CATALYTIC OXIDATIVE AND NON OXIDATIVE STEAM REFORMING OF BIO-ETHANOL FOR HYDROGEN GENERATION

TARAK MONDAL

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2016

CATALYTIC OXIDATIVE AND NON OXIDATIVE STEAM REFORMING OF BIO-ETHANOL FOR HYDROGEN GENERATION

by

TARAK MONDAL

DEPARTMENT OF CHEMICAL ENGINEERING

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2016

Dedicated to

My Parents

CERTIFICATE

This is to certify that the thesis entitled, **"CATALYTIC OXIDATIVE AND NON OXIDATIVE STEAM REFORMING OF BIO-ETHANOL FOR HYDROGEN GENERATION"** submitted by **Mr. Tarak Mondal** to the **Indian Institute of Technology Delhi** for the award of degree of **Doctor of Philosophy** is a record of original bonafide research work carried out by him under my guidance and supervision. The thesis has reached the standards of fulfilling the requirements of the regulations of Indian Institute of Technology Delhi for awarding the degree.

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.

Date:
New Delhi

Dr. Kamal K. Pant (Superviser)
Professor
Department of Chemical Engineering
Indian Institute of Technology Delhi, India

Dr. Ajay K. Dalai (Co-superviser)
Professor
Department of Chemical and Biological Engineering
University of Saskatchewan, Canada

ACKNOWLEDGMENTS

First of all I would like to thank my supervisor, Prof. K. K. Pant, Professor, Department of Chemical Engineering for the motivation, inspiration and keen interest throughout my research work. Since last five years, he has been my mentor and a huge source of inspiration. Despite of busy schedules, he used to review all the results, reports, journal papers and thesis progress. His valuable suggestions and corrections helped me to complete this work. Without his unconditional support, the reported work wasn't so easy for me. It was a fortunate and unforgettable experience to work under his reflective and revered guidance. His friendly nature and endless kindness can't be thanked adequately here.

The encouragement, motivating and needful suggestions given by Prof. Ajay K. Dalai (Co-supervisor), University of Saskatchewan, Canada throughout my research work and during my stay in Canada to carry out part of my research work at University of Saskatchewan, Canada through Graduate Student Exchange Program (GSEP) by Canadian Commonwealth Program, are solely acknowledged. Prof. Dalai's consideration during my research period and the support to work at University of Saskatchewan, Canada provided me phenomenal opportunities for which I will always be grateful.

I am also thankful to Prof S. Basu and Prof. R. Khanna, Head, Chemical Engineering Department, for providing me all the necessary facilities during the course of my work at IIT Delhi. The encouragement, critical reviews and important suggestions given by Prof. S. Roy, Prof. S. K. Gupta, Prof. A. Ramanan throughout my research work are greatly acknowledged. I wish to convey my sincere thanks to Prof. S. N. Naik, Dr. U. Sreedevi for their encouragement

and motivation towards the research work. I also wish to thank the other faculty members and office staff of the Department.

The acknowledgement is incomplete without recognition to Dr. Sachchit Majhi, Dr. Snehal Parmar, Dr. Dinesh Kumar, Dr. Sushil Sarawat, Dr. Pravakar Mohanty, Dr. Satyen Kumar Das, Dr. Vikrant Sarin, Mr. Ritesh Mittal, Ms. Sonal, Mr. Samuel Kassaye, Mr. Rohit Kumar, Mr. Sonit Balyan, Mr. Kaushal Parmar, Mr. Saurabh Mishra and Mr. Ejaz Ahmad and all the other Research Scholars with whom I have worked during my Ph.D. at Catalytic Reaction Engineering Laboratory (CRE), IIT Delhi. I am highly obliged to U.G. and P.G. students of CRE Lab, IIT Delhi viz. Mrs. Madhumita Patel, Mr. Tarun Krishna Jindal, Mr. Mukul Sajnani, Ms. Nidhi Kaur, Mr. Omkarram Ajgaonkar, Mr. Pavan Dhamne, Mr. Mohit Khatri, Mr. Kantesh Malviya, Mr. Ayunachew Zewdu, Mr. Mayank Agrawal, Mr. Deepankar Gautam, Mr. Bhuvnesh Sharma, Mr. Satish Kumar, Mr. Manas Mishra and others are highly acknowledged for their concern and support. I am grateful to my friends and colleagues of IIT Delhi Dr. Garima Chauhan, Dr. Jogender Singh, Mrs. Perminder Dua, Mr. Vikash Kardam, Dr. Jay Pandey, Dr. Kishore, Mr. Dinesh Attarde, Mr. Manish Jain, Mr. Rajat Gupta, Mr. Tanmoy Patra and Mr. Deepak Sharma for their help and support during my research work.

