसिक अपशिष्ट बायोमास (गन्ना बैगस) के पायरोलिसिस का अध्ययन करने पर केंद्रित है। इस प्रतिक्रिया में, उत्पादित बायोचार को एक उत्प्रेरक सुधारक के रूप में देखा जाता है। Biochar को डीऑक्सीजेनेटेड बायो-ऑयल और हाइड्रोजन-समृद्ध दहनशील गैसों के उत्पादन में सक्रिय धातुओं की भूमिका को समझने की विशेषता है। सुधारित उत्पादों की अधिकतम उपज प्राप्त करने के लिए प्रक्रिया की शर्तों को अनुकूलित किया गया था। इष्टतम परिचालन स्थितियों के तहत, जैव-तेल प्राप्त 10 wt% से कम ऑक्सीजन होता है जो इस प्रक्रिया को अद्वितीय बनाता है। इसके अलावा, प्राप्त बायोचार में 90 एम 2 / जी से ऊपर का सतह क्षेत्र था, जिससे यह उत्प्रेरक अनुप्रयोगों के लिए उपयुक्त है। इसके अलावा, लगभग 58 wt।% हाइड्रोजन-समृद्ध दहनशील गैसीय उत्पाद इष्टतम ऑपरेटिंग परिस्थितियों में प्राप्त किया गया था।

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