DEVELOPMENT OF CATALYST AND REACTOR FOR ELECTROCHEMICAL CONVERSION OF BIOMASS-DERIVED FURFURAL INTO VALUE-ADDED CHEMICALS

RAM JI DIXIT

(2017CHZ8250)

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

NEW DELHI – 110016

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by

RAM JI DIXIT

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OF

PROF. SUDDHASATWA BASU

PROF. ANUPAM SHUKLA

PROF. VIJAY K. RAMANI

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

NEW DELHI-110016

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Certificate

This is to certify that the thesis entitled "**Development of Catalyst and Reactor for Electrochemical Conversion of Biomass-Derived Furfural into Value-Added Chemicals**" submitted by **Mr. Ram Ji Dixit** to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

Prof. Suddhasatwa Basu
Supervisor
Department of Chemical Engineering
Indian Institute of Technology Delhi

Prof. Anupam Shukla
Co-supervisor
Department of Chemical Engineering
Indian Institute of Technology Delhi

Prof. Vijay K. Ramani
Co-supervisor
Department of Energy, Environmental and Chemical Engineering
Washington University in St. Louis, US

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Abstract

The biomass-derived furfural (FF) transforms into platform chemicals such as furfuryl alcohol (FA), hydrofuroin (HF), furoic acid (FU), and 2(5H)-furanone (FN) for their use in polymer, pharmaceuticals, and bio-fuel industries. Electrocatalytic hydrogenation (ECH) of FF is an appealing process because of the in-situ generation of adsorbed hydrogen, ambient temperature-pressure conditions, and the use of electrical energy generated from renewables. Herein, FF ECH in alkaline medium produced FA and HF, and their selectivity on Cu, Pt, and Ni-foam (NF, 10 cm^2) electrocatalysts showed that their generation was dependent upon the availability of adsorbed hydrogen, which in turn varied with the choice of electrocatalyst and with applied potentials. The etching of Cu from a co-electrodeposited Ni-Cu electrode, followed by a re-electrodeposition of Cu led to the formation of Cu nanoplate, termed as Cu-NPNi/NF. The formation of Cu-nanoplates and bimetallic Ni-Cu for Cu-NPNi/NF resulted an increase in FA and HF formation rates as compared to Cu, Pt, and NF. As alkaline medium widened the scope for the type of materials, FF ECH using metal-oxide (In_2O_3, Co_3O_4, $Pb_2Ru_2O_{7-x}$) electrocatalysts was studied. Through experimental and theoretical studies, we demonstrated that the binding energy and coverage of competing furfural and hydrogen adsorption processes determined the selectivity of FA over HF ($S_{FA/HF}$). The Langmuir-Hinshelwood mechanism was found to be involved during FF ECH with pristine $Pb_2Ru_2O_{7-x}$ electrocatalyst, which resulted in the high surface coverage of FF and hydrogen leading to selective FA formation.

For scaling up of the electrode to enhance FA and HF formation rates, a batch electrochemical reactor was fabricated in which thermally treated large surface area (100 cm^2) 3D-graphite felt cathode yielded the HF formation rate and HF selectivity as 5.2 ± 0.16 mmol h^{-1}, and 65.7 ± 1.9% HF, respectively with a 97.8% conversion in 3 h of ECH. A silver deposited Ni-foam cathode (100 cm^2) was employed in a fabricated continuous flow (flow rate = 10 mL min^{-1})

electrochemical reactor to obtain 10.5 ± 0.5 mmol h^{-1} FA formation rate and 78.2 ± 2.1% FA selectivity. Furthermore, the solar illumination reduced the electrical energy requirement as a photoelectrochemical cell (Cu-NPNi/NF|TiO_2) depicted a lower applied bias to attain a FA formation rate comparable to that achieved from an electrochemical cell (Cu-NPNi/NF|Pt). The FF ECH was paired with photoelectrochemical oxidation of FF to coproduce FA at cathode and FU, FN at photoanode validating the feasibility of solar illumination utilization in biomass conversion. Overall, FA and HF produced from FF ECH had high formation rates and a competitive market pricing, which could be scaled-up and commercialized by the industries.

सार

जैवभार-व्युत्पन्न फरफुरल (एफएफ) वहुलक, औषधि और जैव-ईंधन उद्योगों में उनके उपयोग के लिए फरफ्यूरिल अल्कोहल (एफए), हाइड्रोफ्यूरोइन (एचएफ), फ्यूरोइक एसिड (एफयू), और 2,(5 एच) -फुरानोन (एफएन) जैसे रसायनों में बदल जाता है। एफएफ का विद्युतरासायनिक हाइड्रोजनीकरण (वि.रा.ह.) अधिशोषित हाइड्रोजन के उत्पादन, परिवेश के तापमान-दबाव की स्थिति और नवीकरणीय ऊर्जा से उत्पन्न विद्युत ऊर्जा के उपयोग के कारण एक आकर्षक प्रक्रिया है।

