Synthesis and Characterization of Catalyst for Hydrogen Production from Hydrocarbons

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Dedication

This thesis is dedicated to my Parents and my teacher for their endless support and encouragement.

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Abstract

Depletion of oil reserves, current hike in crude oil prices and air pollution by burning of fossil fuels are factors which induce researchers to make hydrogen available for use as energy resource. Currently, hydrogen is derived from non-renewable natural gas and petroleum, but in principle, could be generated from renewable resources such as biomass or water. Hydrogen, due to its higher energy value, proves to be an alternative energy source. Currently, most common method to produce hydrogen is reforming of fossil fuels. Many studies have been done for the purpose using various feed-stocks. In this research, catalytic performance of supported metals for H_2 production by steam reforming of bio-ethanol in the temperature range of 400-850 ^oC, is presented. Catalysts were prepared by impregnation and sol-gel method. Experimental results based on using catalysts prepared by both methods, suitability of support for bio-ethanol conversion to H_2, and stability of prepared catalysts are evaluated. Co, Ni, Ru were used as active metals supported on Al_2O_3, ZrO_2, CeO_2, SiO_2, ZnO, TiO2 and China Clay. 1-20% metal loading was used. Characterization of catalysts was done by XRD, SEM and BET surface area. Catalysts' activity as well as their selectivity can be controlled by means of pore size and volume during synthesis. It was observed that ethanol conversion increases significantly when Al_2O_3 and ZrO_2 supported catalysts are used with bio-ethanol being almost completely converted to hydrogen and other fractions. These findings suggest that catalytic reforming of bio-ethanol could prove to be suitable for generation of hydrogen rich fuel gas from renewable biomass.

Key words: Hydrogen Production, Steam Reforming, Bio-Ethanol

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List of Abbreviations

SR	Steam Reforming
ESR	Ethanol Steam Reforming
POX	Partial Oxidation of Hydrocarbons
ATR	Auto-Thermal Reforming
WGS	Water-gas Shift Reaction
WEC	World Energy Consumption
W/E	Water/Ethanol (Ratio)
IWI	Incipient Wetness Impregnation
SG	Sol-Gel
FC	Fuel Cell
GHG	Green House Gas
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
S_{BET}	Bet Surface Area
NO_x	Nitrogen Oxides
SO_x	Sulphur Oxides
LHV	Lower Heating Value
HHV	Higher Heating Value
Btu	British Thermal Unit
MPa	Mega Pascal
kPa	Kilo Pascal
NASA	National Aeronautics and Space Administration (USA)
EIA	Energy Information Administration (USA)

ΔH	Heat of Reaction
Kg/m^3	Kilogram per cubic meter (Density)
rxn	Reaction

Conference/Journal Publications

i. Ali Waqas, Shahid Hussain Ansari, Mohammad Bilal Khan, Shahid Naveed, Generation of Hydrogen-Rich Fuel Gas from Renewable Biomass and Low Value Hydrocarbons by Heterogeneous Metallic Catalysis, International Workshop on Renewable Energy Technologies in Pakistan, Dec 16-18, 2014, organized by University of Agriculture, Faisalabad, Pakistan (Accepted)*

ii. Muhammad Ali Uzair, Ali Waqas, Shahid Hussain Ansari, Muhammad Anees ur Rehman, Application of Acid Treated Kaolin Clay for Conversion of Polymeric Waste Material into Pyrolysis Diesel Fuel, International Conference on Energy Systems and Policies (ICESP-2014), Nov, 24-26, 2014, organized by Air University, Islamabad, Pakistan (Accepted)**

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Chapter 1

Introduction

Intensity between this planet and Human systems has increased drastically over the last few decades due to acceleration in development in various socio-economic sectors such as technology, trade, population etc. Due to these undeniably momentous changes, the consequences are also substantial. Natural resources of earth are being consumed at rapid rates; various technological practices cause soil degradation, fuel price escalations, food challenges etc. Three of the many arising problems are closely related to each other [2]: Climate change due to increase in greenhouse gases, Disposal of Waste, and Need of alternate energy resources which pose lesser or no threats to the environment.

1.1 Climate Change

The major factors which indicate the climate change are rise in temperature of air and ocean, melting of glaciers, consequent sea level rise and floods. Temperature of earth surface has been rising at the rate of 0.1-0.16 ^{o}C per decade over last 50 years. Most of the heat (80%) entering the climate is absorbed by oceans. This fact could justify the increase in weather activities in parts of world, some of which are tornado in US (2011), floods in Pakistan (2010), China floods (2011) and many more [2].

1.2 Energy

Energy security is a parameter on which a country's economy of a country depends primarily. Currently, petroleum fuels are being used globally to meet energy demands, but their excessive consumption has resulted in considerably high levels of pollution and fuel prices. In near future, a decline in annual global production of these sources will cause escalation in demand and consequently, in prices of fossil fuels, resulting in higher dependence of economic developments on availability and consumption of these fuels. Greenhouse emissions, acid rain are few of the many environmental issues being faced due to fossil fuel combustion. Rising demand of clean energy resources is comprehensible. Global economic growth can only be supported if energy demands are met efficiently, decreasing harmful effects on atmosphere. World energy consumption in quadrillion Btu is shown in figure 1.1 [8]. 49% increase in energy demand is expected from 2007 to 2035.

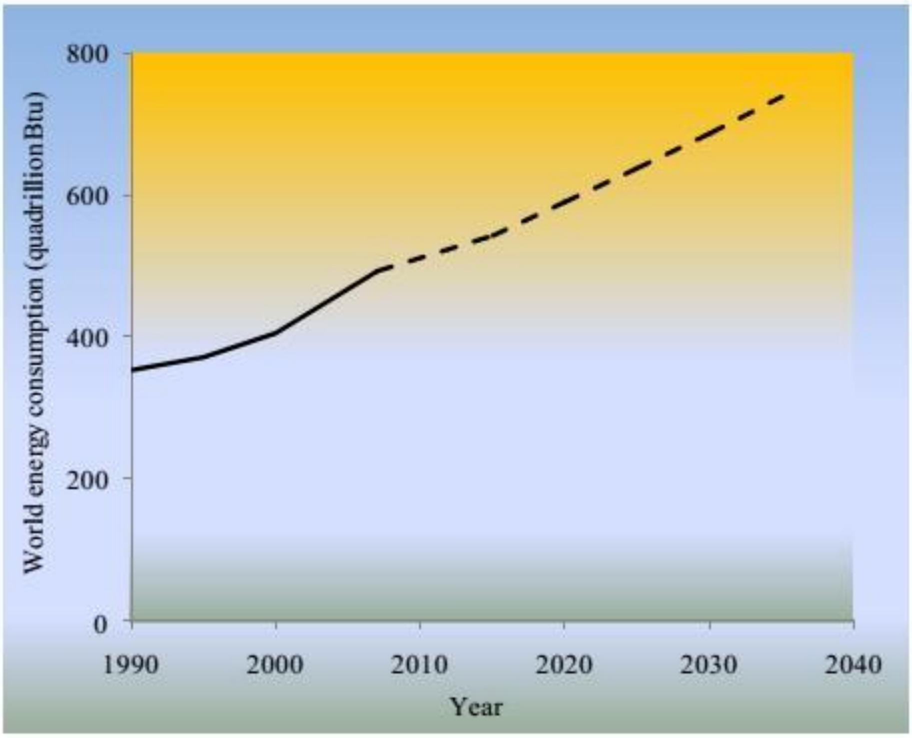

Figure 1.1: World energy consumption. Dashed line is projections from 2009 to 2035. Adapted from EIA [8]

In recent years, development of alternate energy resources has been focused to replace fossil fuels with cleaner, available and renewable energy resources, gradually. Among prospective renewable resources solar, wind and biomass have gained substantial approval. Bio-fuels can prove to be beneficial and effective as they do not affect carbon cycle; they would simultaneously be produced and consumed resulting in a balance of carbon in environment.

1.3 Hydrogen - An alternate energy source

Among many alternate energy technologies, hydrogen and fuel cells seem to be the most efficient substitute of conventional energy systems. Fuel cells use pure hydrogen or hydrogen rich gas, converting its chemical energy to electrical energy.

Hydrogen being an energy carrier can provide a gateway to a variety of new technological options in energy sector. In known universe, hydrogen is most abundant element. It is, however, rarely found on earth. Major reason for this unique existence is the smaller atomic size and chemical activeness. It combines readily with other elements, hence, not found in atomic form on earth [1]. Due to second lowest boiling point (–252.78°C) of all matter, pressurization won't be of greater help to raise its boiling point. Due to this property, storing hydrogen is quite difficult, if not impractical, to store it in liquid form [1]. As a result, hydrogen as an automotive fuel has been stored more often as a pressurized gas than a cryogenic liquid in on-board fuel tank [1]. Due to the smallest size of its molecule, hydrogen can diffuse into materials which are impenetrable by other gases and liquids. Materials can become brittle if they are exposed to hydrogen atmosphere for longer periods. Research and development is underway to develop techniques which could be helpful in developing hydrogen storage, though, there has not been much success in this area so far [1].

Hydrogen gas is combustible having a broad variety of ignition concentrations in air than other available fuels [1]. The hydrogen–oxygen combustion follows the exothermal chemical reaction:

$$2H_2 + O_2 \rightarrow H_2O + \Delta H \qquad (1.1)$$

The enthalpy, *H*, of the combustion product is 285.83 kJ/mol (higher heating value or HHV) and 241.82 kJ/mol (lower heating value or LHV) for the conditions of 25°C and 101.325 kPa [1]. Lower heating value represents the amount of energy which is available for use.

Few basic properties of hydrogen are shown in table 1.1 in comparison with other available fuels. Hydrogen has the highest energy content per kg among all known combustion fuels. Hydrogen itself becomes the energy carrier of the source (biomass, fossil fuels, nuclear etc.) used to produce it. Most common resources for hydrogen production are coal, oil and natural gas.

As compared to gasoline, hydrogen is a low volume-dense fuel. As a result, a gas fuel tank of 7 kg compressed (35 MPa) hydrogen sized to travel a range of 700 km requires a net tank volume of about 300 L in a gas tank, comparing to about 70 L of gasoline tank in a conventional gasoline engine car for the range. Although liquid hydrogen tank requires a third of storage volume of gas tank, this approach incurs energy consumption for hydrogen liquefaction and challenges tank insulation design to prevent boil off [1].

Table 1.1: Comparison of properties of Hydrogen and commercially available fuels

Properties	**Units**	**Hydrogen**	**Methane**	**Propane**	**Methanol**	**Ethanol**	**Gasoline**
Density	kg/m^3	0.0838	0.668	1.87	791	789	751
Boiling Point	^{o}C	-253	-162	-42.1	64.5	78.5	27-225
Lower Heating Value	MJ/kg	120.1	47.141	46.28	20.094	26.952	43.448
Higher Heating Value	MJ/kg	142.18	52.225	50.22	22.884	29.847	46.536

1.3.1 Traditional Uses of Hydrogen

Hydrogen plays significant roles in the world economy today. Global hydrogen production is about 50 million tonnes/year, and in 2008, hydrogen consumption of North America and Asia-Pacific was about 30% each, with Western Europe and other regions following with 18% and 22% respectively [1].

Industries are the main consumers of hydrogen gas. Worldwide, major uses of hydrogen are in the production of ammonia and for petroleum refining, on similar scale in both sectors. Other uses are on much smaller scales such as for semiconductor manufacturing, glass production, food preparation, and chemical production. [1]

Some other main hydrogen uses include:

- Food production (hydrogenation of vegetable oils and unsaturated animal fat for production of butter, margarine, cooking oil)
- Hydrogenation of inedible oils for manufacturing of soaps, creams and plastics.