I was fortunate to have an excellent work environment in Prof. Dalai's laboratory, at Chemical and Biological Department in University of Saskatchewan, Canada which facilitated my work to a great deal. I also acknowledge Saskatchewan Structural Science Centre (SSSC) and Canadian Light Source (CLS) synchrotron facility to provide me the opportunity to work there. I am highly thankful to Dr. Umasankar Das, Ms. Heli Eunike, Mr. Richard Blondin and Mr. R Lee for their constant help in every possible way to carry forward my research there. I am also thankful to Mr. Ashish Somidi, Dr. Kalpana Maheria, Dr. Ashwini Tiloy, Dr. Rajesh

Sharma, Dr. Rambabu Nedunuri, Dr. Jackson Chitanda, Mr. Sandeep Badoga, Mr. Chinmoy Baroi, Mr. Kang Kang, Ms. Prachee Misra and others for their help and support during my stay in Canada.

I wish to thank Chemical Engineering Office staff for their constant support. I wish to thank Library management staff, IIT Delhi for providing all the necessary material (books, e-journals, e-books etc.) to carry forward my research work. I also wish to thank management of Girnar Hostel where I stayed during my tenure. I was fortunate to have an excellent work environment in the laboratory, which facilitated my work to a great deal. For this, I am highly thankful to Mr. Vishesh Kumar, Mr. Krishan Kumar, Mr. Suchit Kumar Pal and Mr. Vijay Pal for their constant help in every possible way to carry forward my research work.

I have no words to express motivation and inspiration given by my father and mother to me, whose courage through their life have been a spiritual inspiration to me and holds no bounds. Their encouraging words and deeds through these tough physical and emotional times will always remain in my heart and soul. I also wish to say thanks to my elder sisters Mrs. Mamata, Mrs. Sabita, and brother-in-law Mr. Pintu Moyra for their help, support and advices during the period. I am also thankful to my friends Mr. Sabir, Mr. Mrinal for their constant moral support during my studies.

Herewith I would like to thank all of those, who have directly or indirectly contributed to the realization of this thesis. Last but not the least, a note of heartfelt devotion to almighty GOD, who has made me capable of accomplishing this acclivitous task.

New Delhi **(Tarak Mondal)**

October 2016

ABSTRACT

Hydrogen production from renewable sources has attracted great attention due to its high energy efficiency, pollutants- free emission and diverse applications. Among various biomass feedstocks available, bio-ethanol is most attractive for large-scale production of H_2, due to its high hydrogen content, non-toxicity, growing availability, renewability and low production cost. Among the several processes available for hydrogen production from bio-ethanol, steam reforming is one of the most promising routes as it gives highest hydrogen yield with negligible CO_2 emission. Therefore developing a stable and highly selective catalyst for H_2 yield maximization and CO minimization during steam reforming of ethanol at optimum conditions is of core importance.

