

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

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**DEPARTMENT OF CHEMICAL ENGINEERING
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by

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DEPARTMENT OF CHEMICAL ENGINEERING

Submitted

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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.

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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 H₂, 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 CO₂ emission. Therefore developing a stable and highly selective catalyst for H₂ 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/CeO₂-ZrO₂ and Rh-Ni/CeO₂-ZrO₂ 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.* N₂ 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 ZrO₂ in CeO₂ 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 H₂ selectivity increased with increasing contact time while CO and CH₄ 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/CeO₂-ZrO₂ catalyst. Rh promoted catalyst exhibited better catalytic activity than 30%Ni/CeO₂-ZrO₂ 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/CeO₂-ZrO₂ catalyst, whereas, higher ethanol conversion (86%) with 73% hydrogen selectivity was achieved using Rh-Ni/CeO₂-ZrO₂ 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.

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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, $\text{m}^2 \text{s}^{-1} \text{mol}^{-1}$
k_i^∞	pre exponential rate constant for reaction i, $\text{m}^2 \text{s}^{-1} \text{mol}^{-1}$
r_i	rate of reaction i, $\text{kmol m}^2 \text{s}^{-1}$ or rate of reaction of formation of component i, $\text{kmol kg}_{\text{cat}}^{-1} \text{s}^{-1}$
S_A	surface area of catalyst, $\text{m}^2 \text{g}_{\text{cat}}^{-1}$
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, $\text{m}^2 \text{g}_{\text{cat}}^{-1}$

$\tau(\theta_p)$	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