- Methanol (CH_3OH) production, a common industrial chemical (H3OCl) (of worldwide demand of about 30 million tons a year) made from hydrogen reacting with carbon dioxide or carbon monoxide; and hydrochloric acid (H3OCl) used in the manufacturing of numerous other chemical products such as vinyl plastic, polyurethane, and food additives.
- Mixed with argon, Hydrogen is used to enhance plasma welding and metal cutting, including welding of stainless steel.
- Reduction of metal ores for metal production such as Tungsten oxide (WO_3)
- Aerospace programs to fuel spacecraft and life-support systems. For example, the U.S. National Aeronautics and Space Administration (NASA) uses approximately 5000 tons per year of liquid hydrogen for space launches including NASA's space-shuttle flights. Hydrogen is fuel for the shuttle main engines and also for on-bound fuel cells used to power the shuttles' electrical systems, the exhaust of which is only pure water used as drinking water by the crews.
- Semiconductor manufacturing where hydrogen is used as a carrier gas for active trace elements and creates specially controlled atmospheres for etching integrated semiconductor circuits.
- High speed generators in large power plants are cooled with hydrogen due to its higher thermal conductivity.

1.4 Technologies for Hydrogen Production

Global hydrogen consumption amount to about 250×10^9 Nm^3/year with refinery industry being a major consumer (>90%) [3].Technically hydrogen can be produced from any carbon source [3]. The main product of conversion of hydrocarbons including major fossil fuels and bio mass is synthesis gas which is a mixture of hydrogen and carbon monoxide, mainly resulting from the processes of steam reforming, partial oxidation (POX), or auto-thermal reforming (ATR). If the hydrogen product is to be maximized, the conversion processes are followed by the water–gas shift reaction. Finally, hydrogen needs to be separated and purified.

1.4.1 Steam Reforming

In steam reforming, gas phase conversion of a hydrocarbon by reaction with water takes place [5]. It is an endothermic process with CO_2 and H_2 being the only products if reaction proceeds in most desirable way. However, by-products such as carbon monoxide, methane, acetaldehyde and ethylene may form [7]. Steam reforming is an established and most widely used hydrocarbon processing technology to obtain alternate fuels. Other hydrogen production technologies have limited application due to cost issues or meager development of suitable technology [6]. 50% of world hydrogen supply is obtained by steam reforming. First established in 1926, now it has become conventional technology in hydrogen production.

Commercially, H_2 can be produced from various resources. Natural gas has been leading fuel source for this process over long period of time. But due to scarcity of fossil fuels and rising demand, alternate feedstocks are gaining attention of researches. Bio-derived hydrocarbons such as acetone, ethanol etc.) are strong alternate candidates in this regard. These resources are sustainable and pose less threat to environment because of fewer or no emissions of NO_X, SO_X.

Basic reaction equation [3] of SR is given as:

$$C_nH_m + nH_2O \rightarrow nCO + (\quad + {}_2)H_2 \tag{1.2}$$

Product mixture is called reformate [5]. Reaction is endothermic, thus requires heat input.

1.4.2 Bio-Ethanol

Bio-ethanol is a highly attractive sustainable energy source for H_2 generation. Bio-ethanol can be renewably produced from fermentation of biomass, including starch, sugar, and cellulitic and lignocellulitic materials. Hydrogen production from biomass or biomass-derived liquids can theoretically be a carbon-emission-free process because all carbon dioxide released can be recycled back to the plants through photosynthesis. In addition, ethanol is free from impurities such as sulfur. Ethanol is non-toxic and easy to transport. [4] It has been accepted by both academia and industry as an economically and environmentally attractive starting material for H_2 production.

Although methane SR to produce hydrogen has been well recognized for many years, commercial catalysts for this process are not suitable for bio-ethanol reforming because ethanol has C-C bonds in the molecule and the reforming process involves a complex reaction network. [4]

Extensive research on catalytic reforming of bio-ethanol has only been performed in the last ten years. Additional fundamental work is needed to truly understand the reaction mechanism and develop efficient catalysts.

1.4.3 Ethanol Steam Reforming

In theory, ethanol steam reforming occurs via the following reaction [4]:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (\Delta H_{rxn} = 347.4\ \text{kJ/mol at } 25\ ^{o}C) \qquad (1.3)$$

In reality, this reaction never proceeds straightforwardly as shown above. Various components lead to diversity in product distribution. Reaction conditions including temperature, pressure, feed composition and reactor design play a determining role. In addition, depending on types of catalysts, alternative reaction pathways may be favored.

ESR might not be easy as compared to SR of commonly accepted feedstocks because ethylene could be one of the primary products which is precursor of coke formation. [3].Below are some of the possible reactions that may take place during the process. [4]

$C_2H_5OH \rightarrow CH_4 + CO + H_2$ (ethanol decomposition) (1.4)

$C_2H_5OH \rightarrow CH_3CHO + H_2$ (dehydrogenation) (1.5)

$C_2H_5OH \rightarrow C_2H_4 + H_2O$ (dehydration) (1.6)

$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$ (incomplete reforming) (1.7)

$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$ (dehydrative coupling) (1.8)

$CO + 3H_2 \rightarrow CH_4 + H_2O$ (methanation) (1.9)

$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ (steam reforming) (1.10)

$CO + H_2O \rightarrow CO_2 + H_2$ (water - gas shift) (1.11)

$2CO \rightarrow CO_2 + C$ (Boudouard reaction) (1.12)

These side reactions not only lead to an extremely complicated reaction network, but also lower the H_2 yield. Dehydration and Boudouard reactions can induce coking on the catalyst surface and cause pressure build-up in the reactor, together with lifetime shortage of the catalysts.

1.4.4 Challenges in Ethanol Steam Reforming

Many Catalysts have been investigated for ethanol steam reforming including Pt, Pd, Rh, Ru, Ni, Co, Cu, Fe with various supports which may include Al_2O_3, La_2O_3, ZnO, MgO, TiO_2, CeO_2, ZrO_2, SiO_2 etc. Catalysts with noble metallic loadings have shown promising results with appreciably good selectivities. However due to higher costs, these catalysts ate not suitable for use in commercial hydrogen production systems. Base metals have essentially high cost-efficiency which is one of the most desirable benefits. Consequently it is required to develop catalysts free of noble metals with high activity and longer life.

Cobalt catalysts have been reported to show best performance in SR reactions. They give higher hydrogen yields comparatively, however, at higher temperatures in long run, these catalysts deactivate significantly due to coke formation. Nickel due to its carbon tolerance is sort of capable candidate for SR catalysts with earth oxide supports.

1.5 Objective of work

This research work was intended to study the synthesis of suitable catalysts, comparison of different metal catalysts, characterization of catalysts prepared by different methods and effect on steam reforming to produce hydrogen from ethanol.

1.6 Thesis Layout

This thesis consists of five chapters. Details of these chapters is shown below:

Chapter 1: Introduction

Climate Change
Energy
Hydrogen – An alternate Source

Hydrogen Production Technologies
Steam Reforming
Bio-Ethanol
Ethanol Steam Reforming

Chapter 2: Literature Review

Steam Reforming
Support Materials for Ethanol Reforming Catalysts
Active Metals for Ethanol Reforming Catalysts
Catalyst Preparation Method

Chapter 3: Methodology

Materials
Catalyst Preparation
Catalyst Characterization
Reaction Testing

Chapter 4: Results and Discussions

Catalyst Activity in Ethanol Steam Reforming
Characterization Results
Flame Test

Chapter 5: Conclusions and recommendations

Summary and Conclusions
Recommendations

1.7 Summary

World is facing energy crisis due to increased exploitation of natural energy resources. Fossil fuels are limited energy resources due to which their prices fluctuate and keep on rising globally. To strengthen the economy, each country needs to develop sustainable energy solutions in near future. Renewable energy resources are viable solution to the rising problem provided that production and maintenance costs are reduced. Solar, Wind, and Biomass are most discussed alternate energy resources. Among resources generated from biomass, hydrogen is a feasible option due to it higher energy content. There are various feedstocks to produce hydrogen by employing different routes. Bio-ethanol can be used as feedstock in steam reforming to produce hydrogen rich gas. In this research, catalyst synthesis for production of hydrogen-rich-gas via ethanol stem reforming has been focused.

1.8 References

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Chapters 2

Literature Review

2.1 Steam Reforming

Bio-ethanol steam reforming has been a point of focus for researchers in recent years. Different aspects of this process have been extensively investigated. Major areas of concern in ethanol steam reforming are: active metal and its percentage, support material, promoters, method of syntheses, treatment, the reaction mechanism, reaction parameters and process design [2, 3]. Efforts are being made to develop catalysts that show efficient selectivity to desired products, active in converting ethanol, and exhibit stability over long duration of process. Fishtik et al [4] performed a thermodynamic analysis of Ethanol steam reforming and found that thermodynamically it is a feasible process.

2.2 Support materials for Ethanol Reforming Catalysts

The support material plays a decisive role in catalyst development. Choice of support can affect loading amount and dispersion of active metals, which can be further associated with catalyst reducibility, selectivity and activity. Auprêtre et al. [5] examined Al_2O_3, CeO_2-Al_2O_3, CeO_2, and Ce0.63Zr0.37O2 as support for different active metals. They found that one key property for the support was high OH group surface mobility. CeO_2 containing supports were investigated to promote activity with the $Ce_{0.63}Zr_{0.37}O_2$ support being the most promising. Burch et al. [6] examined Al_2O_3 and ZrO_2-CeO_2 supported catalysts. Al_2O_3 supported catalysts had high dehydration activity especially at lower temperatures, which led to coking problems. ZrO_2-CeO_2 supported catalysts significantly improved reaction performance, and there was no ethylene formation. Haga and his coworkers [7] evaluated catalytic performance of Co supported on SiO_2, Al_2O_3, ZrO_2, MgO and C. Al_2O_3 was shown to be highly selective because of its ability to suppress CO methanation and ethanol decomposition. Ticianelli et al. [8, 9] studied Co supported on Al_2O_3, SiO_2 and MgO. The interaction between Co species and supports varied, and was related with catalyst reducibility. All supported catalysts had high conversion levels but they promoted different side reactions which led to serious deactivation in less than 10 hrs. Acid sites on Al_2O_3 facilitated ethanol dehydration, whereas Co/SiO_2 favored methanation and Co/MgO produced the highest amount of CO. Llorca and his coworkers[10, 11] performed an exhaustive study on supported Co catalysts by exploring properties of TiO_2,Al_2O_3, SiO_2, MgO, V_2O_5, ZnO, La_2O_3, and CeO_2. The redox and acid-base properties of the oxides can change the catalytic performance dramatically. Acid surfaces promote the dehydration reaction whereas basic surfaces favor the dehydrogenation reaction. The Co/ZnO formulation was proved to be both selective and active in bio-ethanol steam reforming. In a research [12] by Llorca et al., CO-free H_2 was generated through reforming, catalyzed by Co/ZnO catalysts.

After researchers realized the importance of the support acid-base property, they attempted to modify it by using mixed oxide supports. Duprez and his coworkers [13] developed MgxNi1-xAl_2O_4/Al_2O_3 and $MgAl_2O_4$ spinel oxide supports by co-impregnation and solid-solid reactions of precursors, respectively. These supports were non-acidic and moderately basic and were proved to aid the function of active metals to the best extent. The porous structure of the support was also a parameter in determining metal surface densities and dispersion [14]. Depending on the support, interactions between the support and the metals were significantly different [15]. Jacobs et al. studied how Co species interacted with Al_2O_3, TiO_2, SiO_2, ZrO_2-SiO_2 and ZrO_2-Al_2O_3. Differences in Co cluster particle size on the surface, catalyst reducibility and active site availability during reaction were observed. Sun and his coworkers [16] observed similar phenomena regarding effects of support-metal interactions on catalyst selectivity and activity by studying Ni supported on La_2O_3, Y_2O_3 or Al_2O_3. It was concluded that Ni/Y_2O_3 was a promising catalyst for hydrogen production from ethanol steam reforming with its high activity and long-term stability in low and middle temperature ranges. Verykios et al. [17, 18] studied Ni catalysts supported on La_2O_3, Al_2O_3, YSZ, TiO_2 and MgO. From their testing, Ni/La_2O_3 catalysts exhibited long term stability due to removal of the coke deposition on Ni surfaces by formation of lanthanum oxy-carbonate species. Because of its unique oxygen storage property, CeO_2 has been heavily studied as a support for the ethanol steam reforming. Laosiripojana and coworkers [19] employed a surfactantassisted technique to synthesize high surface area CeO_2 and used it as an internal pre-reforming catalyst under solid oxide fuel cell temperatures to convert all ethanol and other high hydrocarbon compounds. CeO_2 showed excellent resistance toward carbon deposition. Song et al. [20, 21] examined nano-crystalline CeO_2 supported Ni-Rh bimetallic catalysts for oxidative steam reforming of ethanol. Their work indicated that CeO_2 support properties (crystal size and surface area) can modify the catalysts properties in terms of geometry (metal particle size and dispersion) and electron transfer (metal-support interaction). Zhang et al. [22] studied CeO_2 supported catalysts and under harsh conditions (stochiometric ratio of ethanol to water), they observed long term stability for 300 hrs.