In the present work, catalytic oxidative and non-oxidative steam reforming of bio-ethanol for hydrogen production was studied over Ni/CeO_2-ZrO_2 and Rh-Ni/CeO_2-ZrO_2 catalysts. The catalysts were prepared by impregnation-co-precipitation method. Physico-chemical properties of the as prepared catalysts were characterized by various characterization techniques *viz.* N_2 adsorption desorption, X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption (TPD), Chemisorption, thermo-gravimetric analysis (TGA), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), scanning electron microscopy (SEM-EDX) and transmission electron microscopy (TEM) techniques. Characterization results showed that addition of ZrO_2 in CeO_2 lattice improves the oxygen storage capacity of mixed oxides support, which in turn improves catalytic activity.

Characterization of metal supported catalysts revealed that the addition of Rh promotes reducibility of NiO at lower temperature for the bimetallic catalysts. Prior to the experiment, thermodynamics analysis for both oxidative and non-oxidative steam reforming of ethanol was carried out by Gibbs free energy minimization method as a function of temperature, steam to ethanol (S/E), and oxygen to ethanol (O/E) molar ratios. Thermodynamic analysis was conducted to improve the understanding of the viability of reaction-product model systems and develop relationships between process variables (i.e., temperature, steam to ethanol ratio (S/E), oxygen to ethanol ratio (O/E)), and the product distribution. Effects of temperature (400-700°C), ethanol/water/oxygen molar ratio, and space time (3.67 to 9.17 kg_{cat} h/kmol[EtOH]) on ethanol conversion and product selectivity were investigated in a tubular fixed bed reactor at atmospheric pressure.

Ethanol conversion and hydrogen yield increased progressively with temperature and reached maxima at 600°C. Conversion and H_2 selectivity increased with increasing contact time while CO and CH_4 selectivity decreased. Compared to SRE, complete ethanol conversion was achieved during OSRE at 600°C with a maximum hydrogen yield of 4.6 mol/mol over 1%Rh-30%Ni/CeO_2-ZrO_2 catalyst. Rh promoted catalyst exhibited better catalytic activity than 30%Ni/CeO_2-ZrO_2 catalyst for both oxidative and non-oxidative steam reforming of ethanol, indicating that addition of Rh improved the catalytic activity significantly by promoting water gas shift and methane steam reforming reactions. During the steam reforming of crude bio-ethanol approximately 81% ethanol conversion was achieved with 59% hydrogen selectivity on Ni/CeO_2-ZrO_2 catalyst, whereas, higher ethanol conversion (86%) with 73% hydrogen selectivity was achieved using Rh-Ni/CeO_2-ZrO_2 catalysts. In oxidative steam reforming of crude bio-ethanol, hydrogen yield and selectivity reduced due to the partial oxidation of oxygenate

compounds present in the feed. The used catalysts were also characterized to identify the cause of catalyst deactivation. The results indicate that the catalyst deactivation occurred mainly due to amorphous and filamentous carbon deposition on the catalysts surface, due to the presence of the impurities in the feed.

The kinetic analysis was carried out for the rate data obtained for oxidative steam reforming of ethanol. Three mechanistic kinetic models were developed using Langmuir-Hinshelwood approach based on three proposed surface reaction mechanisms for the oxidative ethanol steam reforming process. Two distinct types of active sites, one for carbon and oxygen containing species and other for adsorption of hydrogen were considered. The Langmuir-Hinshelwood kinetic model (LH-II) were developed by considering dehydrogenation of adsorbed ethoxy species, decomposition of formate species, and decomposition of acetaldehyde as the rate determining steps for OSRE, rWGS and ED respectively. The model fits reasonably well to the experimental results at all the temperatures (500, 550 and 600 °C) and contact times (0 – 9.17 kg_{cat} h/kmolEtOH) studied. The activation energy for OSRE, WGS and ED reactions obtained were 56.0, 46.1 and 34.8 kJ/mol, respectively.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

