# ETHANOL DRY REFORMING OVER Ce-PROMOTED Ni/$Al_2O_3$ CATALYST FOR $H_2$ PRODUCTION

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We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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Date : JULY 2015

# STUDENT’S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
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Date : JULY 2015

# DEDICATION

This work is dedicated to

My loving mother Tinyai, my beloved father Gira
and all my big family in Sarawak.

# ACKNOWLEDGEMENT

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# ABSTRACT

Ethanol dry reforming show a high potential to become a technology used to produce alternative fuel a transition from traditional petroleum based fuel which continue to increase in price along with its depletion. The product gas is called syngas that consists of CO and $H_2$ gasses, whereby $H_2$ can be used as a clean energy carrier that could help to reduce the emission of GHG. The major problem faced in this process is catalyst deactivation by coking or carbon deposition therefore a lot of effort had been done in researched of catalyst that able to prolong the reaction and also economically feasible. Recently a non noble metal Nickel (Ni) had been a great interest for catalyst for the industrial application because of its cheap in price and high C-C bond breaking activity. The results from characterization of the catalyst based on XRD analysis the calcinations and the addition of Ce promoter did not alter the composition of the catalyst hence the results show consistency with the reading from the data base. TGA analysis illustrates the addition of Ce increase the height and shifts the peaks to the left. The cracks and small catalyst size from SEM results tells that alumina has high degree of dispersion and lastly from BET study the deposition of Ce increase the diameter of catalyst however it decreases the pores surface area. Based on reaction study results by manipulating the feed partial pressure of $CO_2$ at the highest of 50 kPa, the conversion of $H_2$ and $CO_2$ is at the highest up to 90 % for $H_2$. The additions of quantity of $CO_2$ feed ratio allow further decomposition of methane ($CH_4$) thus increase more amount of $H_2$ produced a consistent results with the theory. The results obtained from this research gave positive outcomes in the application of the process in industrial scale by increasing the feed ratio of $CO_2$ to 2.5 to ethanol more $H_2$ in being converted.

# ABSTRAK

Etanol kering pembaharuan menunjukkan potensi yang tinggi untuk menjadi teknologi yang akan digunakan untuk menghasilkan bahan api alternatif peralihan daripada bahan api tradisional berasaskan petroleum yang akan terus meningkat harga selari dengan kekurangan hasil bahan api tersebut. Gas produk dipanggil syngas yang terdiri daripada CO dan $H_2$ gas, di mana $H_2$ boleh digunakan sebagai pembawa tenaga bersih yang boleh membantu untuk mengurangkan pelepasan gas rumah hijau. Masalah utama yang dihadapi dalam proses ini adalah pemangkin penyahaktifan oleh pemendapan karbon disebabkan hal yang demikian banyak usaha telah dilakukan dalam kajian mangkin yang dapat memanjangkan tindak balas dan juga dilaksanakan dari segi ekonomi yang berpatutan. Sejak kebelankangan ini, logam tidak adi nikel (Ni) telah menjadi suatu kepentingan yang besar untuk pemangkin kepada aplikasi perindustrian kerana harga yang murah dan C-C leraian bon aktiviti yang tinggi. Hasil keputusan daripada pencirian mangkin berdasarkan analisis XRD yang pengkalsinan dan penambahan Ce sebagai pengalak pemangkin tidak mengubah komposisi pemangkin oleh itu hasil kajian menunjukkan konsistensi dengan bacaan dari pangkalan data. Analisis TGA menunjukkan penambahan Ce meningkatkan ketinggian puncak dan beralih puncak ke kiri. Retakan dan saiz pemangkin yang kecil dari kajian SEM menunjukkan bahawa alumina mempunyai kadar serakan tinggi dan akhir sekali kajian BET pemendapan Ce meningkatkan diameter pemangkin walau bagaimanapun ia mengurangkan luas permukaan liang. Berdasarkan hasil kajian tindak balas dengan memanipulasi nisbah punca tekanan $CO_2$ di tertinggi 50 kPa, penukaran $H_2$ dan $CO_2$ adalah di kedudukan paling tinggi sehingga 90% bagi H. Penambahan kuantiti punca nisbah $CO_2$ membolehkan penguraian ikatan metana ($CH_4$) seterusnya meningkatkan lagi jumlah $H_2$ menghasilkan keputusan yang konsisten dengan teori. Hasil kajian yang diperolehi daripada kajian ini telah memberikan hasil yang positif dalam penggunaan proses dalam skala industri dengan meningkatkan punca nisbah gas $CO_2$ kepada 2.5 kepada etanol mampu menghasilkan gas $H_2$ dalam ditukarkan.

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| | |
|---|---|
| ${}^{o}C$ | Degree Celsius |
| Ce | Ceriun |
| $CH_4$ | Methane |
| Co | Cobalt |
| $CO_2$ | Carbon dioxide |
| CO | Carbon monoxide |
| Cu | Copper |
| g | Gram |
| g/mol | Molar mass |
| $H_2$ | Hydrogen |
| K | Kelvin |
| $Kg/m^3$ | Density |
| $KJmol^{-1}$ | Energy |
| kWh | Power |
| Mpa | Mega pascal |
| $Ni/Al_2O_3$ | Nickel alumina |
| Pt | Platinum |
| ppm | Part per million |
| RT10 | Ramping 10 ${}^{o}C$/min |
| RT15 | Ramping 15 ${}^{o}C$/min |
| RT20 | Ramping 20 ${}^{O}C$/min |
| $\Delta H^o$ | Ethalphy |
| % | Percentage |

| | |
|---|---|
| *EDR* | Ethanol dry reforming |
| ESR | Ethanol steam reforming |
| BET | Brunauer, Emmett and Teller |
| GHG | Green house gas |
| NASA | National Aeronautics and Space Administration |
| SEM | Scanning Electron Microscopy |
| TGA | Thermogravimetric analysis |
| USA | United State of America |
| IT | Information Technology |
| VS | Versus |
| XRD | X-ray Diffraction |

# 1 INTRODUCTION

## 1.1 *Background*

Human population increase as much as 1.3 % ever year nonetheless this consider to be smaller compare to in 1965-1970 which is 2.1% (globalchange.umich.edu). In spite of that today at much larger population number it is consider as exponential growth rate and must be taken seriously. Experts acknowledge that the world's current rate of energy consumption is at alarming rate and will be lacking of power unless we find a new alternative form of renewable energy source to confront with the world energy crisis.

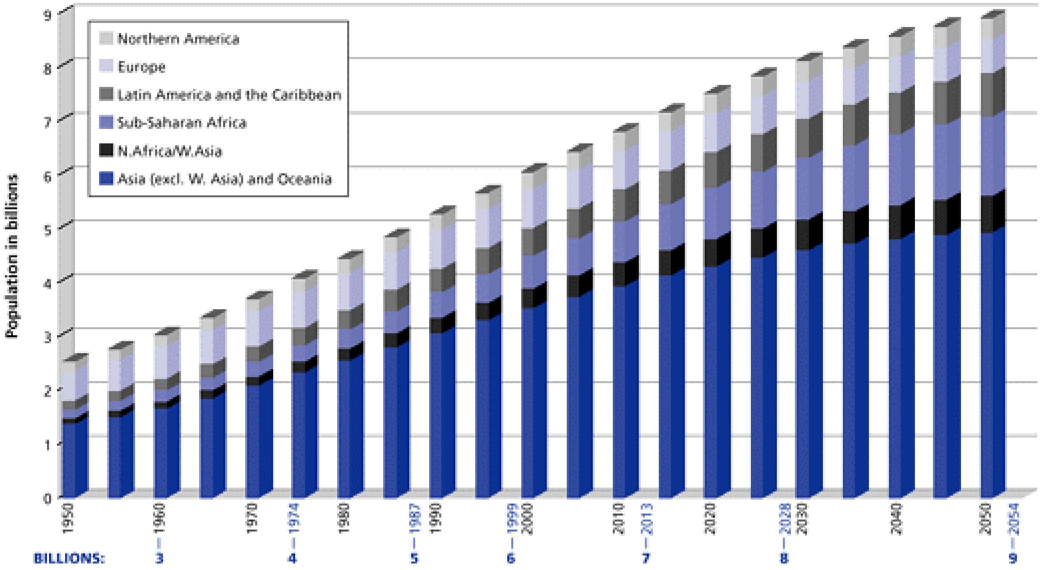


Figure 1-1 : Projected world population growth

According to The World Bank Working for a World Free of Poverty website 3 045.01 kWh of Earth electricity consumption per capita in 2011 compare to 2 582 kWh in 2004 approximately 17.9% increase over 6 years period(worldbank.org). The demands for electric power increase immensely especially in developing countries such as in China and South Korea to satisfy the energy requirement for their power plants.

The main challenge is not so much about whether oil will continue to exist, but whether there will be sufficient supplies at affordable prices. For countries such as the United States, who import from others countries for a steady supply of oil, availability and price will be their ultimatum. As oil or resources being use worldwide at rapid rate this lead to acutely surge the market price (fueleconomy.gov)(eni.com).

In a sense of global issues however Middle-Eastern politics plays a major role here since there are a huge amount of energy resources available. These have become a great interest of western economies such as France, Britain, USA and former Soviet Union. Over the past decades Middle East had suffered wars, overthrow of democratically elected leaders, and puppet governments and dictatorships that all rotated around the world’s energy crisis (worldenergy.org).

In conclusion hydrogen will be the new clean energy carrier to replace the world thirst of energy where hydrogen is use in fuel cell engine to provide power. Fuel cells will be available to a wide range of products, from a miniature size use in portable devices such as laptops and hand phones, to huge engine of cars, ships, and airplanes, likewise to provide power in industrial sector (fuelcellenergy.com).

Additionally applying hydrogen in fuel cell systems emit no harmful emissions by products as a matter of facts NASA spaceships burned hydrogen gas leaving clean drinking water for the astronauts (nasa.gov). They are also excellent in Medical and IT field since it make low noise and high power output. Hydrogen and Fuel Cells will serve a better future for both man and environment unlike other resources either toxic or harm to the environment.

## *1.2 Motivation*

Currently as global demand of petroleum based energy increases exponentially each every year, a new more sustainable energy is highly desired. Thus transition from traditional petroleum based energy to hydrogen economy is one of the best solving answer, since hydrogen is a clean energy carrier (Xun Hu. 2014). Moreover, hydrogen is expected to be one of the most important fuels where it can be use in fuel cell to generate electricity and in hydrogen internal combustion engine vehicles (Murat CİNİVİZ. 2012). The benefits of it all are such as to reduce the dependence on non-renewable resources which are very costly and gradually to continue with it depletion, decrease in emissions of greenhouse gases (GHG) and others harmful air pollutions from the combustion of petroleum based fuel. Other than that hydrogen is also used widely in the production of pharmaceuticals, fine chemicals and bulk chemicals such as ammonia and methanol (Wenju Wang, 2009).

Hydrogen can be produced from diverse energy resources, using varieties of processes technologies such as thermochemical, biological, electrolytic, and photolytic. Bio-derived liquid (ethanol) undergo reforming, which is the most plausible way to produce hydrogen since ethanol is a non toxic nature substance, high availability, cheap and a renewable resource. 95% of ethanol production is by fermentation called bioethanol the raw products comes from various range of biomass resources such as cellulose of plant, argro-industrial wastes, forestry materials and municipal solid waste, in Canada they uses grains, Brazil; sugarcane and in the United State; corn. Apart from that ethanol is feasible for large scale production because it is easily to store, handle and transport due to its volatility. The dry reforming of ethanol reaction is as follows (A. Zawadzki.2014).

A non noble metal such as Ni is currently a great interest to be use as catalyst since Ni has high C-C bond breaking activity overall it is cheaper, compare to other noble metals such as Rh, Ru, Pd and Pt (Nader Rahemi. 2013). However the acid sites of Al2O3 promote ethanol dehydration, Ni/Al2O3 catalyst suffers carbon deposition. To subdue deactivation alkaline oxides such as MgO and CaO is use as additives by neutralizing the acidity, apart from that ZrO2 added to Ni/Al2O3 catalyst to improve stability and boost adsorption and dissociation of water on the surface of nickel catalyst (Seung Ju Han. 2014).

The catalyst Ni/Al2O3 is synthesis by wet impregnation process as it is most prefer in industrial level. The simplicity of the methodology and the convenience make impregnation method is attractive for industrial scale up purpose and much research has been dedicated to improving the preparation method.

Dry reforming or carbon reforming is a process used to produce syngas from reacting carbon dioxide with hydrocarbon or other volatile fossil fuels (K. De Oliveira-Vigier. 2008). It was first developed by Franz Fisher and Hans Tropsch in Germany in 1928. Their researched was mainly about production of syngas from coal and gaseous fuels and production liquid fuel from syngas, since Germany is a place with abundant supply of coal but scarce of petroleum.

## *1.3 Problem statement*

$21^{1st}$ century monumental dilemma is too much dependency on the limited fossil fuels where the use of fossil fuels consequencing high emission of harmful GHG disturbing the environment such as global warming.

## *1.4 Objectives*

The following are the objectives of this research:

- Examine the effect of feed composition on 3%Ce-10%Ni/$Al_2O_3$.
- To investigate the effect of reaction condition such as feed composition and reaction temperature on catalytic selectivity and activity from ethanol dry reforming over 3%Ce-10%Ni/$Al_2O_3$.

## *1.5 Scope of this research*

In order to achieve all the objectives, several scopes have been identified. First procedure is the pre-treatment of alumina($Al_2O_3$) support, done by calcinations process at temperature of 600 $^oC$ for 5 hours. Secondly is the synthesis of catalyst, nickel(II) nitrate $Ni(NO_3)_2$ dissolve in water and continuously stir for 3 hours and left to dry over night at 110 $^oC$. Once dried the catalyst then undergo calcinations for 5 hours at 500 $^oC$. Catalyst characterization will be conduct which are are Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM), X-Ray Diffraction(XRD), and Temperature-Programmed Reduction (TPR). The gas product from the reaction will be test by Gas Chromatography (GC).

## *1.6 Organisation of thesis*

This thesis is about the production of hydrogen gas from ethanol via dry reforming and it begins with the background and literature review. In chapter 2 literature review talks about fuel cells technology, production of hydrogen from renewable and non-renewable sources, comparison of ethanol dry reforming versus ethanol steam reforming and catalyst deactivation.

Chapter 3 discussed about materials used and methods for synthesizing the catalyst. Catalysts (10%-$Ni/Al_2O_3$ and 3%Ce-10%$Ni/Al_2O_3$) were prepared via wetness impregnation is illustrated using flow chart. Calculation on how to measure the right amount of catalyst for synthesizing is also shown in this chapter.

Chapter 4 includes results from the two catalysts characterization. In this chapter also include the results from preliminary runs of reaction study that are detailed. Where the reactions were conducted at fixed temperature and pressure but manipulated partial pressure and catalysts used.

Chapter 5 provides the overall results finding for the thesis and recommendations for future work.

# 2 LITERATURE REVIEW

## 2.1 Overview

The world is currently in its early stage of undergoing dramatic change, all these are influence by the depletion of fossil fuels and the soaring increase average global temperature or global warming. To overcome with the situation implementing clean energy technology such as ethanol dry reforming for hydrogen production could save our world from the energy crisis and reduce pollution.

The process of taking $CO_2$ a harmful gas for the environment and making it into something more valuable is interesting and beneficial(Atashi H, 2010)(Pholjaroen B, 2009). There has been a lot of research and patents done on the subject but little is known and understands, clearly renewable energy is the key for our sustainable development.