2.3 Active Metals for Ethanol Reforming Catalysts

Another important component for ethanol reforming catalysts is the active metal. The nature of the metals can determine ethanol absorption on catalyst surface and reaction pathway. There are two major categories of active metals: noble metals and common metals. Ni, Co, Cu and supported noble metals, like Rh, Pd and Pt have been proven dominant active metals for this process [2].

Nickel has been extensively examined with supports such as Al_2O_3, MgO and ZnO [23]. Fatsikostas et al. reported that for nickel-based catalysts, the Al_2O_3 carrier promoted carbon development. Addition of Lanthana suppressed carbon deposition significantly [24, 25]. Batista et al. performed ethanol steam reforming over Al_2O_3 and SiO_2 supported Co catalysts containing 8 and 18 wt.% cobalt [26]. Only 70% conversion could be achieved at 400 ^{o}C.

Auprêtre et al. [5] compared Rh, Pt, Ni, Cu, Zn and Fe for ethanol reforming. A combination of Rh and Ni led to both high conversion and selectivity. Rh/Al_2O_3 was studied by Cavallaro et al. [28] and Rh greatly promoted the conversion of C2 species produced in the reforming process. Frusteri et al. [29] tested MgO supported Pd, Rh, Ni and Co catalysts supported on MgO for molten carbon fuel cell ethanol reforming. Rh/MgO showed the best performance, though H_2 selectivity was moderate. Other metals suffered from serious sintering at high operating temperature (650 ^{o}C). Rh/CeO_2-ZrO_2 catalyst was evaluated by Idriss et al. [30] and a H_2 yield as high as 5.7 mol per mol of ethanol was achieved at temperature ranges of 350-450 ^{o}C when water was in excess. Rh was also examined by Verykios et al [18] and found to be other noble metals when metal loading was low. Ru supported catalyst activity was dramatically improved with increased loadings. Piscina et al. [31] studied the Pd/ZnO system and activity was attributed to Pd-Zn alloy formation. However, CO and acetaldehyde selectivities were quite high with this catalyst. Pd was impregnated on Al_2O_3 by Tsiakaras et al. [32] and they conducted lots of reaction condition studies using this system.

Ni is the active metal for commercial methane steam reforming catalysts and is still being used in ethanol steam reforming catalytic system [16, 33-34]. Cu-Ni-K/Al_2O_3 formulation was developed in Laborde's group [35, 36]. This system exhibited high ethanol reforming activity at 300 ^{o}C which could be ascribed to the combined promotional effects of all components. Metallic Cu facilitated fast ethanol dehydrogenation to acetaldehyde. Ni favored C-C bond breakage to convert liquid products and produce methane and carbon monoxide. Potassium acted as a neutralizer to balance the acidic sites on the support so as to minimize dehydration reaction. Llorca et al. [10-11, 37-38] conducted extensive work on a Co supported system and Co/ZnO was proven to be an excellent ethanol reforming catalyst with high activity and selectivity to desired products. Ir was found to interact strongly with the CeO_2 support and this resulted in high dispersion, less sintering and resistance to coking over a long period of time [22].

Liguras et al. investigated Pt, Pd, Rh and Ru catalysts containing 1 wt.% of the noble metal on an Al_2O_3 carrier at S/C 1.5 at temperatures from 600 to 850 ^{o}C [27]. Most active catalyst was Rh which also showed the lowest selectivity towards acetaldehyde and ethylene. Upon increasing Rh wt.% to 2%, by-product formation could be further suppressed. Rhodium is most expensive noble metal, so it is not advised to use it in catalysts for commercial hydrogen production processes. Due to Rh higher costs, Ru was then examined and optimized by Liguras et al. Increasing the loading (wt%) of Ru to 3 wt.% enhanced the activity and selectivity, however, further increase in wt% didn't show any improvement. As a next step, ruthenium catalysts made from Al_2O_3, MgO and TiO_2 carrier material were compared, with each containing 5 wt.% ruthenium. The Al_2O_3 support showed the highest activity and least selectivity towards undesired products.

2.4 Catalyst Preparation Method

Researchers prepare catalysts by different methods to check the characteristics of developed catalysts and consequently behavior in reactions. Lingzhi [1] studied the effect of synthesis on catalyst properties. They prepared Cobalt catalyst supported on Zirconia by IWI and Sol-gel. It was found that catalysts prepared by sol-gel method showed better stability comparatively. Co-ZrO2 catalysts with different Co loadings (10%, 20%, and 30%) were evaluated for their ethanol steam reforming activity.

2.5 Summary

In this chapter, a review of literature related to research on catalyst synthesis for ethanol steam reforming has been done. First, steam reforming has been reviewed. A thermodynamic analysis was performed by Fishtick et al and it was found that ESR is a feasible process. Various studies have been conducted on support material for catalysts. Al_2O_3, TiO_2, ZnO and ZrO_2 have reported as most suitable supports for catalysts to be used in ESR. Out of many tested active metals for this process, Ni, Co are reported to best metals for ESR in base metal category. Rh is reported to be the best active metal in both ethanol conversion and hydrogen selectivity, followed by Pt, in noble metals' category.

2.6 References

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Chapter 3

Methodology

3.1 Materials

3.1.1 Ethanol

Commercially available industrial grade ethanol mixed with water was used as feedstock for hydrogen production.

3.2 Catalyst Preparation

Catalysts were prepared by employing different methods i.e. incipient wetness impregnation technique and sol-gel method. Activity of catalysts prepared by both methods was compared. Based on previous studies, Co, Ni, and Ru were chosen as active metals with SiO_2, TiO_2, Al_2O_3 and ZrO_2 as supports. Cobalt nitrate ($Co(NO_3)_2.3H_2O$), Ruthenium (III) nitrosyl nitrate ($HN_4O_{10}Ru$) and Nickel nitrate hexa-hydrate ($Ni(NO_3)_2.6H_2O$) were used as precursors for active metals. Ruthenium (III) nitrosyl nitrate was bought from Santa Cruz, USA. Cobalt nitrate and Nickel nitrate hexa-hydrate were bought from VWR International, USA.

3.2.1 Incipient Wetness Impregnation

SiO_2 was first washed with de-ionized water and dried at 120 ^oC for 12 hours. Then, it were calcined for 3.5 hours at 500 ^oC before impregnation. Calculated $Co(NO_3)_2.3H_2O$ solution was added to dried SiO_2 to get 10% Co loading in final samples. Impregnated sample was dried in air at 110 ^oC for 24 hours, then calcined at 550 ^oC for 4 hours in air. Similar procedure was followed to prepare catalysts of different metal loadings using various supports. A summary of prepared samples is given in table 3.1.

3.2.2 Sol-Gel Method

In sol-gel preparation, 0.5M KOH solution was added to SiO_2 to prepare 100mL solution. Suitable volume of water was added to Nickel nitrate hexa-hydrate. This solution was added drop-wise into SiO_2 solution with constant stirring. Gel was obtained in a rotary evaporator bath at 120 ^oC in 12 hours. Gel was then filtered and filtrate was dried at 90 ^{o}C overnight. Prepared sample with 10% Ni loading was calcined at 550 ^{o}C for 3.5 hours and stored for testing. Similar procedure was followed to prepare catalyst samples using Cobalt and Ruthenium precursors with different supports. A summary of synthesized samples by sol-gel method are given in the following table:

Table 3.1: Prepared Catalyst samples by IWI method, with Metal loading (%)

Prepared Samples	**Metal %**	**Support %**
Co-Si	Cobalt 10%	SiO2 90%
Co-Ti	Cobalt 10%	TiO2 90%
Co-Al	Cobalt 10%	Al2O3 90%
Co-Zr	Cobalt 10%	ZrO2 90%
Co-TiZr	Cobalt 10%	TiO2 45%, ZrO2 45%
Co-Ru-CC	Cobalt 10% Ruthenium 2%	China Clay 88%
Ni-Si	Nickel 10%	SiO2 90%
Ni-Ti	Nickel 10%	TiO2 90%
Ni-Al	Nickel 10%	Al2O3 90%
Ni-Zr	Nickel 10%	ZrO2 90%
Ru-Zr	Ruthenium 3%	ZrO2 97%

Table 3.2: Catalyst samples prepared by Sol-Gel method, with Metal loading (%)

Prepared Samples	**Metal %**	**Support %**
Co-Si-SGP	Cobalt 10%	SiO2 90%
Co-Ti-SGP	Cobalt 10%	TiO2 90%
Co-Al-SGP	Cobalt 10%	Al2O3 90%
Co-Zr-SGP	Cobalt 10%	ZrO2 90%
Co-TiZr-SGP	Cobalt 10%	TiO2 45%, ZrO2 45%
Co-Ru-CC-SGP	Cobalt 10% Ruthenium 3%	China Clay 87%
Ni-Si-SGP	Nickel 10%	SiO2 90%
Ni-Ti-SGP	Nickel 10%	TiO2 90%
Ni-Al-SGP	Nickel 10%	Al2O3 90%
Ni-Zr-SGP	Nickel 10%	ZrO2 90%
Ru-Zr	Ruthenium 3%	ZrO2 97%

3.3 Catalyst Characterization

Different characterization techniques were used to study catalyst surface and structural properties, which can be used to correlate with catalytic performance and guide catalyst design. Following techniques were used in this work.

3.3.1 XRD

X-ray diffraction (XRD) was used for the detection and identification of bulk crystalline phases within the selected catalysts. XRD was done using Philips Analytical instrument. The powder diffraction patterns were recorded in the 2θ range from 20^{O} to 90^{O}. The catalysts were kept at isothermal steps for half hour before data collection and the ramp rate between the isothermal steps was kept at 10ºC/min.

3.3.2 SEM

The scanning electron microscope (SEM) tool was used to study surface morphology of catalysts. JSM-6490 (LA) was used for this purpose.

3.4 Reaction testing

Analysis of catalytic performance in reaction is a significant step in catalyst development. Evaluation of catalyst was done using steady state reaction. Reaction experiments for ESR were performed using a fixed-bed tubular reactor flow system using a reactor made of stainless steel. 1 g of catalysts were used in each test. Initially, catalysts were loaded in the reactor and sandwiched by two glass wool layers, then, heated to 500 ^{o}C and then reduced in pure hydrogen flow at same temperature for 1 hour. De-ionized water and industrial grade ethanol was used to prepare the required water-ethanol mixture. 25 mL flask was used as feed reservoir. The solution of water and ethanol with W/E molar ratio of 6:1 was fed through a stainless steel line to the system using a micro-pump at a federate of 7.5 mL/min, been evaporated at 90 ^{o}C. An electrically controlled heater was used to obtain required temperatures. Temperatures were monitored and adjusted using a K-type thermocouple. Reaction was carried out at different temperatures under the same feed stream. Each catalytic run was carried out for one hour. First catalysts were evaluated at low temperature reaction, before moving on to consequent higher temperatures step-by-step. Conversion of feed was tested by collecting outlet samples.

3.4.1 Parameters

Effect of several parameters towards ethanol conversion and hydrogen production were studied in order to optimize reaction conditions. Temperature was the primary parameter studied. Temperature range of 400-850 ^{o}C was chosen based on previous studies. Performance of different catalysts was analyzed at optimum temperature conditions.

3.4.2 Catalyst activity

Ethanol conversion was calculated using following equation:

$$(\%) = \frac{(2\ 5\ \ ) - (2\ 5\ \ )}{(2\ \ \ 5\ \ \ )} \times 100 \qquad (3.1)$$

$_{2\quad 5}$

Presence and concentration of product (H_2) were tested using flame tests.