D_{eff}	effective diffusivity, $m^2\ s^{-1}$
D_{AB}	bulk diffusivity of component A in B, $m^2\ s^{-1}$
ε	void fraction
τ	tortuosity factor
E_i	activation energy for rate constant of reaction i, kJ mol^{-1}
H_i	enthalpy of species i of reactants or products, kJ mol^{-1}
ΔH_i	heat of adsorption for species i, kJ mol^{-1}
ΔS_i	entropy of adsorption for species i, J $mol^{-1}\ K^{-1}$
λ_{eff}	effective thermal conductivity, kJ $m^{-1}\ s^{-1}\ K^{-1}$
λ	molecular thermal conductivity, kJ $m^{-1}\ s^{-1}\ K^{-1}$
N_{Re}	Reynolds number based on particle
C_{A_s}	concentration of ethanol at the pellet surface, kmol m^{-3}
C_{A_C}	concentration of ethanol at the centre of the pellet, kmol m^{-3}
$-r_{A_{obs}}$	observed rate of reaction, kmol $m^{-2}\ s^{-1}$
L	characteristic length of catalyst pellet, m
h	heat transfer coefficient of fluid, kJ $m^{-2}\ s^{-1}\ K^{-1}$

ρ_C	pellet density, kg m^{-3}
ρ_b	bulk density, kg m^{-3}
R_C	radius of the catalyst particle, m
k_C	mass transfer coefficient, m s^{-1}
n	reaction order
K_i	equilibrium constant of reaction i or adsorption coefficient for surface species i
k_i	rate constant for reaction i, m^2 s^{-1} mol^{-1}
k_i^∞	pre exponential rate constant for reaction i, m^2 s^{-1} mol^{-1}
r_i	rate of reaction i, kmol m^2 s^{-1} or rate of reaction of formation of component i, kmol $kg_{cat}^{-1}s^{-1}$
S_A	surface area of catalyst, m^2 g_{cat}^{-1}
C_S	concentration of site S, mol m^{-2}
C_{S_i}	concentration of site S_i, mol m^{-2}
C_T	total surface concentration of site S, mol m^{-2}
C_{T_i}	total surface concentration of site S_i, mol m^{-2}
d_p	average pore diameter, m
V_g	volume of liquid adsorbate, cm^3
S_g	BET surface area, m^2 g_{cat}^{-1}

$\tau(\theta_p)$	profile t value for parameter θ_p
$\delta(\theta_p)$	standardized value of parameter θ_p
P	operating pressure, atm
P_i	partial pressure of component i, atm
T	temperature, K
T_m	mean temperature, K

Subscripts

1	for active site S_1
2	for active site S_2
i	reaction or product species

Superscripts

	for reaction mechanism 1, RM-I
'	for reaction mechanism 2, RM-II
''	for reaction mechanism 3, RM-III

Greek letters

λ	X-ray wavelength
κ	constant in XRD
θ	radiation angle
β	peak width at half height

Acronyms

Atm	atmosphere
BJH	Barrett-Johner-Halenda
BE	binding energy
BET	Brunauer-Emmett-Teller
DTA	differential thermal analysis
ID	inner diameter
FID	flame ionization detector
FTIR	Fourier transform infrared spectroscopy
GHSV	gas hourly space velocity
JCPDS	joint committee on powder diffraction standards
LH	Langmuir-Hinshelwood
MRSS	mean residual sum of squares
PID	proportional integral derivative
RDS	rate determining step
RM	reaction mechanism
SEM	scanning electron microscopy
EDX	energy-dispersive X-ray spectroscopy
TEM	transmission electron microscopy
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near edge structure
EXAFS	extended X-ray absorption fine structure

HXMA	hard X-ray Micro-Analysis
SGM	spherical grating monochromator
CLS	Canadian light source
STP	standard temperature and pressure
TCD	thermal conductivity detector
TGA	thermal gravimetric analysis
TPD	temperature programmed desorption
TPR	temperature programmed reduction
TOS	time-on-stream
W/F	weight of catalyst/molar flow rate of ethanol
WI	wet impregnation
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy
OSRE	oxidative steam reforming of ethanol
SRE	steam reforming of ethanol
POX	partial oxidation of ethanol
WGS	water gas shift
rWGS	reverse water gas shift
ED	ethanol decomposition
Eq	equation
Rxn	reaction