## 2.2 Introduction

This chapter explained the history of fuel cells technology and how the basic device works. Next is describing advantages and disadvantages of how hydrogen is produce from both renewable and non-renewable sources. Lastly is the comparison of ethanol dry reforming versus ethanol steam reforming.

## 2.3 Fuel Cells

Fuel cells are devices that convert hydrogen (fuel) and oxygen (oxidant) into water along while generating electricity. It was first invented by a British scientist Sir William Robert Grove in the 19th centuries, he was experimenting electrolysis of water that let him to discovered the new technology (J. Laminie. 2003). During the time fuel cell technology was only for the purpose of space applications, since the cost of manufacturing the technology was quite high at the time. Fuel cells are electrochemical devices which will not be subjugated by thermodynamic laws of heat which is by combustion.

Hydrogen is fed in the anode where its electron is stripped thus ionized the hydrogen atoms. The ions then pass through a conductive electrolyte to combine with oxygen at the cathode. The negatively charged electrons provide the current through wires to do work. The electrolytes play a very important role by permitting only the appropriate ions to pass between the anode and cathode. There are a few types of electrolytes available in today markets that are proton exchange membrane (PEM), solid oxide alkali, molten carbonate and phosphoric acid (Smithsonian Institution. 2008). Basic overall reaction of fuel cell is shown below.

$$\mathbf{H_2 + \tfrac{1}{2}O_2 = H_2O} \qquad \mathbf{(1)}$$

(Pilatowsky 2011)

## *2.4 Hydrogen Production (renewable)*

### *2.4.1 Electrolysis of Water*

Hydrogen produce by electrolysis is basically by running electricity through two electrodes in water, oxygen is gathered at the anode while hydrogen is at cathode. There are three type of industrial electrolysis two of which either bipolar or unipolar using aqueous solution of potassium hydroxide (KOH) and thirdly is a solid polymer electrolyte electrolyser. The production cost of the process is dependent on the economic factors of the electricity used. Other threats to the process are today’s technologies are too small for high hydrogen demand and the electricity is generated by burning fossil fuels (Francois Leveque 2010).

### *2.4.2 Photolysis*

Hydrogen is produce by splitting hydrogen molecule from water compound by solar energy. A photoelectron-chemical cell used to carry out photoelectrolytis reactions that comprised of semiconductor to absorbs solar energy and produces electric energy used to separate water molecule. Integrating solar energy and water electrolysis into one single photoelectrode revolutionize the technology cutting the cost of power generator and electrolyzer. However phoelectrolysis is still in experimental stage and the cost is still very expensive for scale up (J.D. Holladay. 2009).

## *2.5 Hydrogen Production (non-renwable)*

### *2.5.1 Methane Steam Reforming*

Steam reforming of methane is the most study process, it is a catalytic process by reacting methane with steam in the presence of catalyst at high pressure and temperature to produce syngas of $3H_2$ and CO (Rostrup-Nielsen, 1984). Nonetheless the process is an endothermic process, a huge amount of energy are been used making the process expensive. However, high quantities of carbon dioxide are emitted during the reforming processes. Besides that the raw product to obtain methane is from natural gas non-renewable resource therefore it is not a viable process for long term usage.

$$\mathbf{CH_4 + H_2O \leftrightarrow CO + 3H_2} \quad \mathbf{(2)}$$

$$\mathbf{CO + H_2O \leftrightarrow CO_2 + H_2} \quad \mathbf{(3)}$$

(Sofia D. Angeli. 2014)

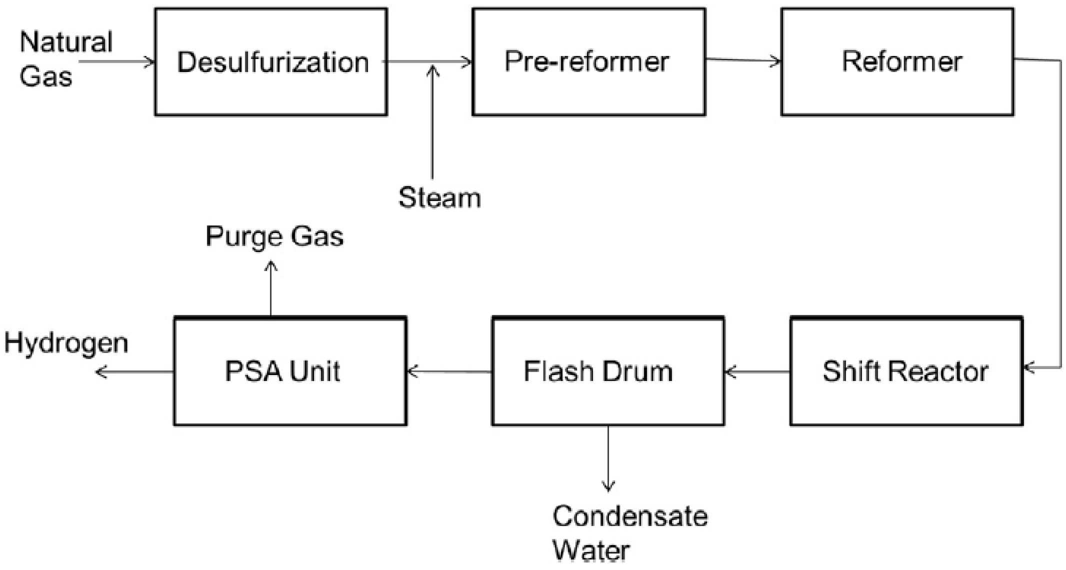


**Figure 2-1: Block flow diagram for steam methane reforming. (Mondal, 2014)**

### *2.5.2 Coal Gasification*

Gasification is a process of converting coal into syngas by partial oxidation in presence of steam, the technology been around since 1800. A gasifier converts hydrocarbon feedstock into syngas by applying heat under pressure. The coal is chemically broken apart due to the heat and pressure from the gasifier thus producing syngas. The main problems faced today with the process are water contamination and the harmful impact to the environment (land).

### *2.5.3 Bioethanol*

Bioethanol along with biodiesel has become one of the most promising biofuels today, in conjunction to uncertain fuel supply and efforts to reduce carbon dioxide emissions. Bioethanol is seen as a feasible fuel alternative because the source crops can be grown renewably by harvesting the energy of the sun in most climates around the world. This can be accomplish during the growing phase of the source crop, CO2 is absorbed by the plant and oxygen is released in the same volume that CO2 is produced in the combustion of the fuel.

**Figure 2-2: Advantages of ethanol in catalytic reaction**

Bioethanol in the modern day are being used as a biofuel for transport such as in Europe, where the country is blending 5% of ethanol with petrol. Other than that ethanol can be used in a number of chemical industries such as pharmaceuticals, cosmetics, beverages and medical sectors as well as for industrial. Improvement can be seen in the performance when ethanol is used as a substitute for lead as an oxygenating additive and has a high octane rating.

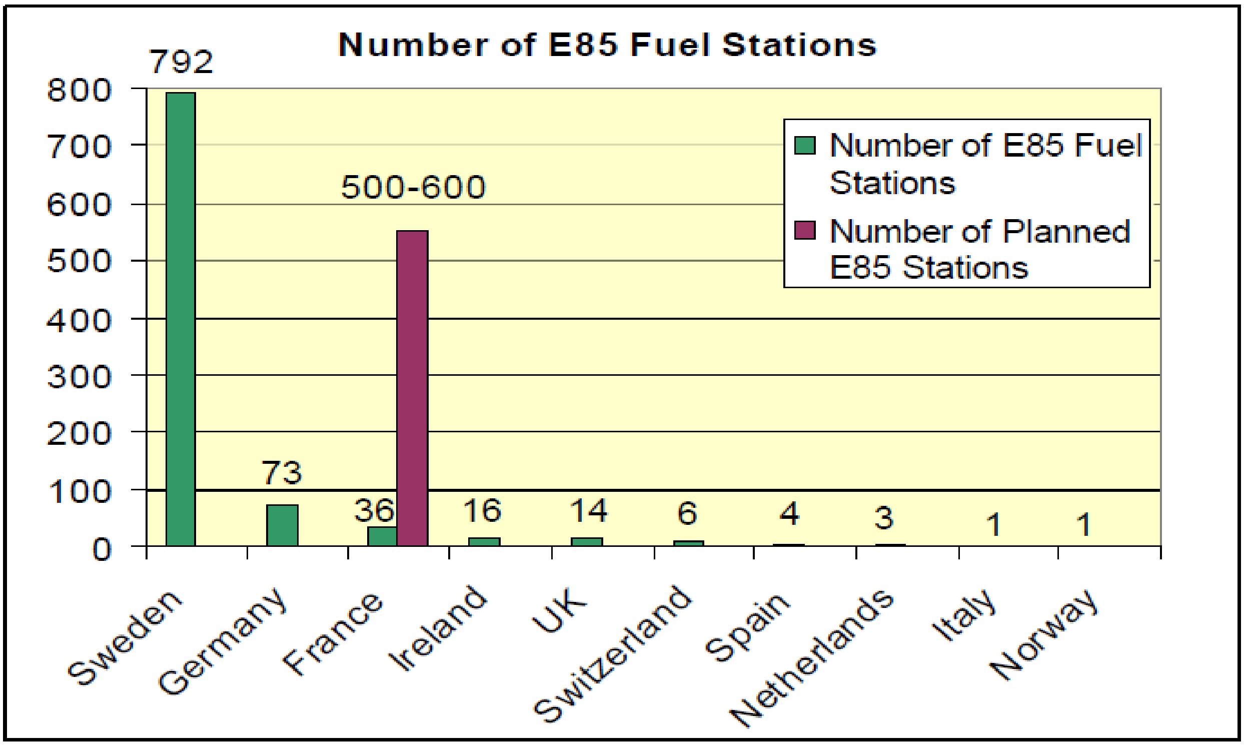


**Figure 2-3 : Number of E85 fuel stations in Europe countries**

The figure above shows leading Europe countries in bioethanol fuel stations. The highest number of fuel station is Sweden, follow by Germany. Meanwhile others countries are just starting on the new technology with lest that half of amount in Germany. Fuel cells are another potential area for ethanol use to produce heat and power. USA and Australia are the only two countries that managed to manufacture fuel cells technologies (Acumentrics made by USA and Ceramic Fuel Cells made by Australia) where bioethanol can be use straight away with the need of reformer to convert the ethanol to hydrogen gas. (Europa.eu)

## *2.6 Malaysia Market for Bioethanol*

National Green Technology Policy was launched in 2009 by Malaysia Prime Minister Datuk Seri Najib Razak, the objective of this policy is to be a driver in the national economy and promote sustainable development. On the other hand the policy is in conjunction with Economic Transformation Programme (ETP) and Renewable Energy Act 2011. The function of Renewable Energy Act 2011is to implement and establish a special tariff system to catalyze the generation of renewable energy and to provide any related matters. Overall the purpose of all the initiatives is to achieve the biomass industry potential.

In 2011 Malaysia launched National Biomass Strategy (NBS) 2020, an innovative on how to benefit from biomass for downstream activity in term of sustainable economic and social benefits. Malaysia has a big advantage when it comes to biomass, as the land is fertile for agriculture industry. Apart from that Malaysia is one of the world’s largest producers of Crude Palm Oil (CPO) and generates about 12% of National Gross Income (NGI) from agriculture sector. Making it more lucrative, in 2012 it was estimated 83 million tonnes of dry biomass and expected to increase to 100 million tonnes by 2020. Among the 83 million tons of solid biomass (biomass (empty fruit bunches, fibers) and 60 million tons of palm waste liquid as a result of the production of palm oil, with 90% of this being discarded without being used.(Asiabiomass.jp)

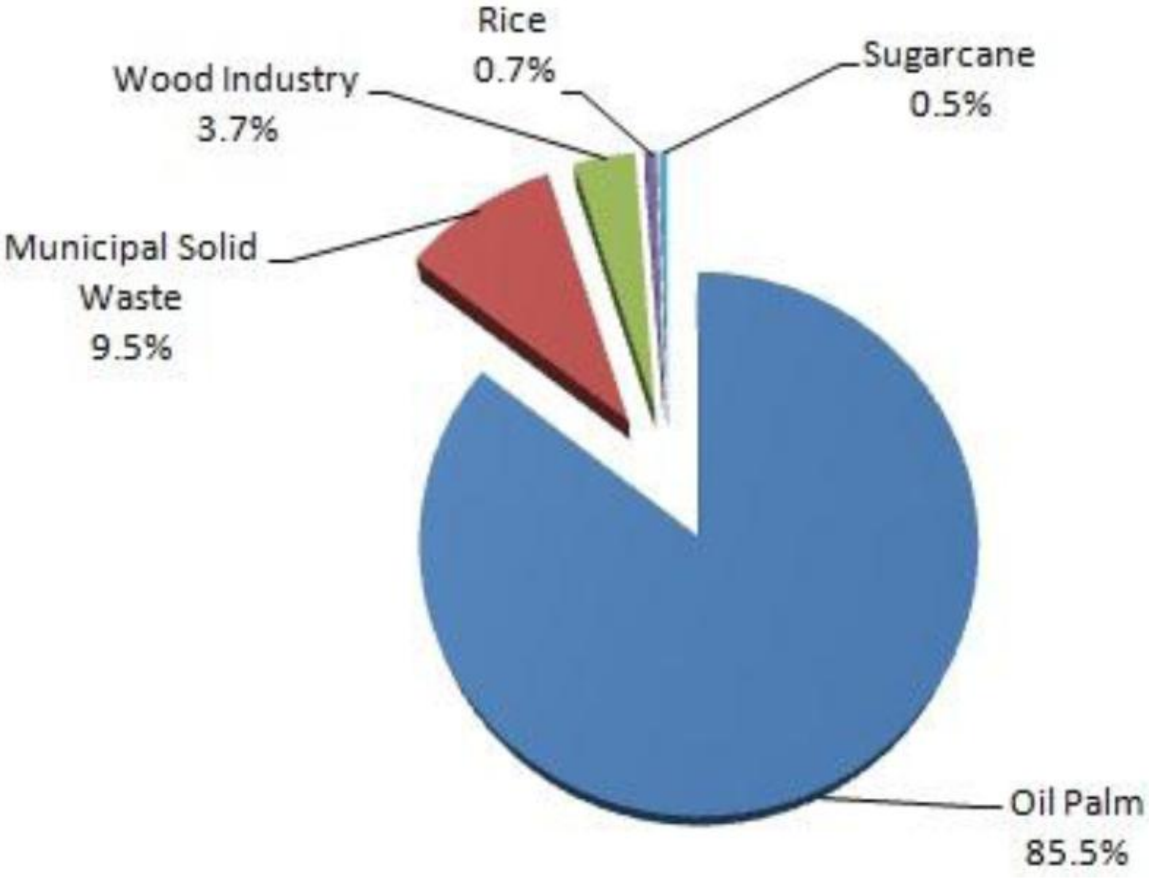


**Figure 2-4: Malaysia $H_2$ prospect**

Being a second largest producer and exporter of oil palm in 2006, Malaysia’s oil palm industry produced huge amount of biomass wastes that contribute about 85.5% of total biomass available in the country. To put in perspective Malaysia can generate up to RM 30 billion contribution to GNI by utilizing the biomass only from palm oil industry waste. This will also helps fellow Malaysians to have more and better jobs, estimated about 66 000 by 2020 together growing alongside with the industry. Malaysia has a solid track record in palm oil industry that produces a lot of usable waste thus putting Malaysia in the centre of the spotlight attracting international attention for its potential in sustainable source of biomass feedstock.