A schematic diagram of reaction setup is shown in the figure 3.1:

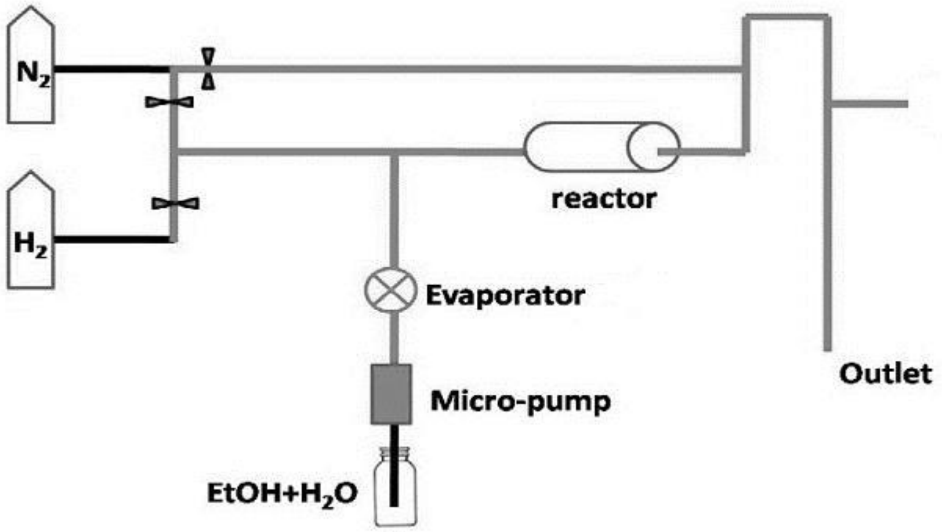

Figure 3.1: Schematic illustration of reaction system for ESR

3.5 Summary

In this chapter, experimentation related to this research has been presented. Catalysts were synthesized by two methods i.e. IWI and Sol-gel. Various samples were prepared using Ni, Co and Ru as active metals, supported on Al_2O_3, ZrO_2, TiO_2, CeO_2 and china clay. Afterwards, catalysts were characterized using XRD and SEM. SG prepared catalysts showed nearly expected results in characterization and were used in ESR. Reaction was carried out in temperature range of 400-850 ^oC.

Chapter 4

Results and Discussions

4.1 Catalytic Activity in Ethanol Steam Reforming

Catalysts prepared by sol-gel processing were used in reaction testing. Among all samples, Co-Si, Co-Al, Co-Zr, Ni-Zr and Ru-Zr showed considerably good performance. Ni-Al promoted carbon deposition at higher temperatures as indicated by Rossetti et al [3]. Ni-Zr exhibited best activity in converting ethanol. 92% ethanol conversion was achieved using sol-gel prepared Ni-Zr catalyst. This catalyst significantly repressed coke deposition for a wider temperature range.

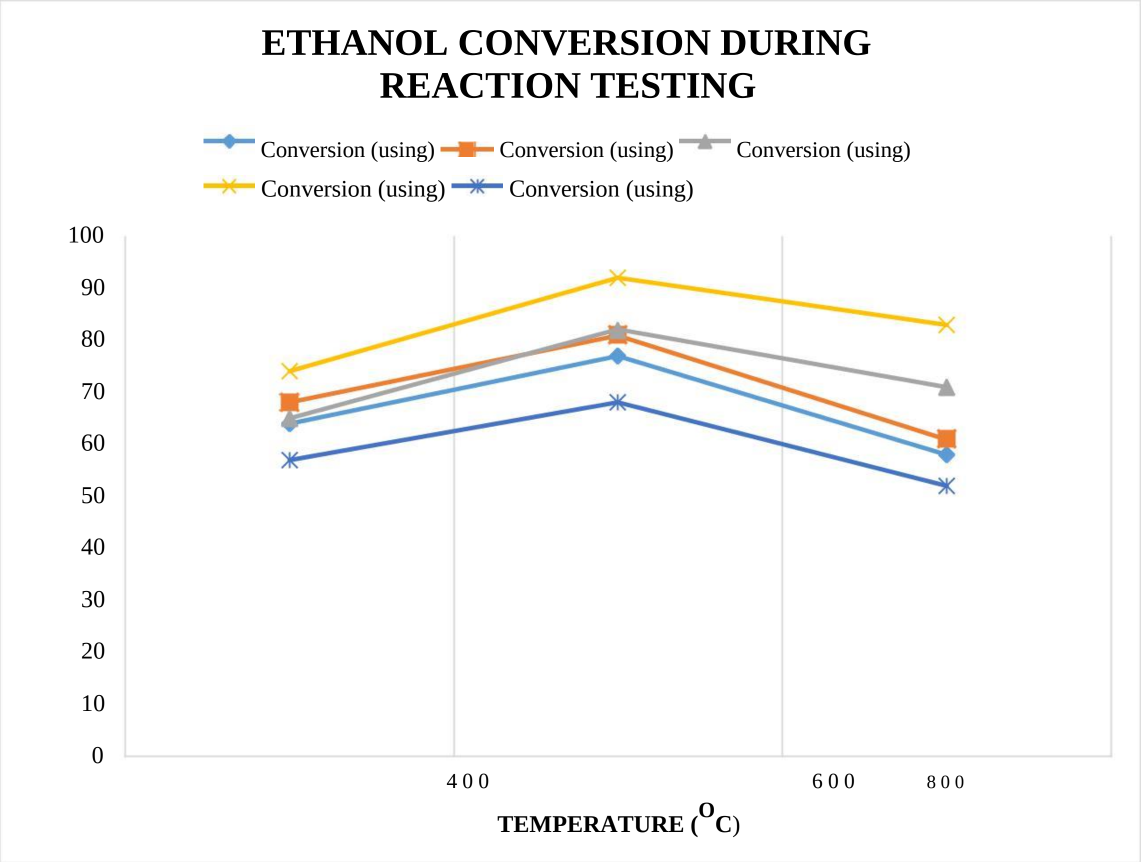

Figure 4.1: Ethanol Conversions (%) during reaction testing

Summary of sol-gel catalysts which showed better ethanol conversions is shown in table 4.1.

Table 4.1: Summary of Sol-gel prepared Co, Ni, and Ru catalysts which showed above 50% ethanol conversion during reaction testing

Catalyst	Support	Temperature (^{0}C)	Ethanol Conversion (%)
Co	SiO_2	400	64
		600	77
		800	58
Co	Al_2O_3	400	68
		600	81
		800	61
Co	ZrO_2	400	65
		600	82
		800	71
Ni	ZrO_2	400	74
		600	92
		800	83
Ru	ZrO_2	400	57
		600	68
		800	52

4.2 Characterization Results

4.2.1 XRD Results

XRD analyses were used to observe the structure of catalysts which produced considerable results in reaction testing. Figure shows the profile of Cobalt-Silica sample (Co-Si-SG). XRD of the catalyst sample clearly shows the reflections at 2 theta valued of 21 and 27.

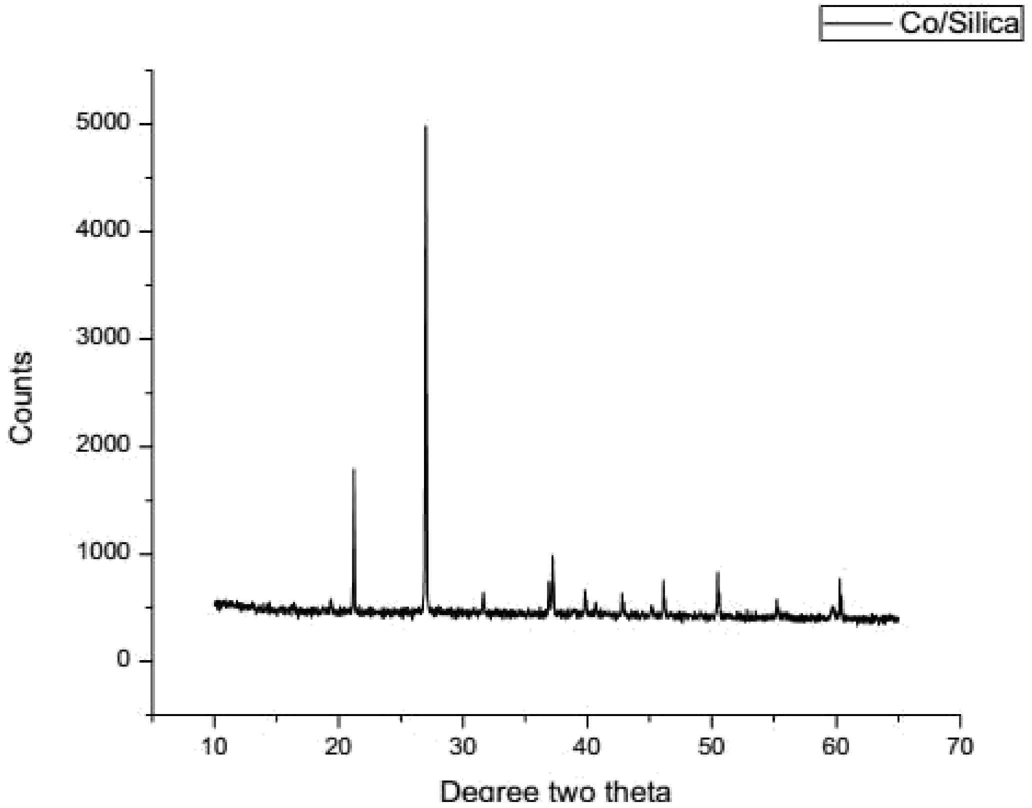

Figure 4.2: XRD Profile of Co-Si-SG

Diffraction patterns of Cobalt-Alumina (Co-Al-SG) are shown in following figure (4.3). The peaks, however didn't show the desired results. By examining the peaks and previous works, it can be said that Cobalt species was not scattered completely on the surface of support, probably due to which in reaction testing, it didn't show better results comparatively.

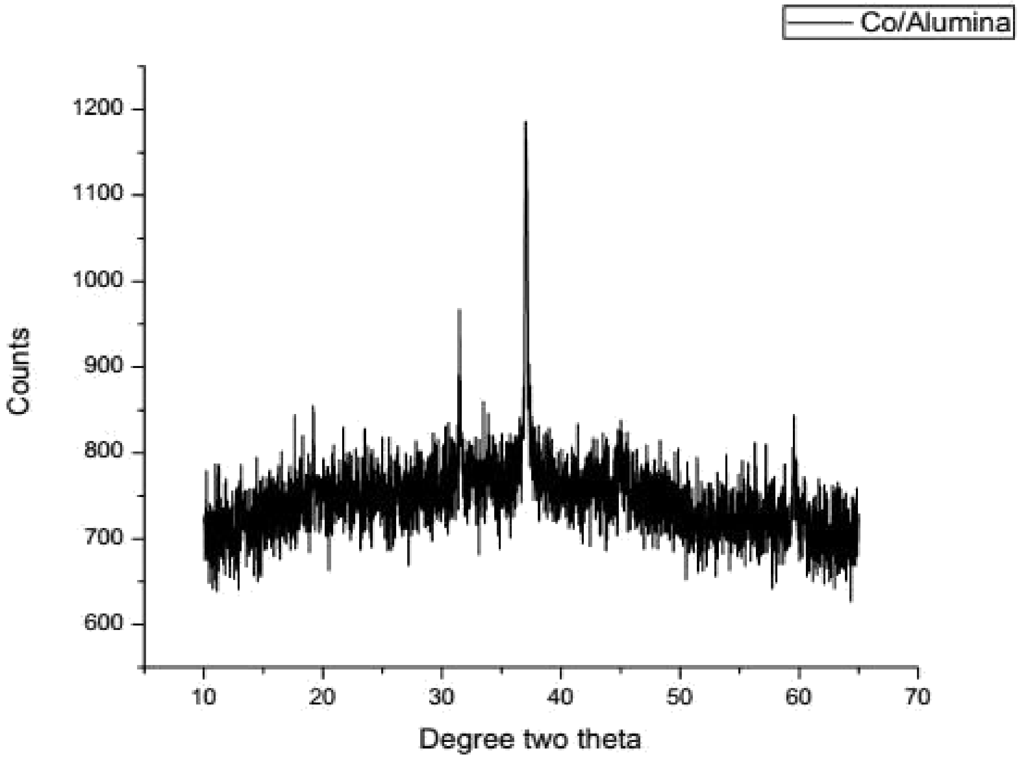

Figure 4.3: XRD Profile of Co-Al-SG

Figure 4.4 shows the profile of Cobalt-Zirconia sample (Co-Zr-SG). XRD of the catalyst sample clearly shows the reflections at 2 theta valued of 28 and 33. Similar peaks were observed in another research. [1]

