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It is certified that the work contained in the thesis titled "**Renewable hydrogen production by catalytic steam reforming of ethanol**" by **Mr. Ashutosh Kumar** has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. Degree.

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DECLARATION BY THE CANDIDATE

I, **Ashutosh Kumar**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of **Prof. Yogesh Chandra Sharma** from July-2012 to July-2017, at the **Department of Chemistry**, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

Date: 04/01/18

Place: Varanasi.

Ashutosh Kumar

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CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my/our knowledge.

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List of Abbreviations

Å	Angstrom
cps	Counts per second
eV	Electronvolt
F	Molar flow rate
FT-IR	Fourier transform infrared
g	Gram
GC	Gas Chromatography
GHG	Greenhouse Gases
h	Hour
IEA	International Energy Agency
JCPDS	Joint Committee on Powder Diffraction Standards
Kg	Kilogram
KJ/mol	Kilojoule per mole
kV	Kilovolt
M	Molar
mA	Milliamppere
mg	Milligram
min	Minute
MJ	Megajoule
mmol/g	Millimole per gram
N	Stoichiometric factor
nm	Nanometre
pH	Potential of hydrogen
rpm	Revolution per minute
SH_2	Selectivity of hydrogen
SCO_2	Selectivity of Carbon Dioxide
SCO	Selectivity of Carbon Monoxide

SCH_4	Selectivity of Methane
SC_2H_4	Selectivity of Ethylene
SCH_3CO	Selectivity of Acetone
SCH_3CHO	Selectivity of Acetaldehyde
SC_2H_6	Selectivity of Ethane
$SC_4H_8O_2$	Selectivity of Ethyl acetate
T	Temperature (K)
W_{cat}	Weight of catalyst
wt%	Weight percent
X	Conversion
°C	Degree Celsius
K	Kelvin
λ	Lambda
μm	Micrometre
%	Percent
θ	Theta

Preface

The factors contributing the climate change, pollution or greenhouse gasses must be check for the betterment of upcoming generations. Sustainability of future energy sources is still a matter of debate. Recently, there is a successful commercialization of fuel cell technology and other appliances to practice the hydrogen as an energy carrier. The future fuel cell technology in market required more renewable hydrogen generation in the near future. The huge amount of hydrogen production is vital to fulfilling our requisite but not at the cost of environmental disputes. Hence, it requires the renewable sources of hydrogen. On industrial scale, thermal steam reforming is upcoming sustainable approach comparative to other available options. Considering these scenario ethanol steam reforming (ESR) is one of the best option for hydrogen generation in the near future. The cost of catalyst contributes the overall cost of hydrogen. Recent studies confirms that the noble metal catalysts are more active compared to non-noble, but noble metal catalysts are not cost effective. However, noble metal catalysts are typically highly stable, but deactivation by carbon deposition were reported too. Hence, the deactivated catalyst regeneration or catalyst reformulation from deactivated catalyst could be a cost effective approach. If the high temperature tolerant catalyst can be synthesized then after carbon deposition it can be regenerated by oxidation of carbon at optimum temperature.

Among non-noble metal catalyst Ni and Co has viable catalytic performance regarding hydrogen selectivity. In metallic state, Co is not only active to perform the ESR but also facilitates the filamentous carbon formation and get deactivated. Study of temperature program reduction showed that reduction of NiO is easy if the interaction between the support and metal is weak. But it is not only facile to be sintered but also resulted in formation in larger particles, vulnerable for carbon formation. However, this deactivated form of metal and carbon mixture contains highly dispersed metal. The strong interaction between metal and support leads to lower generation of carbon. A number of workers studied ESR on the noble and non-noble metal over different kinds of oxide support such as Al_2O_3, CeO_2, ZnO, MgO, ZrO_2 and SiO_2 with variation of metal loading.

Therefore, considering these scenario this work includes the active non noble metal catalyst, the deactivation of catalyst, reformulation of deactivated catalyst, effect of pre-treatment conditions on catalyst for ESR and bimetallic non noble nano catalyst for ESR. The physico-chemical properties of catalysts were characterised with several instrumental techniques such as HR-XRD, ATR-FTIR, HR-SEM, TEM with SAED, EDAX, surface area analyser and TPR. The carbon deposition mechanism involved in Co catalyst was explored. The perovskite-cobalt composite catalyst was prepared via nanocasting approach from the spent catalyst deactivated by carbon deposition. The reduction atmosphere as well as redox atmosphere effects on product selectivity by nano Co/CeO_2 based catalyst was analysed. The special structured mixed metal oxide such as spinel, perovskite and hydrotalcite have a homogenous distribution of atoms as well as excellent sintering stability. Therefore, ZSM-5 supported Ni and Co based catalyst was used for ESR performance. The bimetallic effect of Ni and Co was also evaluated and CeO_2 supported nano bimetallic catalyst was optimized for ESR reaction. The novel route of nano catalyst was also discovered and the activity of synthesized catalysts were evaluated by performing ESR. Investigations were carried out on influence of reaction variables such as loading of active bimetallic catalyst, water: ethanol molar ratio, reaction temperature, and catalyst reusability to find out optimal reaction conditions.