4 million hectares of land under oil palm plantation. 75% of total area planted is located in just four states, Sabah, Johor, Pahang and Sarawak, each of which has over half a million hectares under cultivation. (bioenergyconsult.com). The country is looking to lead Southeast Asia to turn agricultural waste into useful biofeul. Where else in Sarawak the opportunities start with 2nd Generation biethanol and Bio chemical production facility for sustainable feedstock supply for downstream operations. Agensi Inovasi Malaysia (AIM)

**Table 2-1: Advantages of hydrogen fuel cells**

| | |
|---|---|
| High energy efficiency | Potential for a high operating efficiency (typically between 40% to 60% efficiency), and is not dependant on system size. |
| Scale of design | Highly scalable, modular and compact design based on power requirements. |
| Fuel/energy sources | Numerous types of potential fuel sources are available, mainly pure hydrogen, natural gas and methanol. |
| Moving/rotating components | The cell itself has no moving parts, allowing for quite and highly reliable operation. |
| Emissions | Produces zero or near-zero greenhouse emissions. |
| Recharge capability | Nearly instantaneous recharge capability compared to batteries. |

A significant advantage of a hydrogen fuel cell is that only heat and water (or water vapour) is directly produced, eliminating the pollutants normally associated with combustion based power systems. Its green technology is an ideal replacement to conventional power systems as far as environmentalists are concerned. Besides that, fuel cells offer other unique advantages, such as summarized in Table 2-1.

## 2.7 *Ethanol steam reforming (ESR) versus Ethanol dry reforming (EDR)*

Ethanol is prefer because it is produce from a renewable source, safer and contains higher number of hydrogen per molecule as compare to methanol and methane. In past few years has there been growing interest to produces hydrogen from clean renewable of ethanol via steam reforming. However ethanol steam reforming is at disadvantage since the process is an endothermic that requires huge energy input to derive the reactions.

$$\mathbf{CH_3CH_2OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad \Delta H^o\ 298 = +347\ kJmol^{-1}} \qquad \textbf{(4)}$$

With the growing concern of environmental issues the selected process would have to meet the requirement. In a case of EDR it is prefer because even thou steam reforming produces more $H_2$ at the same time also producing $CO_2$ however EDR is $CO_2$ free. According to thermodynamics researched done by Wenju Wang ethanol dry reforming almost achieved complete conversion of 94.75-94.86% yield of hydrogen. The yield of hydrogen depends on the complex manner on process variables such as pressure, temperature, $CO_2$:$C_2H_5OH$ ratio, etc.

$$\mathbf{CH3CH2OH + CO2 \rightarrow 3H2 + 3CO\Delta H^o\ 298 = +229.6\ kJmol^{-1}} \qquad \textbf{(5)}$$

(A. Zawadzki. 2014)

Other possible reaction of DRE, the reaction is an endothermic reaction $\Delta H^o = 296.7$ KJ mol$^{-1}$ and produces carbon monoxide and hydrogen at optimum and if reacts in most desirable condition.

**$C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2$ (6)**

Dehydrogenation of ethanol will produces acetaldehyde and hydrogen.

**$C_2H_5OH \rightarrow CH_3CHO + H_2$ (7)**

Decomposition of acetaldehyde produces methane and carbon dioxide or a second reaction into hydrogen and carbon monoxide.

**$CH_3CHO \rightarrow CH_4 + CO$ (8)**

**$CH_3CHO + CO_2 \rightarrow 2H_2 + 3CO$ (9)**

However dehydration of ethanol can produce either ethylene or ether.

**$C_2H_5OH \rightarrow C_2H_4 + H_2O$ (10)**

**$C_2H_5OH \rightarrow \frac{1}{2}C_2H_5OC_2H_5 + \frac{1}{2}H_2O$ (11)**

Polymerization of ethylene produces carbon and hydrogen.

**$C_2H_4 \rightarrow \text{polymers} \rightarrow 2C + 2H_2$ (12)**

Next is decomposition of ethanol will forms carbon monoxide, methane, carbon dioxide, hydrogen and acetone.

**$C_2H_5OH \rightarrow CO + CH_4 + H_2$ (13)**

**$C_2H_5OH \rightarrow CO_2 + CH_4$ (14)**

**$C_2H_5OH \rightarrow CH_3COCH_3 + CO + H_2$ (15)**

Formation of methane through methanation reaction from transformations of carbon monoxide and carbon dioxide.

**$CO + 3H_2 \rightarrow CH_4 + H_2O$ (16)**

**$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (17)**

Dry reforming of methane is an endothermic reaction and forms hydrogen and carbon monoxide at optimum and if reacts in most desirable condition.

$$\mathbf{CH_4 + CO_2 \rightarrow 2CO + 2H_2} \qquad \mathbf{(18)}$$

At lower temperature, during water shift reaction which is exothermic and reversible reaction. The equilibrium tend to shifts to the right and favour the formation of $H_2$ and $CO_2$.

$$\mathbf{CO + H_2O \rightarrow CO_2 + H_2} \qquad \mathbf{(19)}$$

Decomposition of methane produce carbon and hydrogen, meanwhile Boudouard reaction gives out carbon and carbon dioxide.

$$\mathbf{CH_4 \rightarrow 2H_2 + C} \qquad \mathbf{(20)}$$

$$\mathbf{CO \rightarrow \frac{1}{2}CO_2 + \frac{1}{2}C} \qquad \mathbf{(21)}$$

Reduction reaction of carbon dioxide produces carbon and water vapour.

$$\mathbf{CO + H_2 \rightarrow C + H_2O} \qquad \mathbf{(22)}$$

$$\mathbf{CO_2 + 2H_2 \rightarrow C + 2H_2O} \qquad \mathbf{(23)}$$

Based on Gibbs energy analysis, hydrogen production varies significantly with different reaction pathways. Therefore in order to maximize the hydrogen gas produce, it is pivotal to provide sufficient amount of $CO_2$ and by minimizing the possibilities of dehydration and decomposition of ethanol.

## *2.8 Catalyst Deactivation*

Stand for the loss of time of catalytic activity or selectivity (Morris D. 2013), there are two types of catalyst deactivation that are chemical and physical and commonly divided into poisoning, coking or fouling, sintering and phase transformation. In industrial scale catalyst deactivation is a major threat, it can cost a great loss to a company not only in terms of money but also time. The replacement of new or regeneration of catalyst required a lot of money and also time for shutdown operation, moreover it is an inevitable process but the decay can be slow down.

**Table 2-2: Mechanisms of catalyst deactivation**

| Mechanism | Type | Definition |
|---|---|---|
| Poisoning | Chemical | Strong chemisorption of species on catalytic sites which block sites for catalytic reaction |
| Vapour formation | Chemical | Reaction of gas with catalyst phase to produce volatile compound |
| Vapour-solid and solid-solid reactions | Chemical | Reaction of vapor, support, or promoter with catalytic phase to produce inactive phase |
| Attrition/crushing | Mechanical | Loss of catalytic material due to abrasion; loss of internal surface area due to mechanical-induced crushing of the catalyst particle |
| Fouling | Mechanical | Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores |
| Thermal degradation | Thermal | Thermally induced loss of catalytic surface area, support area, and active phase-support reactions |

### *2.8.1 Poisoning*

Poisoning is a strong chemisorption on the active sites of impurities present in the feed stream that result in the loss of activity. An example of poisoning during isomerization of catalyst is the adsorption of basic compound onto an acid catalyst. Poison may affect by blocking the adsorption sites, adsorbed poisons may induce alteration of electronic or geometric structure of catalyst surface. In addition catalyst also suffers changes in chemical nature of active sites or formation of new compounds by reconstruction, hence disturbing the performance. The difference between poisons and inhibitors is the interaction. In general, poison has a very strong interaction with the active site and the process is irreversible vice versa to inhibitors. Catalyst poisons is characterize by their chemical makeup, selectivity for active sites and types of reactions poisoned.

**Figure 2-5: Common poisons classified according to chemical structure.**

| Chemical type | Example | Type of interaction with metals |
|---|---|---|
| Group VA and VIA | N, P, As, Sb,<br>O, S, Se, Te | Through *s* and *p* orbitals; shielded structures are less toxic |
| Group VIIA | F, Cl, Br, I | Through *s* and *p* orbitals; formation of volatile halides. |
| Toxic heavy metals and ions | As, Pb, Hg, Bi,<br>Sn, Cd, Cu, Fe | Occupy *d* orbitals;<br>May form alloys. |
| Molecules that adsorb with multiple bonds | CO, NO, HCN, benzene, acetylene, other unsaturated hydrocarbons | Chemisorption through multiple bonds and back bonding |

Table 2-4 illustrate 4 groups of catalyst poisons based on their chemical origin and type of interaction with metals. Group VA-VIIA shows the interaction of the elements with catalytic metal phases that depend on the oxidation state of the former, such as the availability of electrons pairs for bonding and shielding degree of sulphur ion via ligands.

The order of increased shielding via oxygen with the decreasing of toxicity poisoning is $H_2S$, $SO_2$, $SO_4^{2-}$ with dependent of different sulphur species. The increase in atomic size or molecular size and electronegativity attribute the increase of toxicity, nevertheless gasification of poison via $O_2$, $H_2O$, or $H_2$ in reactant stream can decrease the toxicity.

**Figure 2-6: Poisons for selected catalyst in important representative reaction.**

| Catalyst | Reacation | Poisons |
|---|---|---|
| Silica–alumina, zeolites | Cracking | Organic bases, hydrocarbons, heavy metals |
| Nickel, platinum, palladium | Hydrogenation and dehydrogenation | Compounds of S, P, As, Zn, Hg, halides, Pb, $NH_3$, $C_2H_2$ |
| Nickel | Steam reforming of methane, naphtha | $H_2S$, As |
| Iron, ruthenium | Ammonia synthesis | $O_2$, $H_2O$, CO, S, $C_2H_2$, $H_2O$ |
| Cobalt, iron | Fischer–Tropsch synthesis | $H_2S$, COS, As, $NH_3$, metal carbonyls |
| Noble metals on zeolites | Hydrocracking | $NH_3$, S, Se, Te, P |
| Silver | Ethylene oxidation to ethylene oxide | $C_2H_2$ |
| Vanadium oxide | Oxidation/selective catalytic reduction | As/Fe, K, Na from fly ash |
| Platinum, palladium | Oxidation of CO and hydrocarbons | Pb, P, Zn, $SO_2$, Fe |
| Cobalt and molybdenum sulfides | Hydrotreating of residuum | Asphaltenes, Ni, V<br>N compounds, |

Table 2-5 exhibited a common poison for certain catalysts bestow to their reactions. Acidic solids, such as Silica–alumina and zeolites tend to suffer from organic bases and ammonia poisons. At the same time sulphur and arsenic metals normally poison during hydrogenation, dehydrogenation, and steam reforming process. Next, in automotive emissions control, cracking and hydrotreating usually poison by Ni, Pb, V and Zn metals. Lastly ethylene oxidation from acetylene poison and hydrotreating petroleum residuum suffers asphaltenes poison.

### *2.8.2 Fouling (Coking)*

*Fouling* is the physical deposition of species onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores that include mechanical deposits of carbon and coke in porous catalysts. Carbon or coke formation are classified as either coke-sensitive or coke-insensitive as suggested by Menon and stressed the structure and location of coke are more important than its quantity in affecting catalytic activity. In coke-sensitive reactions, unreactive coke is deposited on active sites, result to activity decline, while in coke-insensitive reactions, reactive coke precursors formed on active sites are readily removed by gasifying agents. Menon theory confirmed by observation not only location and structure of coke differ but also its mechanism of formation varies with catalyst.

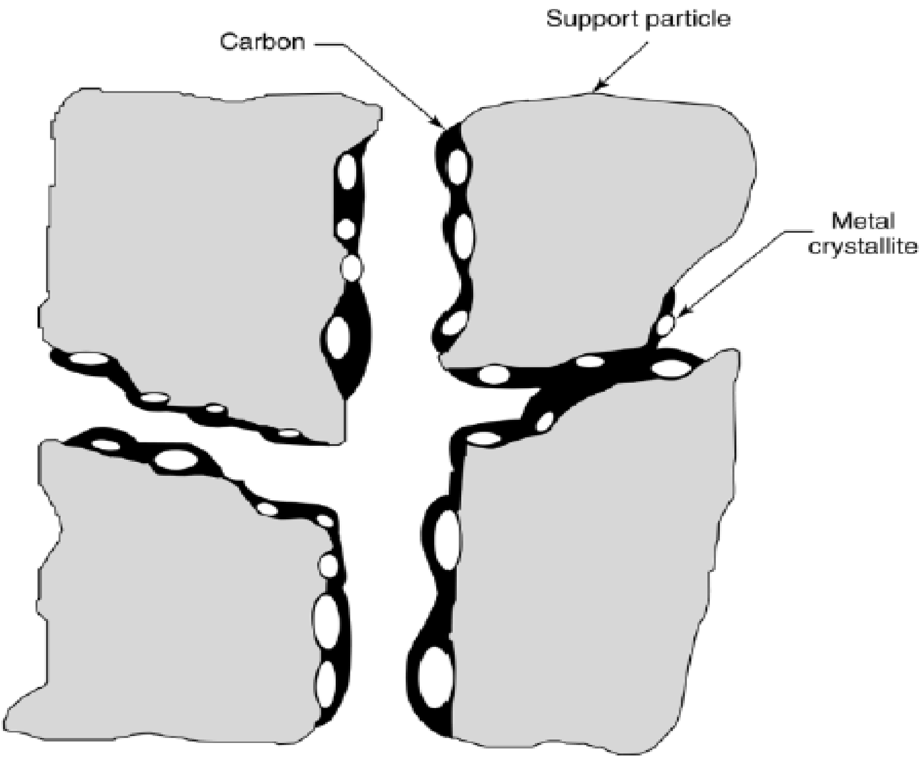


**Figure 2-7**: Conceptual model of fouling, crystallite encapsulation, and pore plugging of a supported metal catalyst owing to carbon deposition. (Wiley-Interscience, 2006)

Previous figure highlight the effects of fouling via carbon coking on support metal catalyst, carbon chemisorb either as monolayer or adsorb physically in the multilayer form a barrier prevent reactant unto active site of metal. The growth of plug micro and mesopores enclose entire metal including the metal pores thus deactivating it. Further coking produces carbon filaments that grow up from inside metal pores consequence stress build up and the support metal to facture causes disintegration of catalyst and overall plugging voids of reactor.

### 2.8.3 *Thermal Degradation and Sintering*

Sintering define as the loss of active surface through structural modification of catalyst that occurs in both supported and unsupported catalyst. In general the process is a thermal activated and physical in nature. Correspondingly reduction of active site occurs by agglomeration and coalescence of small metal crystallites into bigger ones with lower surface-to-volume ratios.