No cobalt oxide crystal phases were seen on sol-gel prepared catalysts, which is suggestive of highly dispersed Co species in the catalyst structure for sol-gel catalysts. [2, 1]

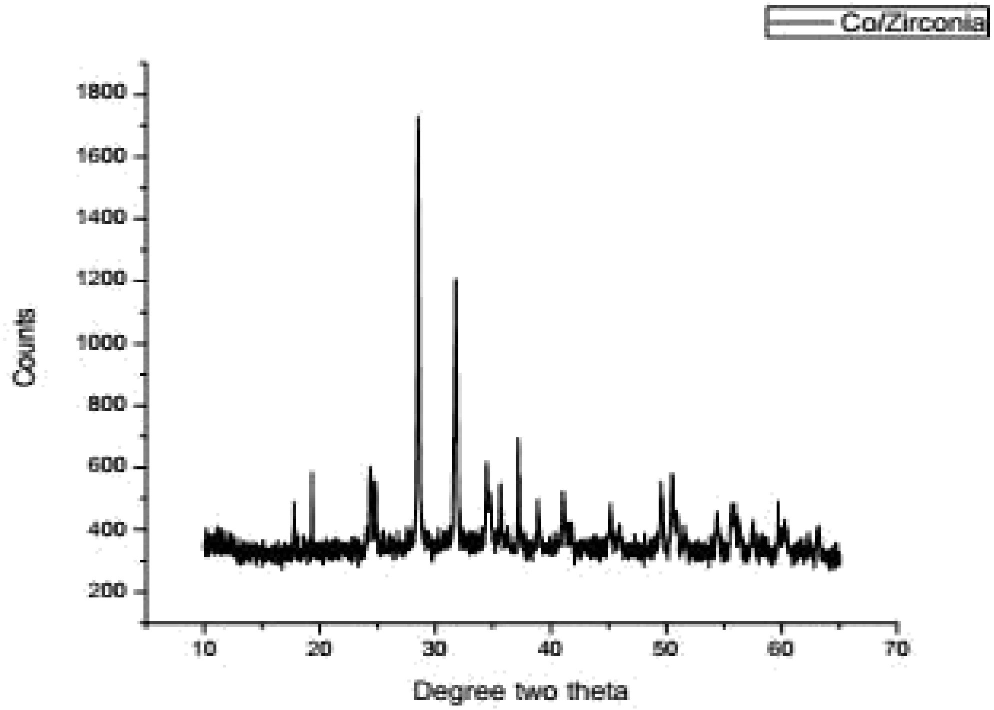

Figure 4.4: XRD Profile of Co-Zr-SG

Nickel Zirconia exhibited best results in this research, as >90% ethanol conversion was achieved. From XRD patterns of this sample, it was observed that tetragonal and monoclinic phases were found.

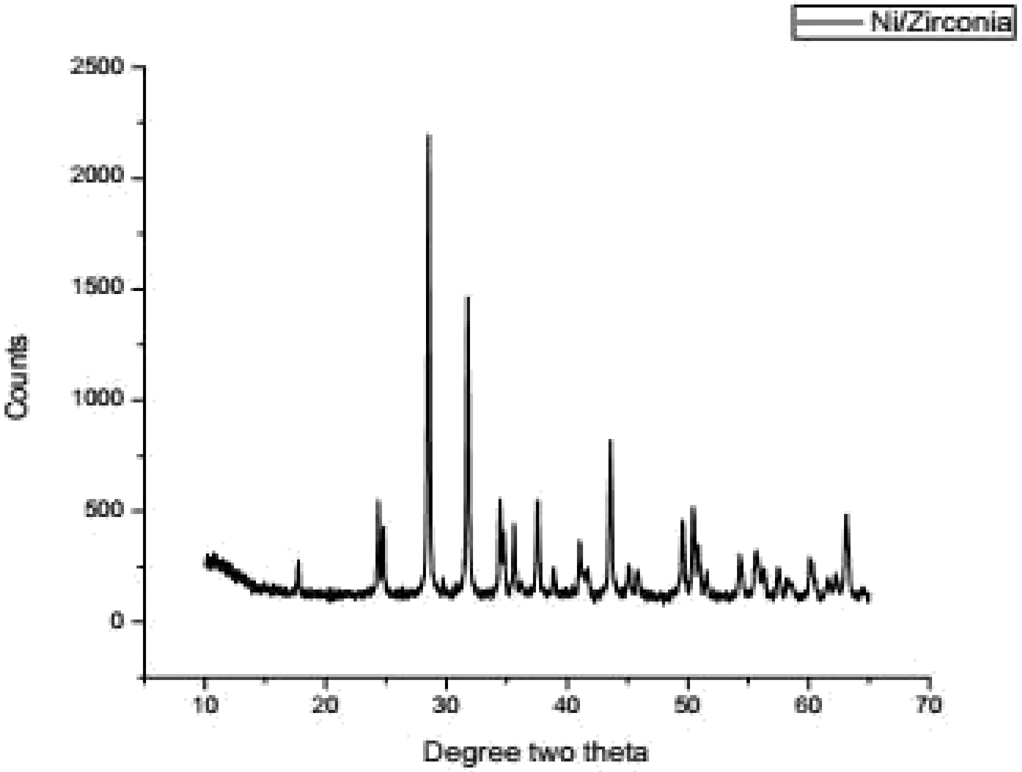

Figure 4.5: XRD Profile of Ni-Zr-SG

4.2.2 SEM Results:

SEM results for Co-Zr-SG and Ni-Zr-SG were obtained to analyze the effect of preparation method on surface morphology of prepared catalysts. Co-Zr-SG results are shown in Fig. 4.6 (a, b). Ni-Zr-SG results are shown on Fig. 4.7 (a, b). In fig. 4.6 (a), bulk particles of Co species can be seen properly. Whereas in Fig. 4.7 (a), it can be seen that metal content (Ni) is quite uniformly dispersed over the surface of support.

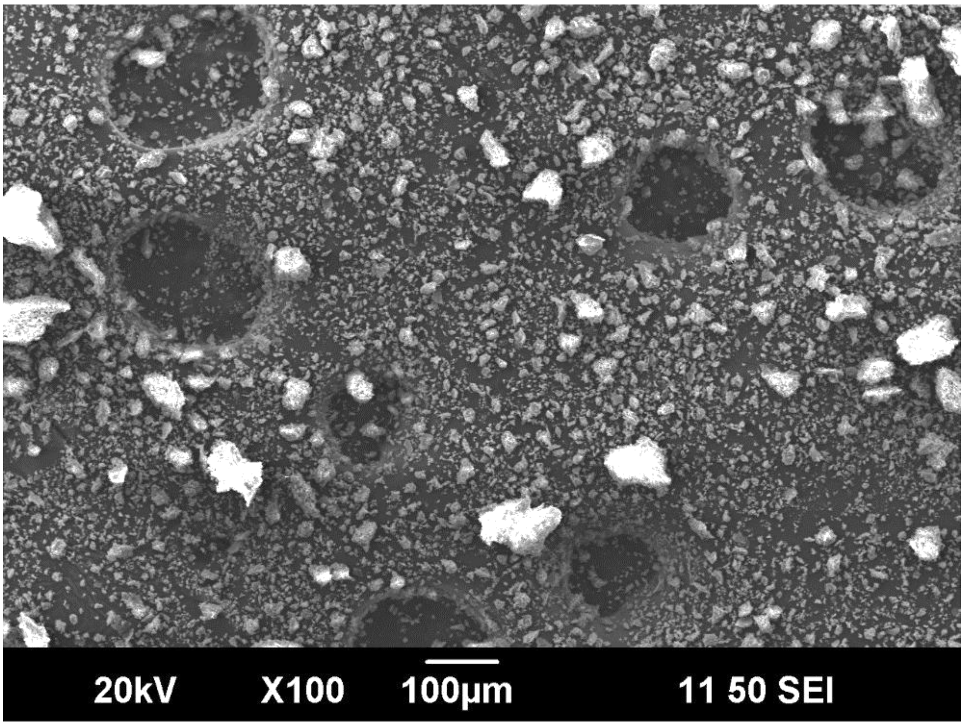

Figure 4.6(a): SEM of Co-Zr-SG

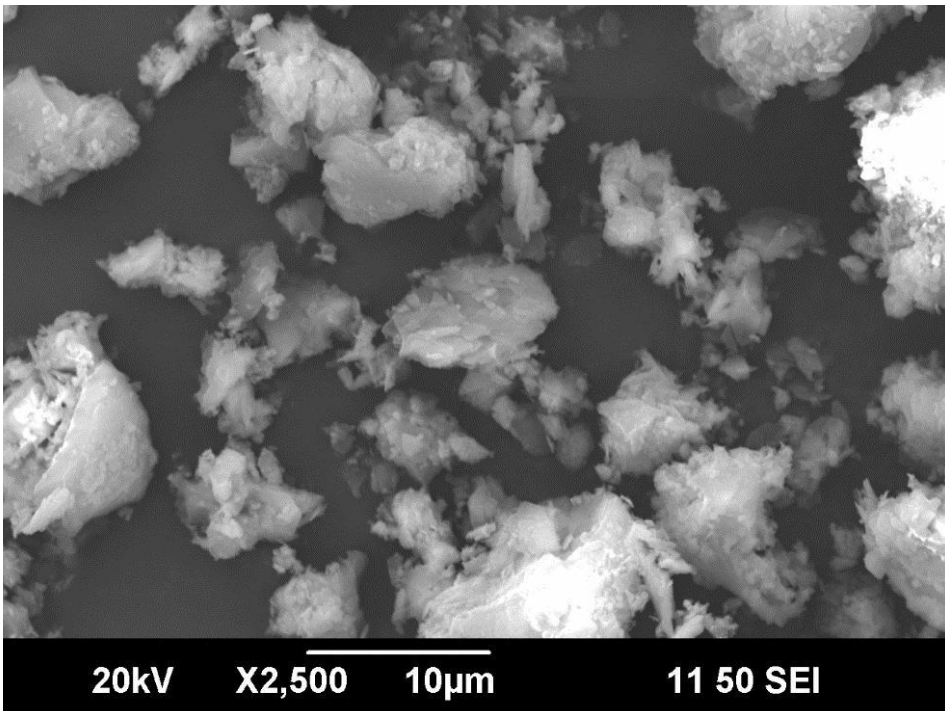

Figure 4.6(b): SEM of Co-Zr-SG (Magnified)