इसमें, क्षारीय माध्यम में एफएफ वि.रा.ह. ने एफए और एचएफ का उत्पादन किया, और Cu, Pt और Ni-Foam (NF, 10 सेमी^{2}) विद्युतउत्प्रेरक पर उनकी चयनात्मकता से पता चला कि उनकी उत्पादन अधिशोषित हाइड्रोजन की उपलब्धता पर निर्भर थी, जो बदले में विद्युतउत्प्रेरक की पसंद और लागू क्षमता के साथ भिन्न थी। एक सह-विद्युतनिक्षेपण Ni-Cu इलेक्ट्रोड से Cu की नक़्क़ाशी, इसके बाद Cu के पुन: स्थिति ने Cu सूक्ष्मचद्दर का निर्माण किया, जिसे Cu-NPNi/NF कहा जाता है। NF के लिए Cu- सूक्ष्मचद्दर और द्विधातु Ni-Cu के गठन के परिणामस्वरूप Cu, Pt और NF की तुलना में एफए और एचएफ गठन दरों में वृद्धि हुई। चूंकि क्षारीय माध्यम ने विद्युतउत्प्रेरक के प्रकार के लिए दायरे को चौड़ा किया, धातु-ऑक्साइड (In_2O_3, Co_3O_4, $Pb_2Ru_2O_{7-x}$) विद्युतउत्प्रेरक का उपयोग करके एफएफ वि.रा.ह का अध्ययन किया गया। प्रयोगात्मक और सैद्धांतिक अध्ययनों के माध्यम से, हमने प्रदर्शित किया कि प्रतिस्पर्धी फर्फुरल और हाइड्रोजन सोखना प्रक्रियाओं की बाध्यकारी ऊर्जा और संग्रह ने एचएफ ($S_{एफए / एचएफ}$) पर एफए की चयनात्मकता निर्धारित की। लैंगमुइर-हिंशेलवुड तंत्र को एफएफ वि.रा.ह के दौरान विद्युतउत्प्रेरक P′-$Pb_2Ru_2O_{7-x}$ के साथ शामिल पाया गया था, जिसके परिणामस्वरूप एफएफ और हाइड्रोजन की उच्च सतह संग्रह हुई जिससे चयनात्मक एफए गठन हुआ।

एफए और एचएफ गठन दरों को बढ़ाने के लिए विद्युतउत्प्रेरक को स्केल करने के लिए, एक गुट विद्युतरासायनिक उपकरण बनाया गया था जिसमें तापीय रूप से बनाए गए बड़े सतह क्षेत्र (100 सेमी^{2}) 3 डी-ग्रेफाइट महसूस कैथोड ने एचएफ गठन दर और एचएफ चयनात्मकता को क्रमशः 5.2 ± 0.16 मिलीमोल घंटा$^{-1}$, और 65.7 ± 1.9% एचएफ के रूप में उत्पन्न किया, जिसमें वि.रा.ह के 3 घंटे में 97.7% रूपांतरण था। एक चांदी जमा NF कैथोड (100 सेमी^{2}) को 10.5 ± 0.5 मिलीमोल घंटा$^{-1}$ एफए गठन दर और 78.2 ± 2.1% एफए चयनात्मकता प्राप्त करने के लिए एक निर्मित निरंतर प्रवाह (प्रवाह दर = 10 मिलीलीटर मिनिट्$^{-1}$) विद्युतरासायनिक उपकरण में नियोजित किया गया था। इसके अलावा, सौर रोशनी ने प्रकाशिक विद्युत् रसायनिकी उपकरण (Cu-NPNi|TiO_2) के रूप में विद्युत ऊर्जा की आवश्यकता को कम कर दिया और विद्युतरासायनिक उपकरण (Cu-NPNi / NF) से प्राप्त एफए गठन दर को प्राप्त करने के लिए कम लागू पूर्वाग्रह को दर्शाया। जैवभार रूपांतरण में सौर रोशनी के उपयोग की व्यवहार्यता को मान्य करने के लिए एफएफ वि.रा.ह को कैथोड और एफयू, एफएन में एफएन को सह-उत्पादन करने के लिए एफएफ के प्रकाशिक विद्युत् रसायनिकी ऑक्सीकरण के साथ जोड़ा गया था। कुल मिलाकर, एफएफ वि.रा.ह से उत्पादित एफए और एचएफ में उच्च गठन दर और एक प्रतिस्पर्धी बाजार मूल्य निर्धारण था, जिसे उद्योगों द्वारा बढ़ाया और व्यावसायीकरण किया जा सकता था।

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ECH	Electrocatalytic hydrogenation
FF	Furfural
FA	Furfuryl alcohol
HF	Hydrofuroin
FU	Furoic acid
FN	2(5H)-Furanone
NF	Nickel foam
HER	Hydrogen evolution reaction
TCH	Thermal catalytic hydrogenation
GF	Graphite felt
T-GF	Thermal treated GF
UT-GF	Untreated GF
OER	Oxygen evolution reaction
HC800	Batch electrochemical reactor
EHG	Electro-hydrogenator
EC	Electrochemical cell
PEC	Photoelectrochemical cell
TEMPO	2,2,6,6-Tetramethylpiperidinyloxyl

List of Abbreviations

PECO	Photoelectrochemical oxidation
CV	Cyclic voltammetry
LSV	Linear sweep voltametry
NMR	Nuclear magnetic resonance
HPLC	High-performance liquid chromatography
ECSA	Electrochemical active surface area
SEM	Scanning electron microscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
R_{FA}	Rate of formation of FA
R_{HF}	Rate of formation of HF
R_{FU}	Rate of formation of FU
R_{FN}	Rate of formation of FN
% S_{FA}	Percentage selectivity of FA
% S_{HF}	Percentage selectivity of HF
% C_{FF}	Percent conversion of FF
$S_{FA/HF}$	Selectivity of FA over HF
H_{ads}	Adsorbed hydrogen
FF_{ads}	Adsorbed furfural

List of Abbreviations

θ_{FF}	Surface coverage by FF_{ads}
θ_{H}	Surface coverage by H_{ads}
BE_{FF}	Binding energy of FF_{ads}
BE_{H}	Binding energy of H_{ads}
O_{vac}	Oxygen-vacancy
J_T	Total current density
J_{FA}	Partial current density for FF
J_{HF}	Partial current density for HF
% Y	Percentage yield
η_s	Electrical energy saving efficiency