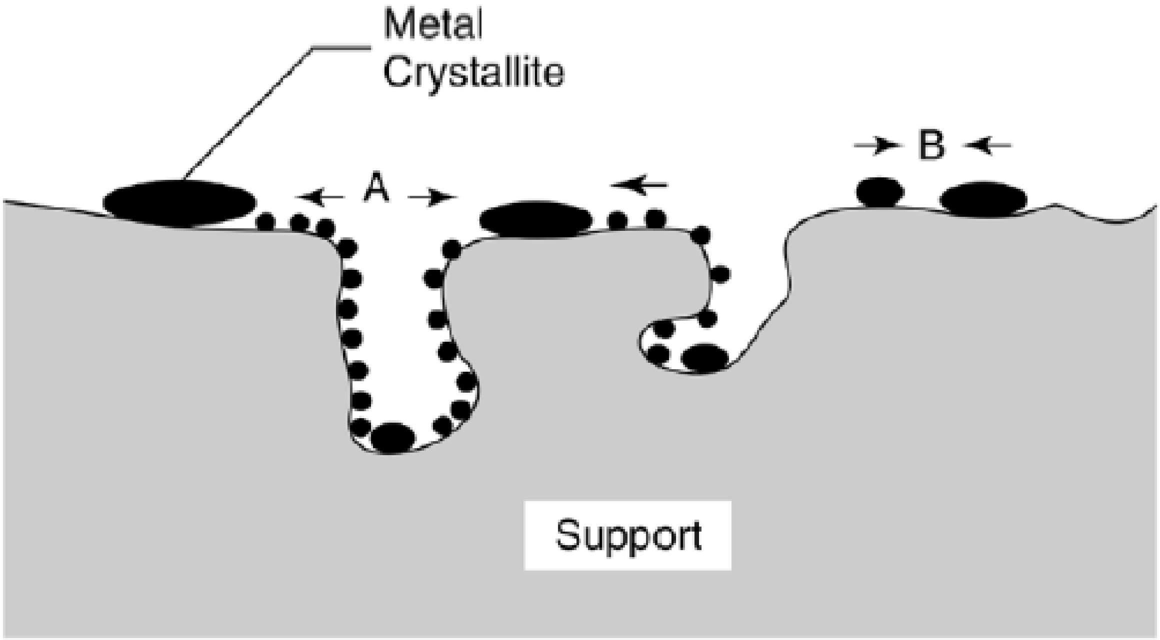


**Figure 2-8**: Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration.(Wiley-Interscience. 2006)

Figure 2-7 represent two cases of sinterings first is (A) atomic migration occurs when atoms from crystallite move across support metal surface thus colliding with other atoms capturing them together. Crystallize migration (B) occur when crystallites migrate along support surface result in collision and coalescence with other crystallites.

Table 2-3 portray Factors Affecting Metal Particle Growth and Redispersion in Supported Metals, sintering rates increase exponentially with temperature. Rapid sintering occurs in oxygen in spite slow in hydrogen with dependence on the support metal. As well as water vapour also increases the sintering rate of support metal.

**Table 2-3**: Effects of Important Reaction and Catalyst Variables on Sintering Rates of Supported Metals Based on General Power-Law Expression

| **Variable** | **Effect** |
|---|---|
| Temperature | Sintering rates are exponentially dependent on $T$; $E$act varies from 30 to 150 kJ/mol. $E_{act}$ decreases with increasing metal loading; it increases in the following order with atmosphere: NO < $O_2$ < $H_2$ < $N_2$ |
| Atmosphere | Sintering rates are much higher for noble metals in $O_2$ than in $H_2$ and higher for noble and base metals in $H_2$ relative to $N_2$. Sintering rate decreases for supported Pt in atmospheres in the following order: NO > $O_2$ > $H_2$ > $N_2$ |
| Metal | Observed order of decreasing thermal stability in $H_2$ is Ru > Ir Rh > Pt; thermal stability in $O_2$ is a function of (1) volatility of metal oxide and (2) strength of metal oxide–support interaction. |
| Support | Metal–support interactions are weak (bond strengths of 5–15 kJ/mol); with a few exceptions, thermal stability for a given metal decreases with support in the following order: $Al_2O_3$ > $SiO_2$ > carbon |
| Promoters | Some additives decrease atom mobility, e.g., C, O, CaO, BaO, $CeO_2$, $GeO_2$; others increase atom mobility, e.g., Pb, Bi, Cl, F, or S. Oxides of Ba, Ca, or Sr are “trapping agents” that decrease sintering rate |
| Pore size | Sintering rates are lower for porous *versus* nonporous supports; they decrease as crystallite diameters approach those of the pores |

### *2.8.4* Catalyst prevention and regeneration

Catalyst prevention is often easier compare to regeneration or curing of catalyst. Poisons and foulants able to be eliminate using guard beds, scrubbers and filters. Fouling, thermal degradation and chemical degradation can be decrease via controlling of operating condition such as decreasing the temperature to lower rate of sintering and via gasification to lower coking. Mechanical degradation able to lower by circumspect choice of carrier materials, coatings, and catalyst particle forming methods.

**Table 2-4**: Type of catalyst deactivation and the prevention measure

| Type of deactivation | Prevention measure |
|---|---|
| Poisoning by impurities | Purification of reactants or mitigation by adding traps (getters) as components of the catalyst. |
| Coking or carbon deposition | Gasification using $O_2$ or $H_2$ gasses and controlling reaction rate regimes |
| Sintering | Minimizing and controlling temperature of reaction. |

Regeneration process is done when the reaction activity had declined to a discerning stage in spite of the prevention efforts. There are a few alternatives had to made when reaction at critical level: (1) restore the activity of the catalyst, (2) use it for another application, (3) reclaim and recycle the important and/or expensive catalytic components, or (4) discard the catalyst. The possibility of regeneration is depending upon the reversibility of the process and the decision is based on the reaction rate. On account of rapid deactivation regeneration becomes economic necessity.

## *2.9 Concluding Remarks*

Every human action is accompanied by a need for energy thus future sustainable energy is most required and it must also meet the requirement of having low or none impact to the environment. This requires innovative strategies for changeover to hydrogen as an energy carrier. Work especially well in country like Malaysia with abundant supply of biomass raw materials for the production of bioethanol.

The opportunity to reduce dependence on fossil fuels, while reducing CO2 is of strategic important today DRE show a great potential to Malaysia market thus can propel the country to great high not only saving millions of money but also helping the citizen by creating jobs and saving the environment too. DRE operates at high temperature thus a suitable catalyst such Ce promoted nickel alumina is one of the priority in making the DRE technology feasible. The process of synthesizing bioethanol need to be improves in order to cut cost and time.

# 3 MATERIALS AND METHODS

## *3.1 Overview*

This paper presents the preparations and method of characterizations between catalysts 10%Ni/$Al_2O_3$ and 3%Ce-10%Ni/$Al_2O_3$.

## *3.2 Introduction*

This chapter provides details and description of materials and equipment used and also the preparation procedures for both catalysts which were done by impregnation method and the characterization procedures of the catalyst shall be described in this chapter.

## *3.3 Materials*

### *3.3.1* Chemicals

All of chemicals used in this research is listed in Table 1. The source of chemicals used named Sigma-Aldrich (Cerium (III) Nitrate Hexahydrate 99.9% trace metal basis, Nickel (II) Nitrate Hexahydrate crystallizes ≥ 97.0%, Aluminium Oxide).

**Table 3-1: List of chemicals and its uses.**

| Materials | Boiling Point °C | Density Kg/m$^3$ | Molecular Weight g/mol | Materials Application |
|---|---|---|---|---|
| **Ethanol** | 78.37 | 789.00 | 46.06 | -Raw product<br>-Use in reforming process |
| **Cerium** | 3257.0<br>795<br>(melting point) | 8.16 | 140.11 | -Catalyst (promoter) |
| **Carbon Monoxide** | -191.5 | 1.15 | 28.01 | -Product |
| **Hydrogen** | -252.879 | 0.08 | 1.00 | -Desire product |
| **Nickel** | 2913<br>1455<br>(melting point) | 8.90 | 58.69 | -Catalyst (supporter) |
| **Alumina** | 2977<br>2072<br>(melting point) | 3.95 | 101.96 | -Support |

### *3.3.2* Gases

The listed of gasses in table 3 were used for the dry reforming reaction throughout this research. All of the gasses used were supplied by Air products Malysia Sdn Bhd. The physical properties are tabulated in the table below.

**Table 3-2 : Specification of gasses used**

| Material | Purity (%) | Molecular weight (g/mol) | Density (g/ml) | Material application |
|---|---|---|---|---|
| Carbon dioxide | 98.97 | 44.01 | $1.98 \times 10^{-3}$ | Reactant<br>GC calibration |
| Nitrogen | 60 ($CO_2$ balance) | 24.02 | - | Diluent<br>BET measurement |
| Helium | 99.999 | 4.0 | - | BET<br>GC |
| Argon | 99.999 | 39.94 | - | TGA carrier |

## 3.4 Ethanol

Ethanol meet all the necessary requirement which are helps to reduces gasoline usage and the dependency on imported oil thus decreases dangerous emission caused by combustion of gasoline. It is approximated that 1 tonne or 1 acre of wheat able to produce 352 litres of ethanol. Moreover ethanol is eco-friendly since the application on of ethanol for the production and use of $H_2$ energy is $CO_2$ neutral ((Athanasios, 2002).

It is also known that ethanol is easy to produce, and is also safe to handle, transport and store (Athanasio, 2004); (Cavallaro, 1996). Furthermore ethanol composition is mostly an oxygenated hydrocarbon, which leads to complete combustion during its application to produce power. As such, little or no CO is produced. Since ethanol does not contain heteroatom and metals, its use as source of energy does not release in emissions of NOx, SOx, particulates and other toxics. Unlike hydrocarbons such as natural gas (methane), ethanol is easier to undergo reforming reaction and is also free of sulphur, which is a catalyst poison in the reforming of hydrocarbons (Cavallaro et al., 1996). Compare to reforming of methanol, which is sourced from hydrocarbons (Klouz, 2002) and it has a relatively high toxicity, ethanol is completely biomass based and has low toxicity.

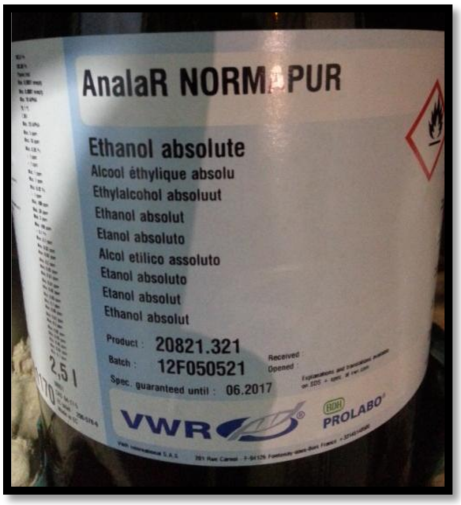


**Figure 3-1: Liquid ethanol that was used for researched.**

### *3.5 Cerium promoter catalyst*

Catalyst play an important role in industry, it help to seep up the rate of reaction by lowering the activation energy in a reaction but at the end of the reaction the catalyst is chemically unchanged. Catalysts help to gain profit in industry by increasing efficiency and productivity.

**Figure 3-2 : Cerium (III) nitrate hexahydrate (left) and $CeO_2$ particle at x6 million magnifications**

Cerium is a common naturally occurring element and is characterized chemically by having two valence states, +3 and +4. Cerium can be use in a wide varies of commercial applications which are metallurgy, glass and glass polishing, ceramics, phosphors and catalysts. In catalytic reaction, cerium is used in the form of cerium (IV) oxide, $CeO_2$. Cerium oxide is a highly stable, nontoxic, refractory ceramic material.

Cerium as catalyst plays a major role because of its ability to transform from the stoichiometric $CeO_2$ (+4) state to the $Ce_2O_3$ (+3) valence state via a relatively (at least in comparison with other oxides) low energy reaction. Apart from that Cerium has high thermal stability that results in $Ce_2O_3$ re-oxidizing and remaining active after initial combustion cycle.

## 3.6 Nickel catalyst

Nickel is most widely used due to low cost, high catalytic activity, high degree of dispersion, small crystallite size result in reasonable large surface area. In some cases metal supporter such as Pt, Co and Cu is added to improve the catalytic activity canal. Nickel catalyst is enhances in reactivity of reaction by forming strong interaction with the metal promoters.

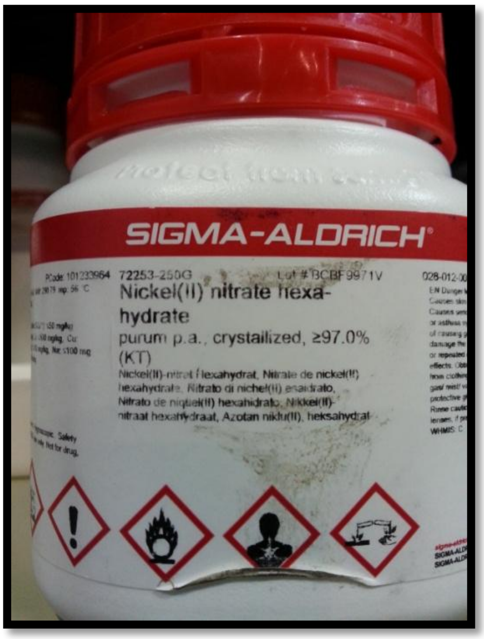


**Figure 3-3 : Nickel (II) nitrate hexahydrate catalyst**

Catalyst deactivation or coke formation on catalyst is the main concern, the metal promoters also help in retardation of coke deposition by enhance the dispersion of nickel catalyst. In a recent discovery exposing nickel catalyst to a small amount of sulphur reduces the catalyst decomposition or coke formation due to the sulphur hinder the active site necessary for carbon whisker growth.

Other research, explained that to prolong the catalyst activity extra effort is done by reducing sulphur concentration from raw products to an amount of less than 0.5 ppm (Sunggyu Lee, 2nd edition). It was reported that impregnation method significantly affected the structure, dispersion, and chemical states of nickel metal (J. Braz. Chem. 2014).

## *3.7 Support*

Aluminium oxide or alumina ($Al_2O_3$) is made from bauxite ore from weathering aluminium rich rocks. The alumina was used as support was made by Sigma-Aldrichh type WN-6. Aluminium Oxide has two types of sites, *hexagonal* and *octahedral* it is a very hard material and its hardness is exceeded only by diamond and a few synthetic substances such as *carborundum*, and *silicon carbide* high melting point above 2000 °C, which makes it useful as a refractory and as linings of special furnaces.