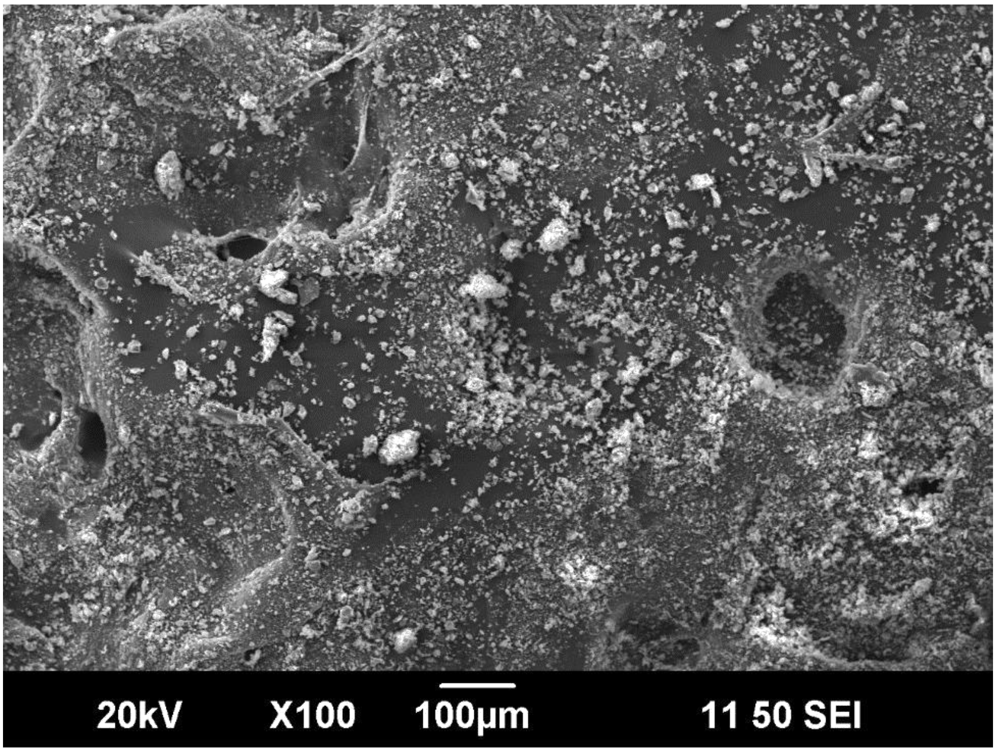

Figure 4.7(a): SEM of Ni-Zr-SG

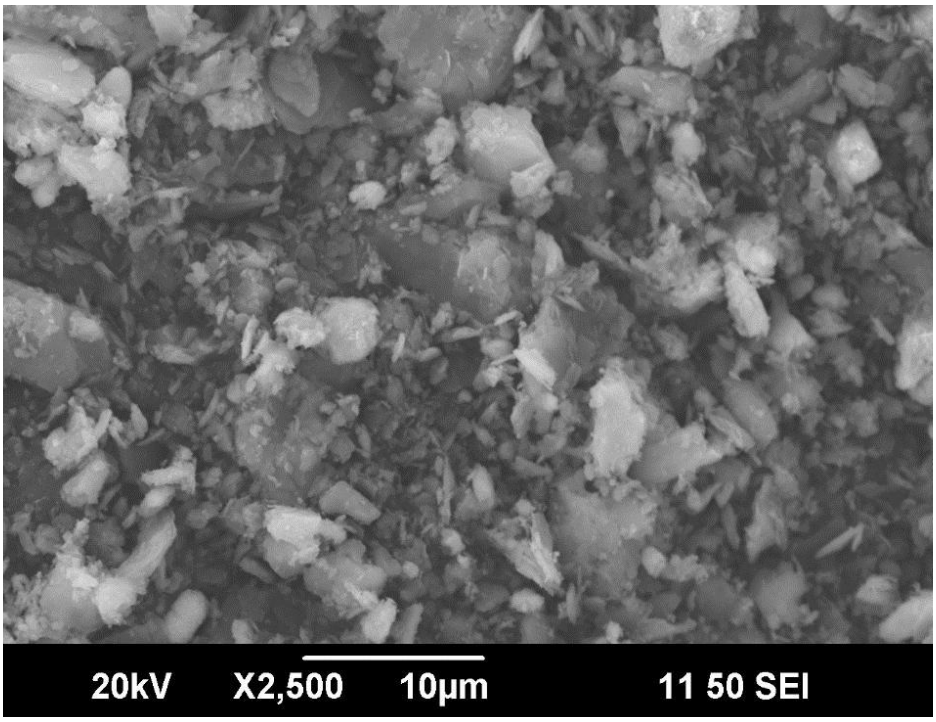

Figure 4.7(b): SEM of Ni-Zr-SG (Magnified)

4.2.3 Specific Surface Area

Specific surface areas of catalysts were measured by BET surface area method. Values of different catalysts are shown in the table 4.2.

Table 4.2: Specific Surface Area results of catalysts

Catalyst	**Metal %**	**S_{BET} (m2/g)**
Co-SiO_2	10	154.6
Co-Al_2O_3	10	178.2
Co-ZrO_2	10	192.7
Ni-ZrO_2	10	215.4
Ru-ZrO_2	3	236.1

4.3 Flame Test

Hydrogen enriched gas was detected during experimentation by flame test. The flame color and pop sound ensured the presence of hydrogen enriched gas. Test was done several times during experimentation but flame could only be prominently observed in case of Nickel-Zirconia and Cobalt-Zirconia catalyzed reaction.

Fig. 4.8: Flame test of presence of hydrogen rich gas

4.4 Summary

Results of experimentation are discussed in this chapter. Among various catalysts used in reaction testing, Co-Zr-SG and Ni-Zr-SG exhibited best results with maximum ethanol conversions at 600 ^{o}C. XRD, SEM and BET surface area results of successful catalysts are shown. XRD profile of Ni-Zr-SG was similar to many successful results shown in literature review. SEM results showed that among SG-prepared catalysts, surface morphology of Co-Zr and Ni-Zr was suitable for proceeding with reaction testing. Hydrogen flame test was conducted for each ESR test and it complemented the other results, with better flame in case of Ni-Zr-SG and Co-Zr-Sg catalysts.

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Chapter 5
Conclusions & Recommendations

5.1 Summary and Conclusions

Critical appraisal of the literature shows that various studies have been carried out to examine ethanol steam reforming using different catalysts under different reaction systems. A number of catalysts have been developed based on the research results, globally, by many researchers. However, there are certain problems yet to be dealt with. Current challenges include the need for reduction in developing costs of catalysts, operating costs of process, reusability of catalysts, reduction in carbon deposition, improving the selectivity of products and feed conversion. One of the possibilities to reduce costs is to develop an efficient catalyst based on materials which are abundant and are commercially available in the market. In this study, commercially available precursors have been used to develop and analyze catalysts for conversion of ethanol to hydrogen.

Steam reforming of catalysts was studied by employing many catalysts developed by IWI and sol-gel method, after several experiments. Nickel, Cobalt and Ruthenium were used as active metals with SiO_2, ZrO_2, Al_2O_3, and CeO2 as supports. Catalysts developed by both methods were analyzed by characterization and reaction testing. For ESR, ethanol-water mixture was used. Process was carried out under different temperatures (400-850 ^{o}C) at atmospheric pressure.

Following conclusions were made based on results obtained from this research:

5.1.1 Catalyst synthesis

For better active metal deposition, sol-gel method showed better results as compared to IWI. This method generates a strong bonding between active metal and support, thus resulting in higher metal loading. Reducible metal species were very less in sol-gel catalysts.

5.1.2 Catalyst Activity in Steam Reforming of Ethanol

Evaluation of catalysts showed that sol-gel catalysts showed better results in the process. Comparable ethanol conversion was achieved using sol-gel catalysts. Among many catalysts developed, Nickel supported on Zirconia showed 92% ethanol conversion, highest among the tested catalysts, with Cobalt supported on Zirconia being the second, with 82% ethanol conversion. Both active metals showed promising results with Zirconia as support. However, carbon deposition increased with increase in temperature when Cobalt-Zirconia was used. Ceria supported catalysts showed poor ethanol conversion in comparison with Zirconia supported catalysts but carbon deposition was considerably less.

5.1.3 Reaction Parameters

Further efforts were made to analyze reaction temperatures while maintaining the catalysts. Above 60% ethanol conversions were achieved in all tests of sol-gel catalysts at 400 ^{o}C except in case of Ruthenium supported on Zirconia, which showed 57% conversion. 600-650 ^{o}C was the optimum temperature range in all cases with highest ethanol conversions achieved in tested temperature range. Higher temperatures affected the conversion adversely and conversion dropped significantly with increase in carbon deposition on catalyst surface.

5.2 Recommendations

Further studies are critical to establish a linkage between surface structure and catalyst performance in reaction. Based on this study, following recommendations can be made:

- Bio-ethanol is promising feedstock for hydrogen production via steam reforming. Its performance should be investigated by developing small scale catalytic steam reforming systems.
- Materials like La_2O_3, CeO_2, MgO, ZnO, should be used in combination with Al_2O_3 as promoters to optimize catalyst stability in the reaction as they have been reported to inhibit the coke deposition on acidic sites [1, 2]
- Nickel weight content needs to be optimized to obtain apt dispersion on promoted catalysts.

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Annex I

Generation of Hydrogen-Rich Fuel Gas from Renewable Biomass and Low Value Hydrocarbons by Heterogeneous Metallic Catalysis

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Abstract:

Depletion of oil reserves, current hike in crude oil prices and air pollution by burning of fossil fuels are factors which induce researchers to make hydrogen available for use as energy resource. Currently, hydrogen is derived from non-renewable natural gas and petroleum, but in principle, could be generated from renewable resources such as biomass or water. Hydrogen, due to its higher energy value, proves to be an alternative energy source. Currently, most common method to produce hydrogen is reforming of fossil fuels. Technological advancements are required to produce hydrogen from water as precious metals' catalysts are used to bring about the required decomposition which also involves higher energy consumption. Many studies have been done for the purpose using various feed-stocks. In this research, catalytic performance of supported metals for H_2 production by steam reforming of bio-ethanol in the temperature range of 400-850 ^{o}C, is presented. Catalysts were prepared by impregnation and sol-gel method. Experimental results based on using catalysts prepared by both methods, suitability of support for bio-ethanol conversion to H_2, and stability of prepared catalysts are evaluated. Co, Ni, Ru were used as active metals supported on Al_2O_3, CeO_2, SiO_2, ZnO, TiO2 and China Clay. 1-

20% metal loading was used. Characterization of catalysts was done by XRD, SEM and BET surface area. Catalysts' activity as well as their selectivity can be controlled by means of pore size and volume during synthesis. It was observed that selectivity of hydrogen production increases when CeO_2 and TiO_2 supported catalysts are used, with bio-ethanol being almost completely converted to hydrogen and other fractions. These findings suggest that catalytic reforming of bio-ethanol could prove to be suitable for generation of hydrogen rich fuel gas from renewable biomass.

1. Introduction

Hydrogen has been identified as an ideal energy carrier to support sustainable energy development [1–3]. It can be used as feed in fuel cells for power generation with high efficiency [4–6] and it is extremely clean as the only by-product is water. Among the various feed-stocks, ethanol is very attractive because of its relatively high hydrogen content, availability, non-toxicity, storage and handling safety, and more importantly, it can be produced by fermentation of biomass.

Among various reforming technologies, steam reforming has been considered as the most promising process for hydrogen production due to its high hydrogen yield. Ethanol may be converted into hydrogen by steam reforming (SR) according to the stoichiometric reaction:

$$CH_3CH_2OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad (\Delta H^\circ = +173.7\ \mathrm{kJ/mol}) \qquad (1)$$

This apparent simple reaction in fact summarizes a very complex overall process since several reaction pathways are involved which depend on the nature of the catalytic material and the reaction conditions [7, 8].

The most important problem which faces catalytic materials used in SRE is deactivation and it is generally attributed to deposition of carbonaceous species as well as sintering or oxidation of the metallic particles. Some of the parallel reactions taking place during SRE can lead to catalyst deactivation through carbon deposition [9]: ethylene polymerization (2), decomposition of hydrocarbons such as methane (3) and ethylene (4) and the Boudouard reaction (5).

$$C_2H_4 \rightarrow \mathrm{coke} \qquad (2)$$

$$CH_4 \rightarrow C + 2H_2 \qquad (3)$$

$$C_2H_4 \rightarrow 2C + 2H_2 \qquad (4)$$

$$2CO \rightarrow CO_2 + C \qquad (5)$$

Transition noble and non-noble metals supported on oxides of a great variety of acid–base properties have been extensively studied for SRE reaction [2, 4, 7, 8, 10, 11]. The steam reforming of ethanol over Ni, Co, Ni/Cu and noble metals (Pd, Pt, Rh) has been extensively studied. The greatest concern lies in developing an active catalyst that inhibits coke formation and CO production. Co and Ni have been reported as active catalysts in ESR [3, 4]. The authors described selectivity in the ESR as sensitive to structure and showed that the amount of CH4 produced decreases with increasing Co particle size. Llorca et al. [20,21] proposed the use of ZnO-supported Co catalysts in steam reforming of ethanol. The use of $Co(CO)_8$ as precursor produced a highly stable catalyst that enabled the production of CO-free H_2 at low temperatures (623 K). They concluded that the method of catalyst preparation affected its performance and structural characteristics. Haga et al. [22] studied the catalytic properties of Co among other metals and found that selectivity to H_2 was in the order Co > Ni > Rh > Pt, Ru, Cu. In another study, they found that the supports vastly influenced the properties of Co catalysts [10]. The formation of H_2 decreased in the order: Co/Al2O3 > Co/ZrO2 > Co/MgO > Co/SiO2 > Co/C. The Co/Al2O3 catalyst exhibited the highest selectivity to H_2 (67% at 673 K) by suppressing methanation of CO and decomposition of ethanol. Similarly, Cavallaro et al. [23] found that Co/MgO is more resistant to coke formation than Co/Al_2O_3 at 923 K.

Kaddouri and Mazzocchia [24] reported high catalytic activity of Co/SiO_2 and Co/Al_2O_3 for steam reforming of ethanol and concluded that the product distribution was dependent on both the nature of the support and the method of catalyst preparation, thereby suggesting metal–support interaction. Batista et al. [25] studied ethanol steam reforming over Co/Al_2O_3 and Co/SiO_2. The catalysts showed average conversion higher than 70% at 673 K. The metal loading influenced ethanol conversion and product distribution.

Nickel catalysts supported on alumina have been widely employed for the steam reforming of ethanol due to their excellent activity and low cost [8, 9]. However, Ni/Al_2O_3 catalysts suffer from significant deactivation caused by carbon deposition during the steam reforming of ethanol. It is known that the identity of support strongly affects the catalytic performance of supported nickel catalysts [10]. Therefore, many efforts have been made to increase both catalytic activity and durability of supported nickel catalysts through the modification of supporting materials [11]. In particular, acidity of support is one of the crucial factors determining the catalytic performance of supported nickel catalysts in the steam reforming reactions [12]. This is because acidity of support is closely related to various reaction pathways in the ethanol steam reforming reaction [13, 14].

The property of active metal is also an important factor determining the catalytic performance in the steam reforming reactions. Metal catalysts supported on CeO_2–ZrO_2 have aroused interest in their activity, thermal stability and the existence of oxygen vacancies. In this work, series of catalysts with different Ni, Co and Pt content (wt %) were prepared by a impregnation and sol-gel method for use in the hydrogen production by steam reforming of ethanol. Effect of metal loading with various supports including Al_2O_3, CeO_2, SiO_2, ZnO and TiO_2 on hydrogen selectivity and ethanol conversion was investigated.

2. Experimental

2.1. Catalyst preparation

Commercially available supports (Al_2O_3, SiO_2, CeO_2, ZnO and TiO_2) were washed in ethanol, dried and calcined at 873 K for 3 h in air. The catalysts with wt% (1-20) were prepared by impregnation of the supports with $Co(NO_3)_2{\cdot}3H_2O$, nickel nitrate hexahydrate [$Ni(NO_3)_2{\cdot}6H_2O$] and platinum chloride solutions separately. The resulting samples were dried in an oven at 333 K for 12 h and then calcined in air at 873 K for 3 h.

2.2. Characterization

Crystalline structures of calcined and reduced catalysts were investigated by XRD. Surface areas of catalysts were calculated by applying the BET method. Metal-support interaction and reducibility of the catalysts were examined by temperature-programmed reduction (TPR) measurements, which were conducted in a conventional flow system with a moisture trap connected to a thermal conductivity detector (TCD). TPR profiles were obtained by reducing 100 mg of catalyst sample with a mixed stream of H_2 (2 ml/min) and N_2 (20 ml/min).

2.3. Experimental procedure

Ethanol steam reforming experiments were carried out in a fixed bed vertical tubular reactor placed inside a cylindrical electrical furnace. One gram of catalyst was loaded in the middle of the reactor of 10 mm inner diameter such that the centre of the catalyst bed corresponded to the central heating zone of the furnace. The catalysts were mixed with inert particles so that the bed height was maintained at 60 mm. The remainder of the reactor was filled with inert ceramic material. Prior to the reaction, catalyst was reduced as well as activated while it was heated to 550 ◦C with the flow of hydrogen (40 cm^3 min^{-1}) for 4 h. The thermocouple inserted into the thermos-well of reactor recorded the catalyst bed temperature.

After catalyst activation, the reaction temperature was fixed at a desired temperature and catalytic steam reforming reaction was performed isothermally at atmospheric pressure. The feed consisting of an appropriate ratio of ethanol–water mixture was pumped at the desired flow rate to vaporize at about 170 ◦C in the preheater before entering the reactor. After passing the outlet product stream through condenser, the liquid was separated in gas–liquid separator and gaseous product stream was analyzed online at different time-on-stream in Gas Chromatography with thermal conductivity detector (TCD). Fig. 1 describes the schematic diagram of the steam reforming setup. The main products are H_2, CO, CO_2, CH_4 and water vapor. No traces of intermediate products such as ethylene and acetaldehyde were found to be formed.

3. Results and Discussion:

Table 2 shows ethanol conversion, hydrogen yield and selectivities of the main products in the

ethanol steam reforming at different temperatures over Ni/SiO2 catalysts with different metal loadings, obtained in the dynamic experiments. Under these conditions, the three catalysts show similar performance. A hydrogen selectivity of 62% is achieved at 500ºC.

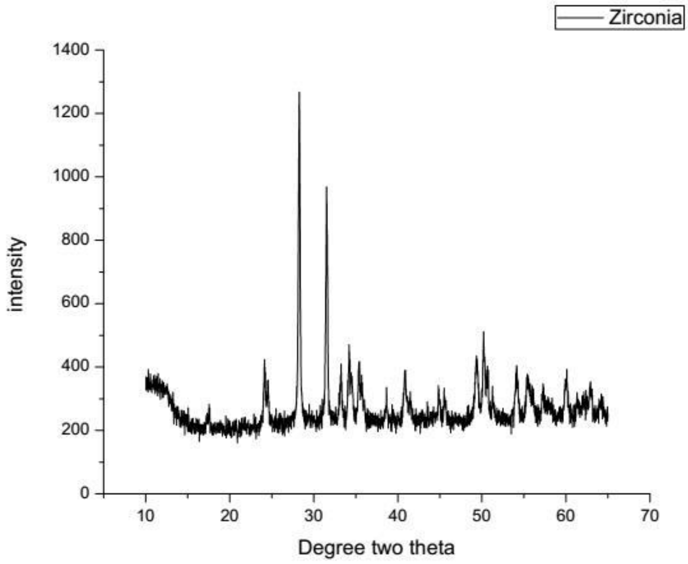
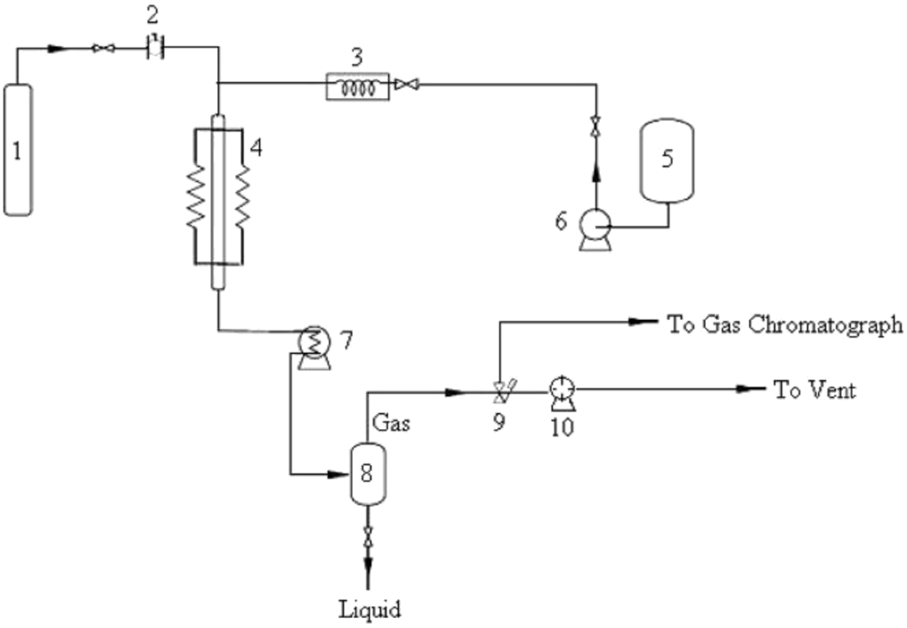


Figure. XRD of Zirconia used as support

The temperature favours steam reforming and decomposition reactions due to their endothermic nature leading to a hydrogen selectivity of 69 % at 600 ºC. These results are in agreement with those obtained in literature (Comas et al., 2004).



1: H_2 Cylinder; 2: Mass flow meter; 3: Preheater; 4: Furnace-Reactor assembly; 5: Ethanol-water storage; 6: Feed pump; 7: Condensor; 8: Gas-liquid separator; 9: Three-way valve; 10: Wet gas meter;

Fig 1. Schematic Diagram of Experimental Set-Up for Steam Reforming of Ethanol

Although CO_2 formation slightly increases with temperature up to 500 ºC, the H_2/CO_2 ratio also increases, which indicates that there is a competition between steam reforming and decomposition reactions. For 20NiSi, catalyst this ratio increased from 3 at 400 ºC to 3.4 and 3.7 at 500 and 600 ºC, respectively. Above this temperature, CO_2 selectivity decreases, indicating that r-WGS reaction is favoured due to its endothermic nature.

The conversion of ethanol, the hydrogen yield and product selectivity have been calculated according to the following expressions (Comas et al, 2004)

$$X_{EtOH} = \frac{F_{EtOH,in} - F_{EtOH,out}}{F_{EtOH,in}} \qquad (1)$$

$$S_i = \frac{x_i \cdot F_T}{F_T - F_{EtOH,out} - F_{H_2O,out}} \qquad (2)$$

$$Y_i = \frac{F_T \cdot x_i}{F_{EtOH,in}} \qquad (3)$$

Table 2. Ethanol conversion, hydrogen yield and selectivities of H_2, CO_2, CO and CH_4 in the 400-600 ºC range, atmospheric pressure, water/ethanol molar ratio 6/1 and space time of 8.3 $g_{catalyst}min/g_{EtOH}$ over Ni/SiO$_2$ catalysts.

Catalyst	T (ºC)	X_{EtOH}	Y_{H2}	S_{H2}	S_{CO2}	S_{CO}	S_{CH4}
5NiSi	400	0.51	0.73	0.46	0.10	0.17	0.20
	500	0.63	1.81	0.62	0.20	0.04	0.12
	600	0.81	3.10	0.68	0.18	0.07	0.04
10NiSi	400	0.58	0.83	0.48	0.13	0.14	0.20
	500	0.75	2.12	0.62	0.20	0.05	0.12
	600	0.89	3.38	0.69	0.18	0.07	0.05
20NiSi	400	0.75	1.27	0.49	0.17	0.08	0.22
	500	0.98	2.70	0.62	0.20	0.05	0.13
	600	0.99	3.91	0.69	0.19	0.07	0.05

Conclusions:

ESR test performed in the range of 400-850 C carried out using different catalysts showed the relevance of support and metal loading on activity, selectivity and stability. In particular Pt/CeO2 sample exhibits complete ethanol conversion without carbon deposition in the whole temperature range. Catalysts' characterization showed that CeO_2 stabilize the Pt in higher oxidation state, with higher dispersion and strong metal-support interaction, resulting in more stable and active catalyst as compared to other supports.

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Application of Acid Treated Kaolin Clay for Conversion of Polymeric Waste Material into Pyrolysis Diesel Fuel

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Abstract**—** *Polymer waste material was subjected to catalytic pyrolysis using acid treated kaolin clay. Waste material was cracked thermally and catalytically in a batch reactor in the temperature range 400-500°C for synthesis of liquid fuel. For this purpose, kaolin clay was first treated with different prepared molar solutions of HCl (1M, 3M and 5 M) under reflux condensation at 100°C and atmospheric pressure in a round bottom flask for 4 hours. The acid treated clay samples were subsequently washed with distilled water and then calcined at 500°C for 4 hours. Cracking activity of untreated kaolin clay was compared with acid treated kaolin clay. It was observed that acid treated kaolin clay performed better than untreated kaolin clay due to high surface area and greater number of acidic sites.*

Keywords—Waste plastic, Pyrolysis, Kaolin, Polypropylene, GC-MS

Introduction

Plastics are one of the greatest innovations of the century and have proved their reputation to be true. Plastics are being used in various ways and we will depend on them in the upcoming years. Plastics are light weight, do not rot or rust, economical, reusable and conserve natural resources. These are the reasons of our dependency on the plastics. Plastics reduce CO_2 emissions during their usage along with conservation of energy. If we want to replace plastics with other conventional materials considering sustainability, then we would have to add 22.4 million tons of crude oil yearly [8]. Plastics have rapidly replaced conventional materials due to continuous advancement in polymer technology, knowledge and economic production.