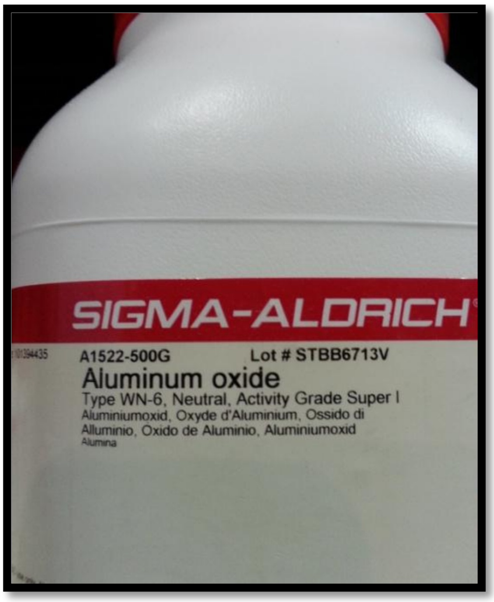


**Figure 3-4 : Alumina that was used during researched**

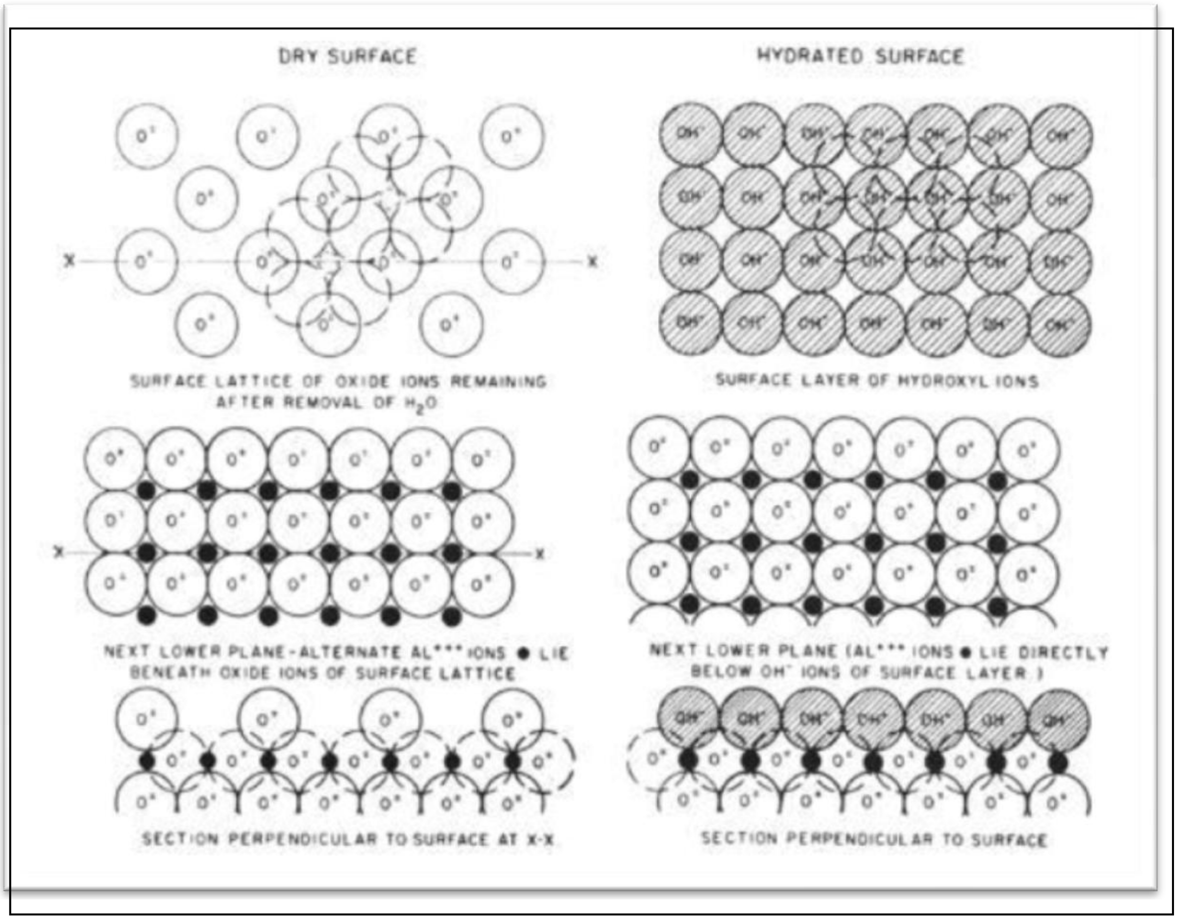


**Figure 3-5: Ideal structure of alumina for dry and hydrated (G. Sposito. 1995)**

It was calcined at 600 $^{o}$C of temperature inside a furnace for 5 hours, the temperature and conditions of the calcinations process determines the crystal structure and the surface area of the alumina. Alumina in general has more acidic sites than basic site as the increase of acidity increase the mobility of hydrogen thus increasing the rate of the dry reforming by enhancing hydrogen spillover and diffusion from the metal through the support.

### *3.8 Catalyst preparation*

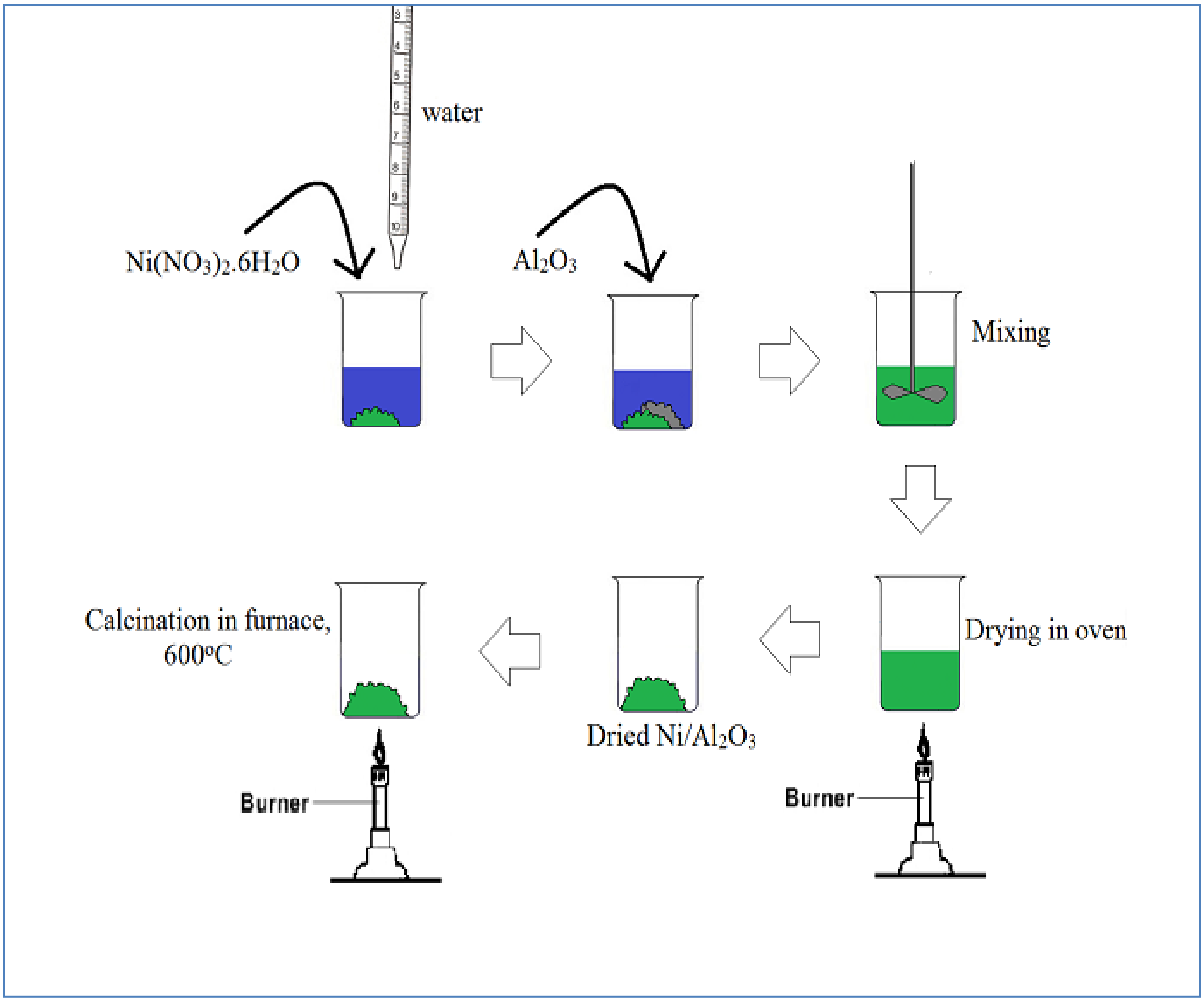


**Figure 3-6 : Impregnation method.**

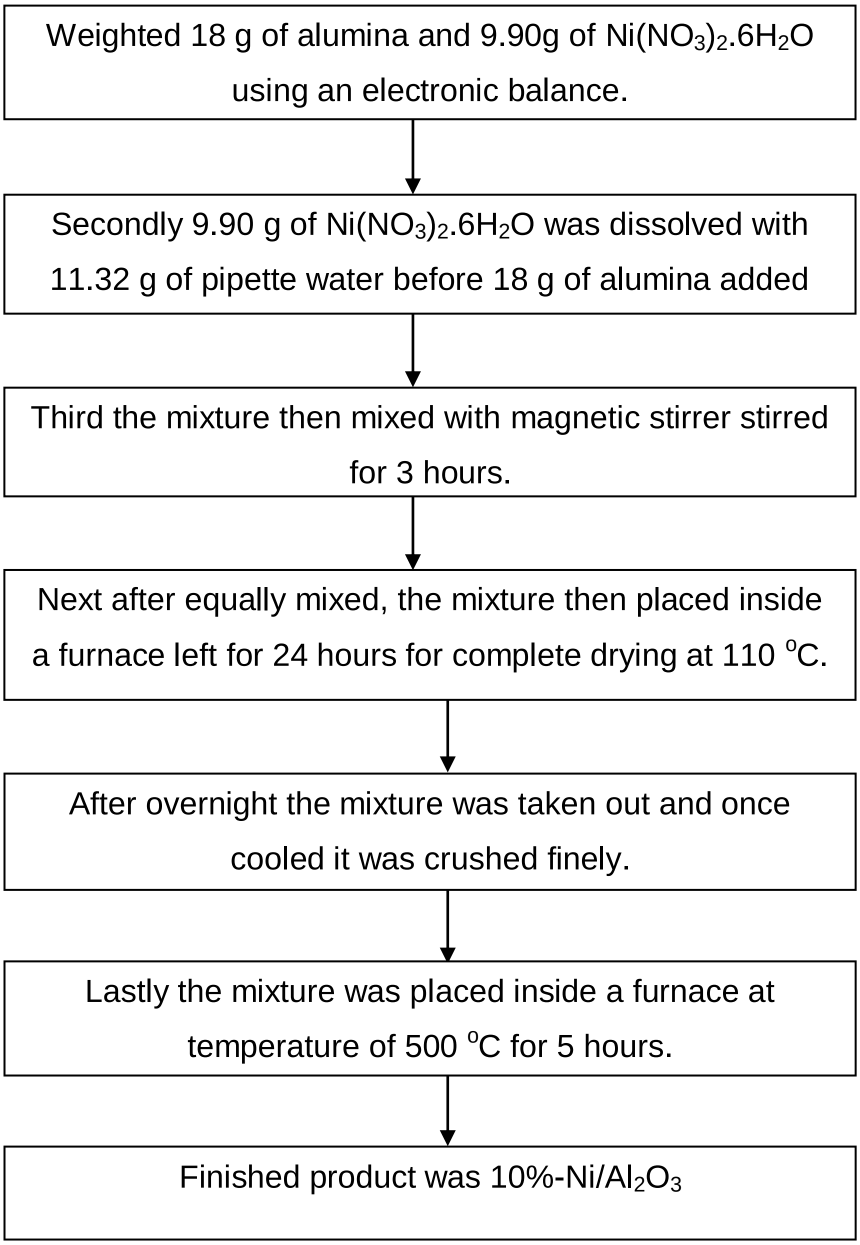
After the catalyst dry overnight, calcination was done in a furnace at 600 $^oC$ for 5 hours. Once done the catalyst was left inside the furnace for further cool down slowly to room temperature. After the calcinations process the catalyst was reduced in size due to the loss of moisture.

Instruments that were used during preparation of catalyst are listed below:

**Figure 3-7 : Oven (left) and muffle furnace (right)**

The catalyst was prepared by wet impregnation method, first nickel (II) nitrate,$Ni(NO_3)_2$ was dissolved with measured water and then mix with the weighted alumina. The solution then stirred for 3 hours before dried over night. Next the mixture was calcined at 500 $^oC$ for 5 hours (Friederike C. Jentoft. 2003).

## Flow chart



Weighted 18 g of alumina and 9.90g of $Ni(NO_3)_2.6H_2O$ using an electronic balance.

Secondly 9.90 g of $Ni(NO_3)_2.6H_2O$ was dissolved with 11.32 g of pipette water before 18 g of alumina added

Third the mixture then mixed with magnetic stirrer stirred for 3 hours.

Next after equally mixed, the mixture then placed inside a furnace left for 24 hours for complete drying at 110 $^oC$.

After overnight the mixture was taken out and once cooled it was crushed finely.

Lastly the mixture was placed inside a furnace at temperature of 500 $^oC$ for 5 hours.

Finished product was 10%-$Ni/Al_2O_3$

**Figure 3-8 : Synthesis of 10%-Ni/ catalyst.**

## *3.9 Catalyst calculation, 20g of 10%- Ni/$Al_2O_3$ catalyst*

Required 2g of Ni and 18 of alumina,

$$\frac{10\%}{100\%} \times 20g = 2g \qquad \textit{(24)}$$

since nickel come in a compound form which is $Ni(NO_3)_2.6H_2O$(Nickel(II) Nitrate Hexahydrate) therefore further calculation found that 9.90g of $Ni(NO_3)_2.6H_2O$ needed to make up for 2g of Ni.

$$\frac{2g \times 290.7949g/mol}{58.6934g/mol} = 9.90g \qquad \textit{(25)}$$

Predetermined 15g of water used to dissolved the mixture, since $Ni(NO_3)_2.6H_2O$ compound already contain water. Calculation of water in compound shall minus with 15g to avoid excess of water.

$$\frac{108g/mol}{290.7949g/mol} = 0.37139 \qquad \textbf{(26)}$$

$$0.37139 \times 9.90\ g = 3.68\ g[water\ inside\ Ni(NO_3)2.6\mathrm{H_2O}] \qquad \textbf{(27)}$$

$$15g - 3.68\ g = 11.32\ g\ (total\ water\ required\ to\ dissolve) \qquad \textbf{(28)}$$

## *3.10 Characterization*

First catalyst characterization is Brumauer-Emmet-Teller (BET) use to measure catalyst surface area, pore size, pore volume and pore distribution. Thermogravimetric analysis (TGA) is use for the uncalcined catalyst to measure weight loss, rate of weight loss and heat effects as function of temperature. To identify the component phases present as a function of synthesis method at different stages Powder X-ray diffraction analysis (XRD) will be use. Temperature-Programmed Reduction (TPR-$H_2$) to determine reducibility and optimum reduction temperature for the catalyst. Lastly is Scanning Electron Mircoscopy (SEM) to show spatial variations in chemical compositions. (Abayomi J. Akande. 2005), ( J. HABER. 1995).

## *3.11 Surface characterization*

Catalyst supports in nature have pores externally on the surface and internally as a well complex network deep inside the catalyst, which high number of pores gives good indication of more active catalyst. These pores serve active sites for metal particles to adhere on the surface due to metal-support interaction. Reactant molecules will undergo adsorption onto the active sites of the porous catalyst result in intermediates reaction thus reacts with other reactant molecules or the intermediates of other reactant to form products.

The surface area and pore size of a catalyst can be determined by gas adsorption technique. When gas is allow to passed through, it will come into contact with the porous surface where some of the gas will be adsorbed which depends on the equilibrium of pressure, temperature and the nature of gas-solid adsorption. The process is called physisorptionin whereby the gas use is an inert gas such as nitrogen ($N_2$). The surface measurements are based on the quantity of gas physisorbed to form monolayer or in practice multilayers. The multilayer formation in small pores may lead to condensation. The relationship between the amount of gas adsorbed ($n_{adsorbed}$), equilibrium pressure ($P$), critical gas temperature ($T$), and saturation pressure ($P0$) of the adsorbate gas at temperature $T$, when adsorption takes place at constant catalyst temperature is given below.

$$n_{adsorbed} = f\left(\frac{P}{P_o}\right)_{\tau} \qquad (29)$$

Brumauer-Emmett-Teller then extrapolated Langmuir kinetic model which was based upon monolayer adsorption into multilayer adsorption that is used to measure the surface area of catalyst. The BET isotherm equation is shown below.

$$\frac{P}{V(P_s - P)} = \frac{1}{cV_m} + \frac{(c-1)P}{cV_m P_s} \qquad (30)$$

Where

$P$ = gas pressure

$P_s$ = saturation pressure of the adsorbate gas

$V$ = volume of gas adsorbed

$V_m$ = volume of gas adsorbed corresponding to a monolayer adsorption

$c$ = constant characterising the adsorbate

A plot of $P/V(P_s - P)$ against $P/P_s$ provides a straight line with an(Chen. L)(Joo, 2002)(A.S.A. Al-Fatesh, 2012) intercept $1/cV_m$ and slope $(c-1)/cV_m$. The slope and intercept value can be used to calculate $V_m$. The value of $V_m$ along with the information of cross-sectional area of the adsorbate gas can be utilised to find the number of gas molecules adsorbed. The surface area per weight unit can be calculated by

$$S_A = \frac{n_m a_m N}{M} \times 10^{-20} \qquad (31)$$

Where

$S_A$ = surface area of solid ($m^2\ g^{-1}$)

$a_m$ = average surface area occupied by a molecule

$N$ = Avogadro's number

$M$ = molecular weight of adsorbate, $N_2$

$n_m$ = monolayer capacity of adsorbate (g adsorbate $g^{-1}$)

**Figure 3-9 : BET device used for characterization**

The measurements of multipoint BET surface area and pore volume were carried out using Thermo Scientific Surfer. For each measurement 0.1 g of the sample was placed in a quartz glass tube and subjected to pre-treatment at 573 K for 3 h under vacuum to remove any moisture and volatile impurities or contamination. After pre-treatment the sample tube was transferred to the analysis port for physical property measurements.

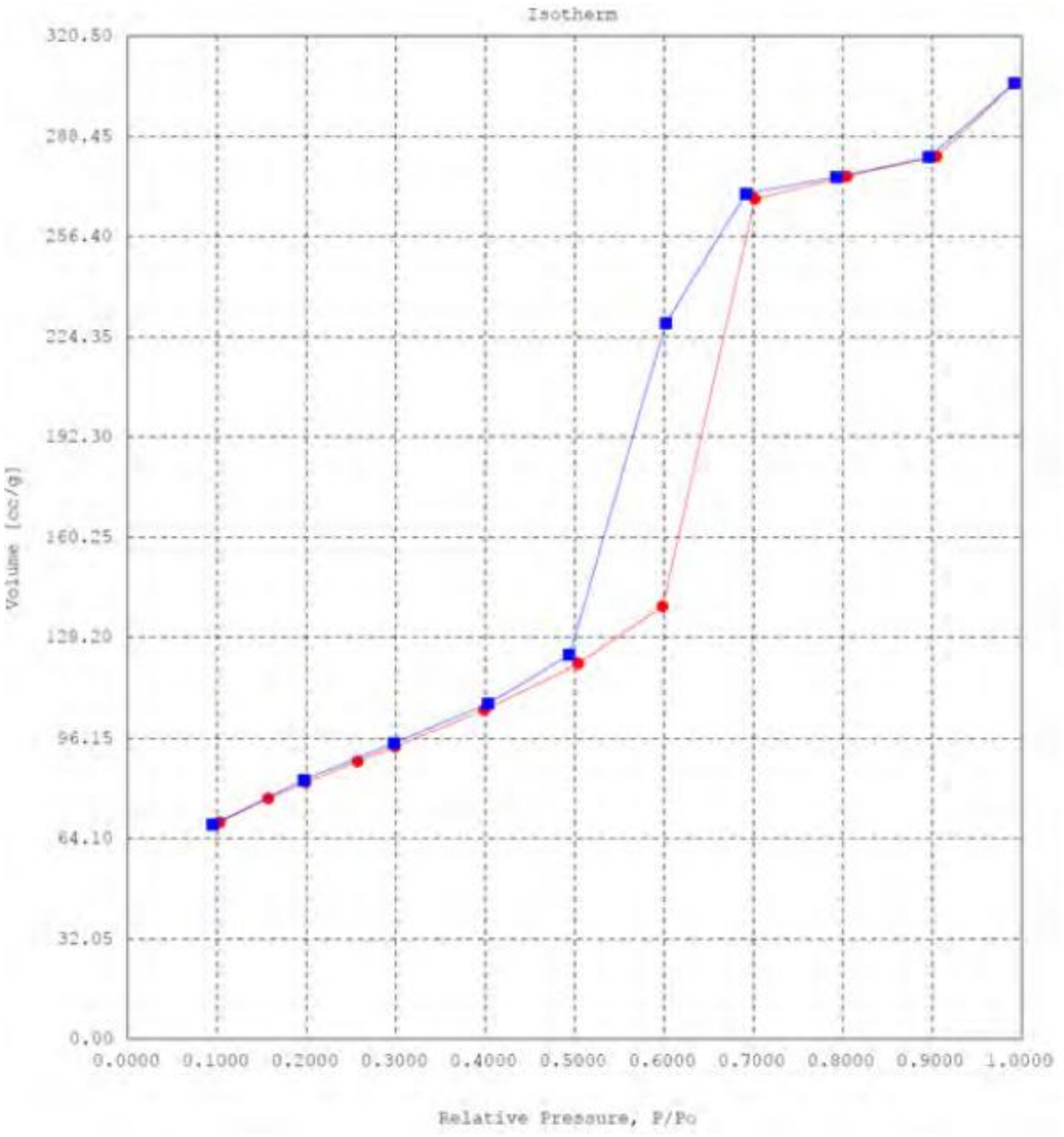


**Figure 3-10: General profile of N2 isotherm**

N2 is use as cold trap which has the cross-sectional area of 16.2 Å2 was used as an adsorbate gas. The adsorption was carried out at 77 K which is the boiling point of N2, at this temperature the adsorption forces involved are same as that of vapor condensation forces such as London dispersion force and short range intermolecular repulsive force. The adsorption isotherm is obtained by successive injection of measured volumes N2 while measuring the equilibrium pressure. On the other hand desorption isotherm is obtained by decreasing the pressure while measuring the quantities of N2 removed from the adsorbent. General profile of N2 isotherm is shown in figure 3-11 where the red and blue lines represent adsorption desorption isotherms respectively.

## *3.12 Scanning Electron Microscopy SEM*

SEM analysis is used to observe the topography or morphology of the catalyst. Surface areas as well as size consistencies plays an important role in catalyst efficiency during a reaction. The working principle of SEM is the specimen is bombarded by a convergent electron beam, which is scanned across the surface. This electron beam generates a number of different types of signals, which are emitted from the area of the specimen where the electron beam is impinging, seen in Figure

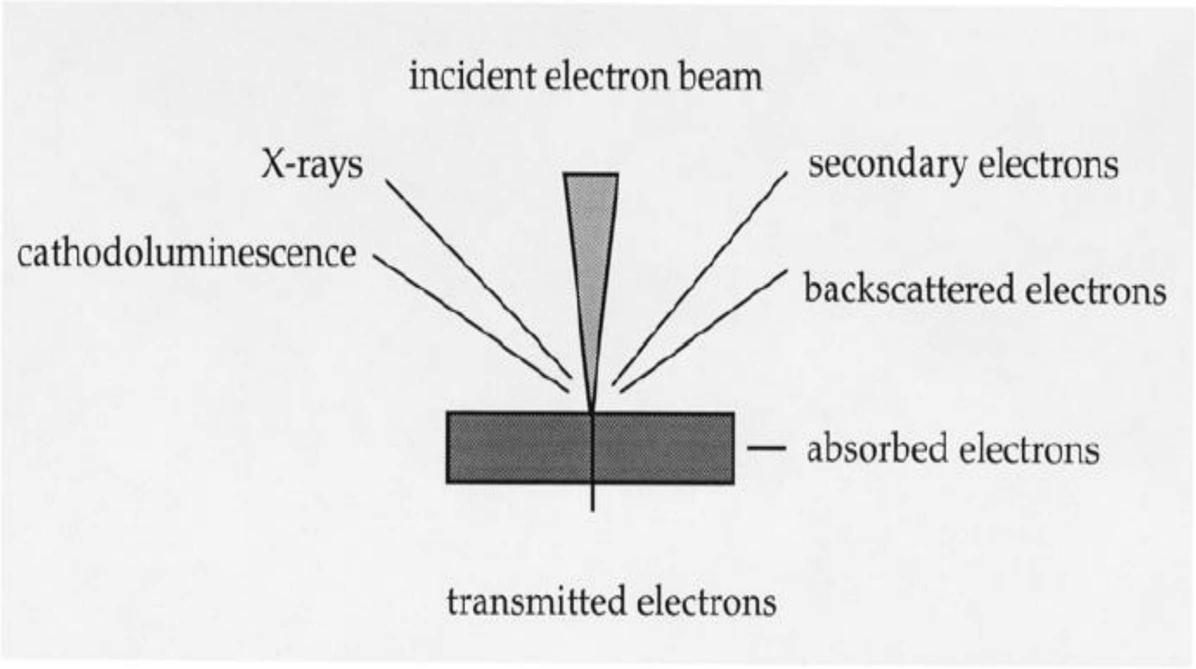


**Figure 3-11 : Woking principle of SEM with different types of signals produced when high-energy electron impinge on a material.**

**Figure 3-12 : Scanning electron microscopy device that was used to observed catalysts**

The induced signals are detected and the intensity of one of the signals (at a time) is amplified and used to as the intensity of a pixel on the image on the computer screen. The electron beam then moves to next position on the sample and the detected intensity gives the intensity in the second pixel and so on.

## *3.13 Thermogravimetric Analysis*

Thermogravimetric analysis is used to study the mass of a substance as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Generally the device is used to characterize a transformation phase while a solid sample is being heated at a constant rate in the presence of a gas. TGA also includes temperature-programmed calcinations. The samples were subjected to heating of 100 $^0$C while $N_2$ inert gas is passing through for 30 minutes to eliminate any remaining moisture and purify the catalyst from impurities. Characterization of all the catalysts we carried out with analysis gas ($4N_2 : O_2$ ) flow rate of 100 ml/min and 10 $^O$C ramping rate, along with 750 $^o$C holding temperature.

**Figure 3-13 : TGA (Research instrument, model: TGA Q500)**

## *3.14 X-ray Diffraction (XRD)*

Powder XRD analyses were performed on the dried, calcined and reduced catalysts to identify the species present in the catalysts by means of lattice structural parameters and estimate particle size. Each crystalline solid has its distinguish characteristic X-ray powder pattern which may be used as a "fingerprint" for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure (Kayani, 2010). X-ray source is bombarded with high energy electrons which then emitted X-rays, whereby result the irraditon of the catalyst. As can seen in Figure , the lattice spacing may be estimated from X-ray diffraction of crystal planes using the Bragg relation

$n_{ref}\lambda = 2d\sin\theta$

where $\lambda$ is the wavelength of the X-rays

d = the distance between two lattice planes

ϴ = the angle between the incident X-rays and the scattering plane

$n_{ref}$ = an integer, the order of the reflection

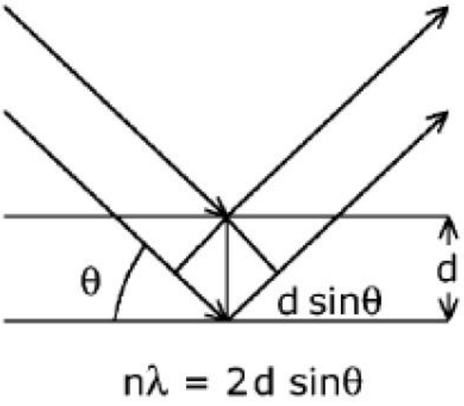


Figure 3-14 : The Bragg Law for XRD measurement

The XRD measurements were conducted using Match! system using Cu Kα target as radiation source with $\lambda$ = 1.5418 Å operating at 30 kV for qualitative crystallographic identification of metal phases on both catalysts. Crystallographic database published by ASM International (Materials Park, Ohio, USA), edited by Pierre Villars and Karin Cenzual was used for analyzing XRD experimental data in all cases.

## *3.15 Ethanol dry reforming process*

The reactor is made up of a series of steel pipes, valves and consists of a few major instruments such as syringe pump, furnace, cold trap, dricite bed and mass flow controller. The function of the mass flow meter is to control the amount $CO_2$ flowing into the furnace. Meanwhile the syringe pump is use to control the amount of flow of liquid ethanol. In the centre of the furnace is a long tube steel cylinder, in this section the catalyst will be put to place by glass wool to hold it in position. This part of the reactor is the most critical since the reaction will take place here and the catalyst can suffer severe deactivation if the condition is not optimum thus blocking the flow and prevent any reaction to occur. Cold trap is use to condense and trap any water droplet that might get into the GC with the help of dricrite bed to further trap any water droplet. Next, bubble flow meter is used to measure the flow of the gasses been release from the furnace. Lastly after the reaction is done, the product gas is collect to be test in gas chromatography machine.

**Figure 3-15: Actual pictures of the reactor used for researched**

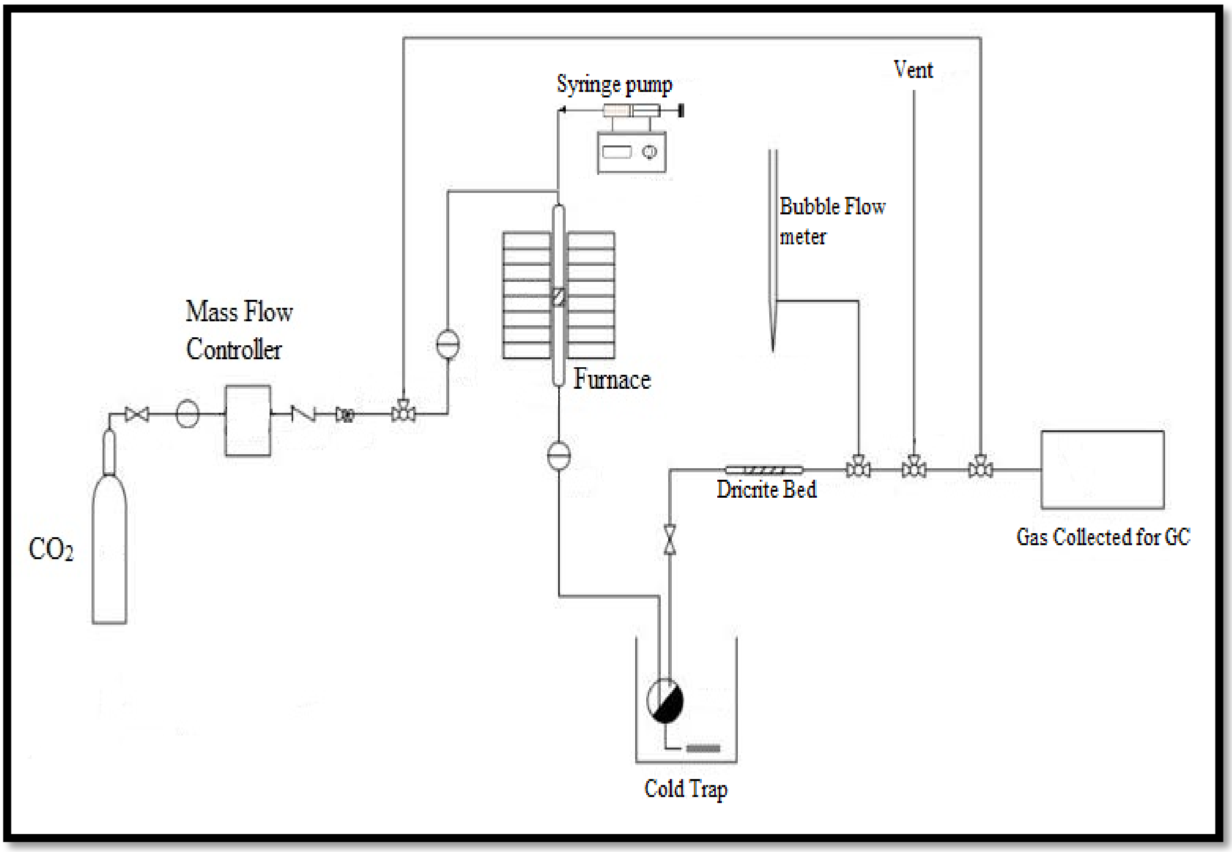


**Figure 3-16: Schematic diagram of ethanol dry reforming process**

All reactions were run at fix condition of 1 atm ambient pressure and 973 K temperature with the same amount of flow rate of liquid ethanol and nitrogen gas, which were 2.1ml/h and 41.1 $m^3$/hr. The manipulated variables was catalyst used and with various partial pressure ratios of $CO_2$:$CH_4$ 1:0 to 1:2.5. Feed and activation gas flow rates were digitally controlled by Brooks Smart mass flow controllers where else the furnace temperatures were controlled by LT Furnance (Model: VTF50/150-1000) controllers. Catalyst that was about to be used was place inside the glass tube before hand and afterward the prefer conditions were keyed in and set to applied but the feed flow of carbon dioxide and nitrogen gasses were switched to bypass the reactor. Once the set point temperature of the reactor had been reached and the liquid ethanol from the syringe pump started to dripped inside the glass tube, the very instant the $CO_2$ and $N_2$ gasses are allowed to pass through the reactor to complete the reaction.