Plastic waste disposal has been identified as worldwide environmental problem. In recent years, attention has been paid more towards the recycling of synthetic polymer waste for solving pollution problems and the reuse of cheap and abundant waste products. Though several methods have been proposed for recycling waste plastics, it is generally accepted that material recovery is not an ideal solution to the present problem, and that energy or chemical recovery is a more attractive one [1].

Catalytic degradation of polyolefins to oil has been preferred over thermal pyrolysis due to narrow product distribution, high reaction rate and lower temperature of degradation. One of the most commonly used solid catalysts in polymer degradation studies are zeolites due to their strong acidity, pore size and specific pore structure effects. Amongst the numerous kinds of zeolites investigated in polyolefin pyrolysis, the most commonly used are Beta, USY, ZSM-11, REY, Mordenite, ZSM-5 etc. Some other solid acid catalysts used for plastic pyrolysis include molecular sieves, silica alumina, and MCM-41. Reports on the use of FCC catalysts are also found in literature. Other catalytic materials such as clays (montmorillonite, saponite), reforming catalysts, activated carbon, metal oxides, metal complexes of the type MCln-AlCl3 or M(AlCl4)n (M=Li, Na, K, Mg, Ca, Ba; n=1–2), and alkali metal carbonates or alkaline metal carbonates have also been tested for polymer degradation [2].

The performance of several differently treated clinoptilolite zeolites (dealuminated clinoptilolite catalysts) in the degradation of polypropylene was investigated in a semi-batch reactor at 400°C [3]. The effects of different zeolites as H-Y, Na-Y, H-mordenite and Na-mordenite on the catalytic degradation of polypropylene were studied using thermogravimetry under nitrogen flow [4]. The catalytic cracking of polypropylene was carried out by silica–alumina and H-ZSM-5 at temperatures between 350°C and 420°C and sulfated zirconia at temperatures below 300°C, and also by means of thermogravimetry under helium flow [5]. Meanwhile, Sakata et al. studied the catalytic cracking of polypropylene with silica–alumina catalyst at 380°C in a semi batch reactor without external gas flow [6]. Ishihara et al. investigated the catalytic degradation of polypropylene by silica–alumina at temperatures between 180°C and 300°C in a semi batch reactor under a nitrogen flow [7].

From the study of previous work done, it was found that suitability of all catalysts used previously is due to their acidity and structure. Kaolin is thermally stable and is mildly acidic in nature, which can support cracking temperatures at high temperatures.

Cost is also less compared to other acidic materials e.g. zeolites. Acid treatment of clay enhances the acidic properties of clay enabling the cracking of plastic at comparatively low temperature. Therefore in this work, studies have been carried out for thermal and catalytic cracking of polypropylene in batch reactor using acid treated kaolin clay.

Experimental

A. Materials:

Waste polypropylene (used plastic disposable glasses) was collected from waste yards of National University of Sciences and Technology NUST. Waste plastic disposable glasses were washed and cut into flakes by scissor. The catalyst employed in this study, commercial grade kaolin clay was obtained from CES, NUST. Hydrochloric acid (36.5 %) was obtained from Sigma Aldrich. Hydrochloric acid, kaolin clay and distilled water were used for the preparation of catalysts.

B. Acid treatment of Clay:

Acid treatment of clay was carried out by adding 50 g of clay to 500 ml of hydrochloric acid solution of different concentrations (1 M, 3M and 5 M). Reflux condensation was used for acid treatment at temperature range of 80-100 °C and atmospheric pressure in a round bottom flask. Reflux condensation was done for 6 hours. 500 ml ice cold distilled water was then added to rapidly quench the clay suspension. Resulting content was repeatedly washed with distilled water and filtered to remove any unspent acid. Drying was carried out in an oven at 120 ° C overnight. Subsequently, calcination was done at 500° C for 4 hours and grounded in mortar pastel to powder form.

C. Experimental setup and procedure: The experimental setup used in this work consists of batch reactor provided with glass tube enclosed in a round bottom flask and open at the other end (Figure 1a and 1b). High temperature furnace is provided by K type thermocouple fixed inside. Vertex PID controller VT9626 with the accuracy of T/C±1°C was used to control the temperature of furnace.

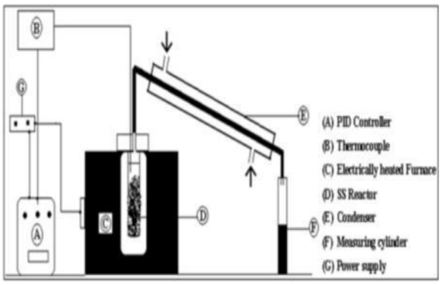


FIGURE 1a. SCHEMATIC REPRESENTATION OF EXPERIMENTAL SETUP

For each experiment, 20 g of waste polypropylene samples were used. In each reaction, kaolin clay treated with different molar concentrations of HCl (1 M, 3M and 5 M) was used for pyrolysis in the batch reactor heated at 20° C/min up to desired temperature. The condensable liquid products were collected at the other end and weighed. After reaction, solid residue left in the round bottom flask at the reaction end was weighed.

FIGURE 1b. EXPERIMENTAL SETUP

Weight of gases was calculated using the mass balance. Operating temperatures for the reaction were in the range of 400-500° C. Reaction time was calculated from the start of reaction exceeding the room temperature till the completion of reaction (the time when no liquid comes from the tube end).

D. Analysis Methods:

Analysis of liquid product was done by GC-MS-QP

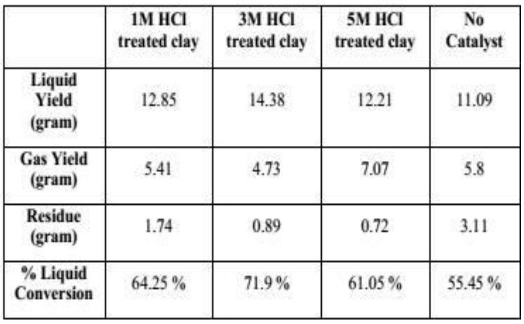
Results and Discussion

Effect of Catalyst

The liquid yield was highest for the reaction when kaolin clay treated with 3M HCl was used as catalyst. Least yield was obtained when the reaction was carried out in the absence of catalyst.

For 3M HCl treated clay, reaction started at 400°C, but reaction completed at 500° C. For 1M HCl treated clay, reaction started at 420°C and completed above 500°C, while reaction started at about 400°C and completed at 470°C for 5M HCl treated clay.

The results of all 4 experiments have been depicted in the table as



	1M HCl treated clay	3M HCl treated clay	5M HCl treated clay	No Catalyst
Liquid Yield (gram)	12.85	14.38	12.21	11.09
Gas Yield (gram)	5.41	4.73	7.07	5.8
Residue (gram)	1.74	0.89	0.72	3.11
% Liquid Conversion	64.25 %	71.9 %	61.05 %	55.45 %

TABLE I YIELD OBTAINED BY CATALYTIC PYROLYSIS OF POLYPROPYLENE AT 500° C

Effect of Temperature on Product Distribution in Thermal Pyrolysis:

Three fractions namely low and high viscous liquid, non-condensable gases and solid residue were obtained as products of thermal pyrolysis. The liquid fraction obtained at 400°C was less viscous. As temperature increased to maximum 500°C for thermal pyrolysis, liquid yield converted to more viscous form. At high temperature, less liquid yield and more gas yield was due to formation of more non-condensable volatile fractions as a result of severe cracking. Product distribution at different temperatures is summarized in figure 2

Characterization of Liquid Product:

The oil sample was characterized using GCMS for detailed composition. The GCMS of oil obtained via thermal and acid treated kaolin catalytic pyrolysis is shown in figure. Different components of oil obtained by comparing NIST library are presented in table. Results obtained reveal that oil is composed mostly of alkenes. Additionally, oxygenated compounds such as alcohols and ketones are also found which may be due to oxidative cracking of polypropylene in the presence of limited oxygen as the reaction was not carried out in absence of air and under inert conditions.

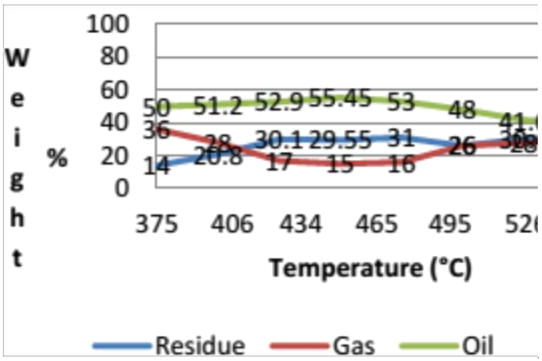


FIGURE 2. EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION OF POLYPROPYLENE

TABLE 2 GC-MS COMPOSITION OF OIL OBTAINED VIA CATALYTIC PYROLYSIS WITH 1:3 CATALYST TO POLYPROPYLENE FEED AT 500° C

Peak	Retention Time in Minute	Area %	Molecular Formula
1	1.3	0.2	C_2H_6O
2	1.87	0.1	C_6H_{12}
3	2.16	1.1	$CHCl_3$
4	2.33	0.09	C_7H_{14}
5	3.02	0.07	C_7H_{12}
6	4.05	0.78	C_8H_{16}
7	4.22	0.8	C_8H_{16}
8	4.47	1.1	C_8H_{18}
9	6.97	2.9	$C_8H_{14}O$
10	7.29	4.4	C_9H_{18}
11	7.4	0.8	C_9H_{18}
12	8.61	1.0	$C_{11}H_{22}$
13	8.93	1.2	$C_{10}H_{18}O_3$
14	11.44	0.8	$C_{11}H_{22}$
15	11.78	1.0	$C_{10}H_{22}$
16	11.86	1.1	$C_{10}H_{22}$
17	12.74	1.0	$C_{12}H_{24}$
18	12.82	0.9	$C_{12}H_{24}$
19	13.13	1.5	$C_{11}H_{24}O$
20	13.2	1.42	$C_{14}H_{30}O_2$
21	14.07	0.9	$C_{17}H_{31}F_3O_2$
22	16.275	1.7	$C_{12}H_{24}$
23	16.38	0.82	$C_{22}H_{40}O_4$
24	16.5	0.85	$C_{11}H_{22}$
25	16.64	1.4	$C_{22}H_{40}O_4$
26	16.75	2.08	$C_{11}H_{24}O$
27	16.87	1.3	$C_{17}H_{31}F_3O_2$
28	17	1.70	$C_{11}H_{24}O$
29	17.33	0.8	$C_{11}H_{22}$
30	19.62	0.8	$C_{30}H_{57}F_3O_2$

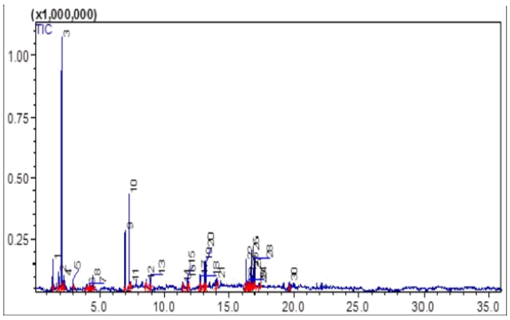


FIG. 3 GC-MS OF OIL OBTAINED VIA CATALYTIC PYROLYSIS WITH 1:3 CATALYST TO POLYPROPYLENE FEED AT 500° C

CONCLUSION

An experimental study on catalytic and thermal pyrolysis of polypropylene was performed to study the effect of catalyst and temperature on the product yield. Acid treated kaolin clay was found to be an efficient and cost effective catalyst for pyrolysis of plastic. Highest yield of liquid hydrocarbons was achieved with kaolin clay treated with 3M HCl. This is due to the fact that acidity of clay increased and thereby increasing the liquid yield. Higher acidity as in the case of kaolin clay treated with 5M increased the gas yield. Furthermore, higher heating rate favors the formation of viscous hydrocarbons. For obtaining low viscous hydrocarbons, less heating is required, thereby compensating the liquid yield.

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