A pair of pressure gauges was connected to the inlet and outlet of the reactor enabled monitoring of the pressure drop as well as at the front of both CH4 and CO2 tanks. When in contact with the hot glass tube surface the ethanol was instantly evaporated into gas form, all the gasses then were mixed and reacted at the applied temperature inside the reactor.

**Figure 3-17 : Example of gas bag that was used to transfer product gas to be analyzed in Gas chromatography.**

The product gas from the furnace was delivered to pass through a condenser and drierite bed to eliminate any moisture. The reactions run were conducted for 8 hours and end product gases were collected for every hour to be analyzed using gas chromatography using gas collecting bags. By the end of $8^{th}$ hour, the reaction was completed and the reactor was switched off and let to cool to ambient temperature. Once cool the used catalyst from each runs was collected and store for future study.

**Figure 3-18 : Gas Chromatography, Agilent Technologies 6890 Series**

Ethanol dry reforming performance was evaluated in terms of conversion, yield, selectivity, products formation, reaction rate and $H_2$/CO and $CH_4$/CO ratios. The following formulas are shown below

$$X_{C_2H_5OH}\ (\%) \ = \ \frac{2F_{H_2}^{Out} + \ 4F_{CH_4}^{Out}}{6F_{C_2H_5OH}^{In}} \times \ 100\%$$

$$Y_{CH_4}\ (\%) \ = \ \frac{F_{CH_4}^{Out}}{F_{CO_2}^{In} \ + \ 2F_{C_2H_5OH}^{In}} \ \times \ 100\%$$

$$Y_{CO}\ (\%) \ = \ \frac{F_{CO}^{Out}}{F_{CO_2}^{In} \ + \ 2F_{C_2H_5OH}^{In}} \ \times \ 100\%$$

$$Y_{H_2}\ (\%) \ = \ \frac{2F_{H_2}^{Out}}{6F_{C_2H_5OH}^{In}} \ \times \ 100\%$$

$$-r_{CO_2} \ = \ \frac{F_{CO_2}^{In} \ - \ F_{CO_2}^{Out}}{W_{Cat.}}$$

$$-r_{C_2H_5OH} \ = \ \frac{F_{C_2H_5OH}^{In} X_{C_2H_5OH}}{W_{Cat.}}$$

$$r_i \ = \ \frac{F_i^{Out}}{W_{Cat.}} \ (i: \ \mathrm{CO, H_2} \ \mathrm{or} \ \mathrm{CH_4})$$

$$S_i\ (\%) \ = \ \frac{r_i}{\sum_{i=\mathrm{CO,H_2,CH_4}} r_i} \ \times \ 100\%$$

# 4 RESULTS AND DISCUSSIONS

## *4.1 Catalyst Characterisation*

### *4.1.1* Introduction

The results of catalyst analysis or catalyst characterization are presented and evaluated in this section. This chapter provide the physiochemical characteristics of the catalyst which is the most important aspects in catalysis. The catalyst characterization techniques used was BET, XRD, TGA and SEM analysis.

### *4.1.2* Physisroption measurements

The surface properties for 3%Ce-10%Ni/$Al_2O_3$ and 10%Ni/$Al_2O_3$ were illustrated in table 4.1. In comparison the density and cumulative pore volume of the catalyst are almost identical, however the surface area and average diameter are differ. The decrease of surface area and an increase of average diameter were probably due to loading of $CeO_2$ metal onto the catalyst, as Ce deposited inside $\gamma$-$Al_2O_3$ pores. In contrast lower $CeO_2$ loading would stabilize $\gamma$-$Al_2O_3$ against surface area loss (Piras *et al.,* 2000; Ozawa and Kimura, 1990). Apart from that $H_2$ chemisorption increase with loading of $CeO_2$.

**Table 4-1**: Surface properties of catalyst

| **Catalyst** | **Density g/cm$^3$** | **Cumulative Pore Volume (cm$^3$g$^{-1}$)** | **Surface Area(m$^2$g$^{-1}$)** | **Average Diameter (Angstrom)** |
|---|---|---|---|---|
| 10%Ni/$Al_2O_3$ | 3.3382 | 0.9910 | 96.6971 | 7.6915 |
| 3%Ce-10%Ni/$Al_2O_3$ | 3.2479 | 0.9910 | 84.2487 | 7.9261 |

### *4.1.3* **Powder X-ray diffraction analysis, XRD**

Powder XRD analyses were performed on the dried, calcined and reduced catalysts to identify the species present. The figure 4-1 below show results obtained from X-ray Diffraction (XRD) analysis a) with Cerium promoter and b) without Cerium promoter. Using Match! program its shows consistence results with the data based. XRD spectra a) showed common peaks correspond to the presence of $CeO_2$ at peaks 2Θ = $28.48^0$, $33.06^o$, $47.46^0$ and $56.33^o$. Moreover the other components are presence in both curves $Al_2O_3$ at peaks 2Θ = $37.36^0$, $43.42^0$ and $67.90^0$, $Al0_3$ at peaks $43.81^0$ and $45.52^0$, Nickel Oxide (NiO) at peak 2Θ = $62.90^0$, Nickel Aluminate $Al_2O_4$ at peaks 2Θ = $49.30^0$, $59.68^0$ and $77.78^0$. Based on the curve obtained, it shows that the diffraction pattern did not alter the structure of the catalysts as the peaks are identical for the every metal which present in both catalysts.

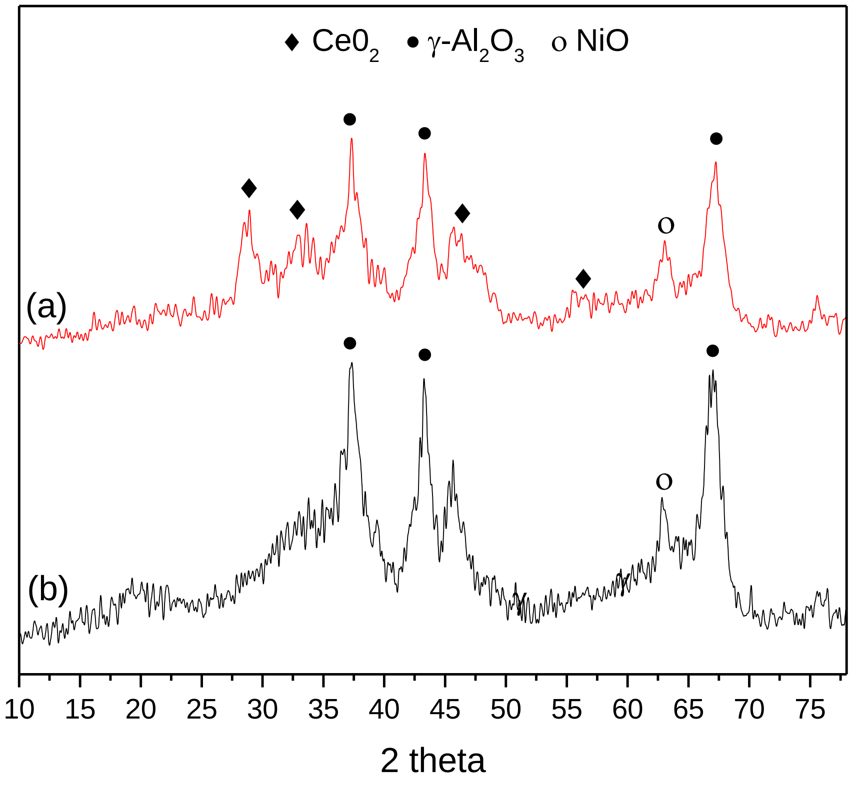


**Figure 4-1: Comparison of catalyst (a) 3%Ce-10%Ni/$Al_2O_3$ with (b) 10%Ni/$Al_2O_3$**

The two catalysts were prepared by wetness impregnation at the same 10% Ni loading but one catalyst has the presence of Ce promoter. Typical XRD spectra common peaks can be seen for both catalysts correspond to nickel oxide (NiO), alumina ($Al_2O_3$) and nickel aluminate ($NiAl_2O_3$). The characteristic of formation of nickel aluminate was due to the interaction between NiO and $Al_2O_3$ at high temperature as shown in equation below. This similar traits also been portrayed from Idem and Bakhshi results, (1996). Formations of nickel aluminate imply strong metal-support interaction.

$$\mathbf{NiO + Al_2O_3 = NiAl_2O_4} \qquad \textbf{(32)}$$

The displays of peaks corresponding to nickel species also denote strong crystallinity of the species and that the monolayer coverage of $Al_2O_3$ is applicable to Ni metals species was in excess. Spinel nickel aluminate formation was observed due to the catalyst prepared by impregnation methods. This tells that at 600 $^{o}$C temperature was not sufficient to reduce all the nickel aluminate species to Ni metal and alumina for both catalysts.

### *4.1.4* Thermogravimetric analysis, TGA

Calcination is a pivotal part in the synthesizing of heterogeneous catalyst since it involves the generation of active phase, structure modification, texture modification and stabilization of mechanical properties and texture modification. At different temperature of calcinations different types of carbon deposited on catalyst surface, thus at 850 K higher activity of catalyst was recorded compare to at 450 K this was discovered by Joo and Jung (2002). In other researched, a higher reduction temperature is necessary to ensure complete reduction of NiO on calcined catalyst such as 773 K to 873 K. However conversion of $CH_4$ and gas selectivity decreases if the calcinations temperature exceeds 773 K to 873 K (Chen et al. 2005).

TGA is important to determine the maximum temperature of catalyst after which the catalyst weight loss is negligible and complete decomposition occurs. Other than that TGA also help to determine the catalyst thermal stability temperature. Based figure 4-2 shows the presence of Ce catalyst shift the peaks to right side and result in much higher peaks compare to the curve without the presence of promoter. The reduction temperature and the peaks widths are indications of reduction and the degree of interaction between different species, respectively. High reduction temperatures illustrate the difficulty in reduction whereas wide peaks indicate degree of interaction between the species and the support. At temperature of 230 $^{o}$C -310 $^{o}$C the $Ni/Al_2O_3$ metal decomposition occurs, in general the temperature below than 400 $^{o}$C suffer from thermal desorption and abstraction of chemically bound water from Nickel (II) Nitrate Hexahydrate.

$$\mathbf{Ni(NO_3)_2 \rightarrow NiO + N_2O_5} \qquad \textbf{(33)}$$

$$\mathbf{2Ce_3(NO_3)_3 \rightarrow Ce_2O_3 + 3N_2O_5} \qquad \textbf{(34)}$$

. First peak at low temperature of 500 - 520 K was due to the decomposition of metal nitrates to the corresponding metal oxides, the equation is given above. The first peak after 400 $^{o}$C until 600 $^{o}$C temperature full decomposition of nickel hydroxide into NiO and $H_2O$ indicates decomposition of catalyst as reported by (Parathasarathi, 2000). The second peak depicts the formation of metals support.

$$\mathbf{NiO + Al_2O_3 \rightarrow NiAl_2O_4} \qquad \textbf{(35)}$$

While the second peak at temperature of 570-620 K represents spinel NiAl2O4 phase formation. Lastly the last peak which is the smallest at temperature 660 K represent the oxidation of $Ce^{3+}$ to $Ce^{4+}$ during air calcinations. The equation is shown below.

$$\mathbf{Ce_2O_3 + 0.5O_2 \rightarrow 2CeO_2} \qquad \textbf{(36)}$$

This result shows a consistency with the XRD reading as can be seen no further peaks exist beyond 700 K, this also illustrate that both impregnated catalysts were thermally decomposed and oxidized completely to stable metal oxides during TPC.

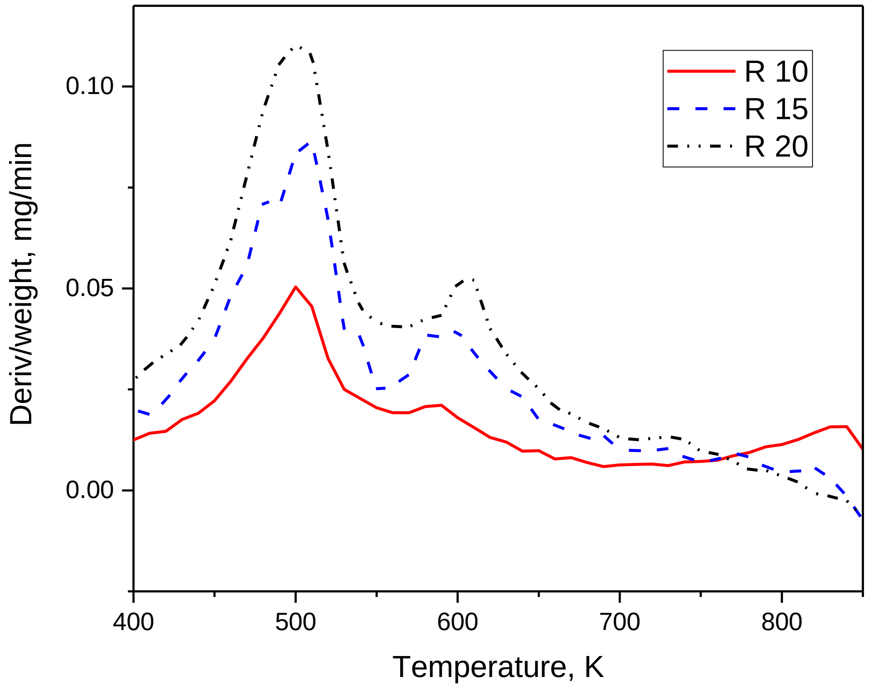


**Figure 4-2 : Derivative weight profiles for temperature-programmed calcination run of 10%Ni/$Al_2O_3$**

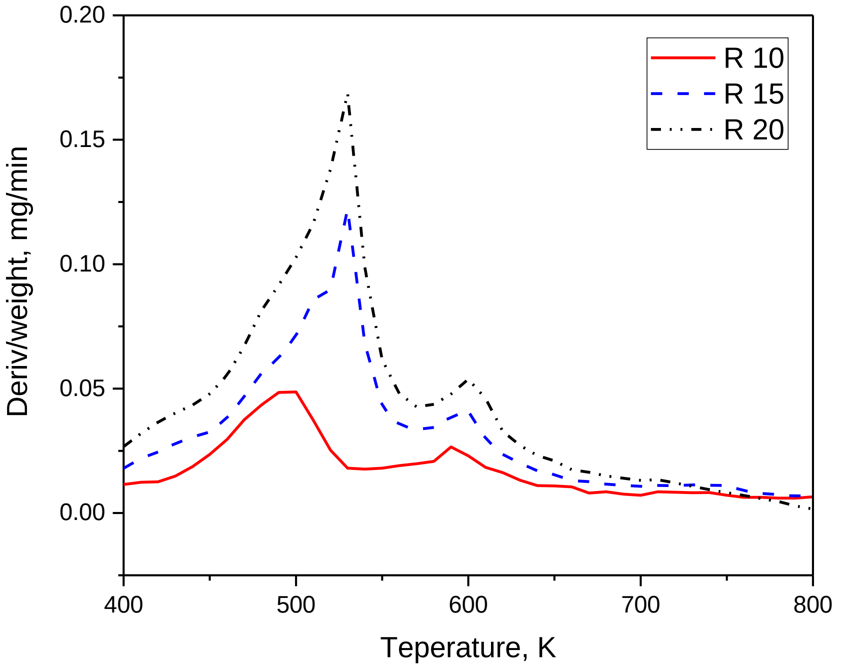


**Figure 4-3 : Derivative weight profiles for temperature-programmed calcination run of 3%Ce- 10%Ni/$Al_2O$.**

### *4.1.5* Scanning Electron Microscopy, SEM

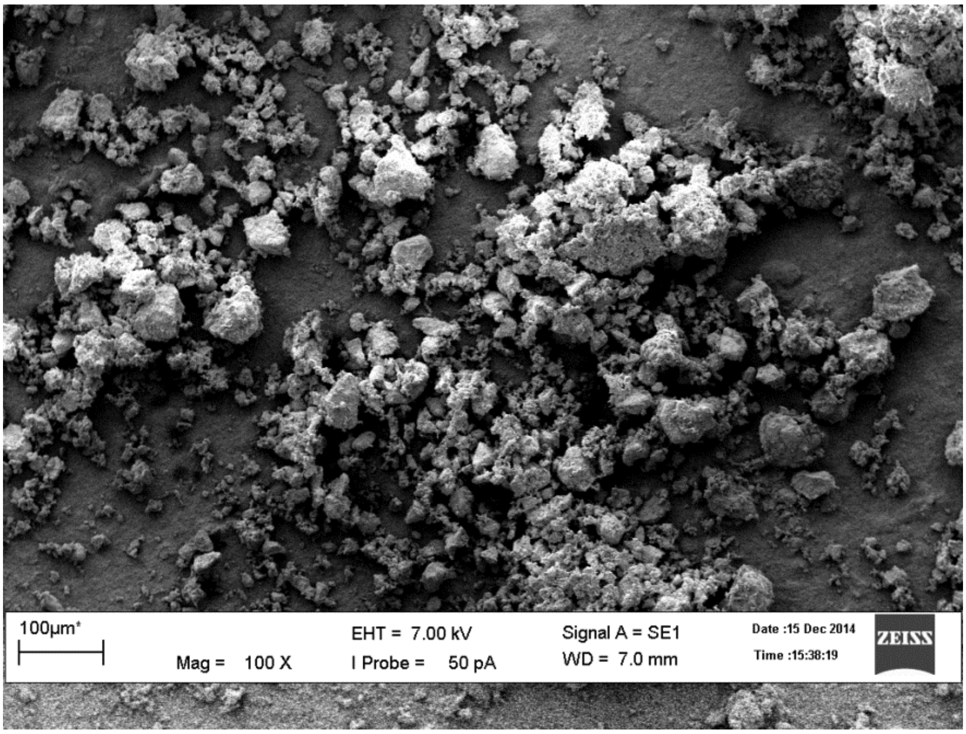


**Figure 4-4 : SEM result 100 magnification 3%Ce-10%Ni/$Al_2O_3$.**

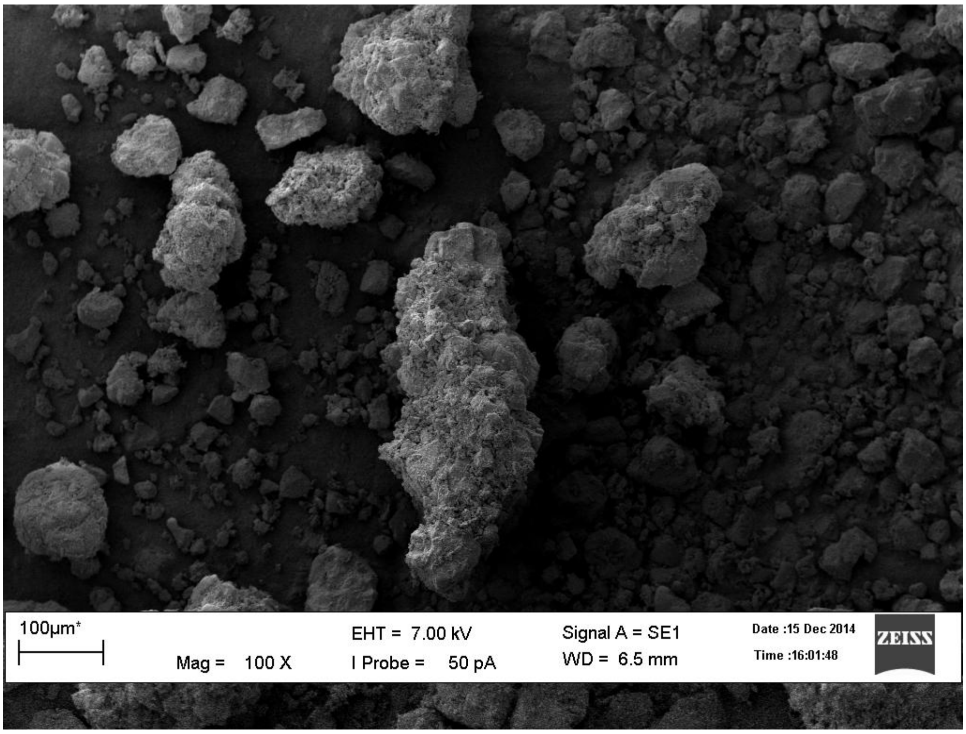


**Figure 4-5 : SEM result 100 magnification 10%Ni/$Al_2O_3$.**

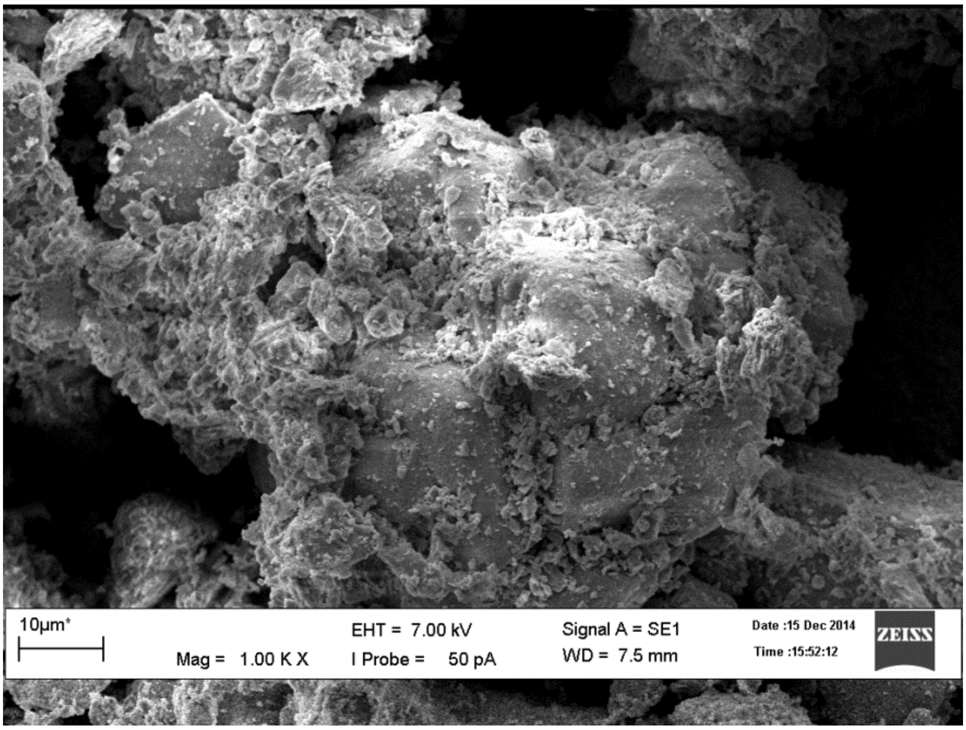


**Figure 4-6 : Figure 4-7 : SEM result 1000 magnification 3%Ce-10%Ni/$Al_2O_3$.**

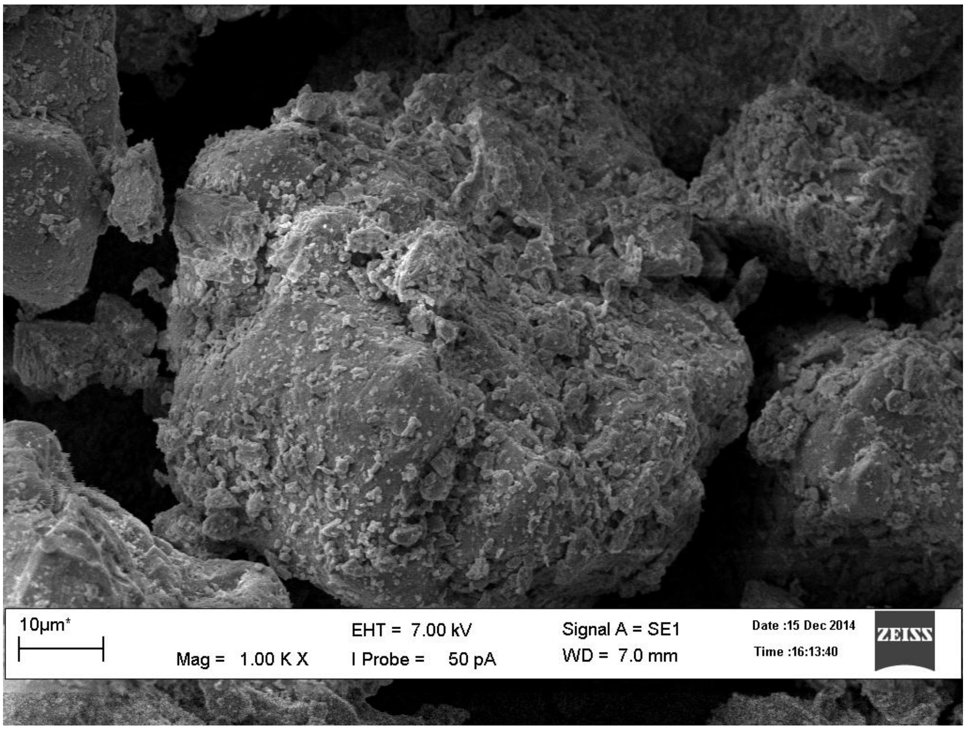


**Figure 4-8 : SEM result 1 000 magnification 10%Ni/$Al_2O_3$.**

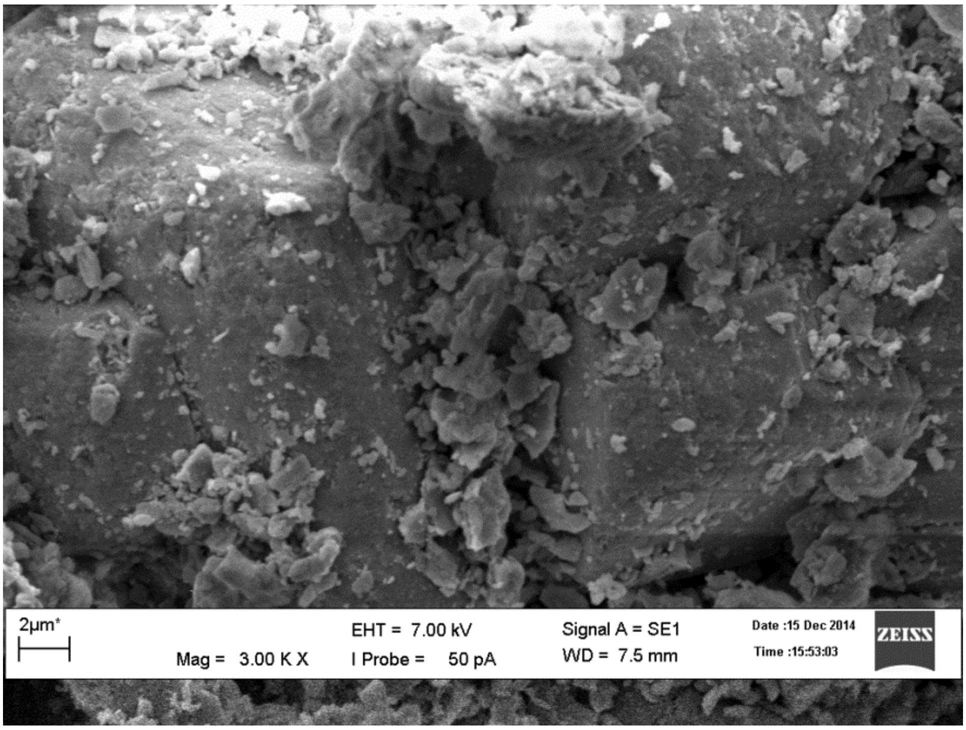


Figure 4-9 : Figure 4-10 : SEM result 100 magnification 3%Ce-10%Ni/Al$_2$O$_3$.

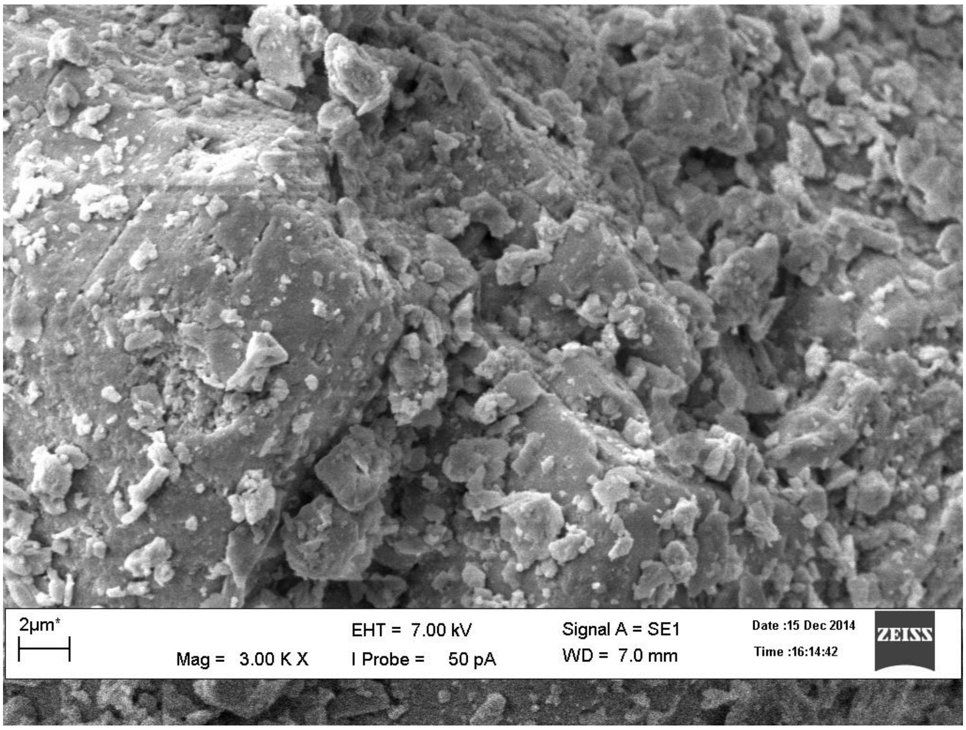


Figure 4-11 : SEM result 3 000 magnification 10%Ni/Al$_2$O$_3$.

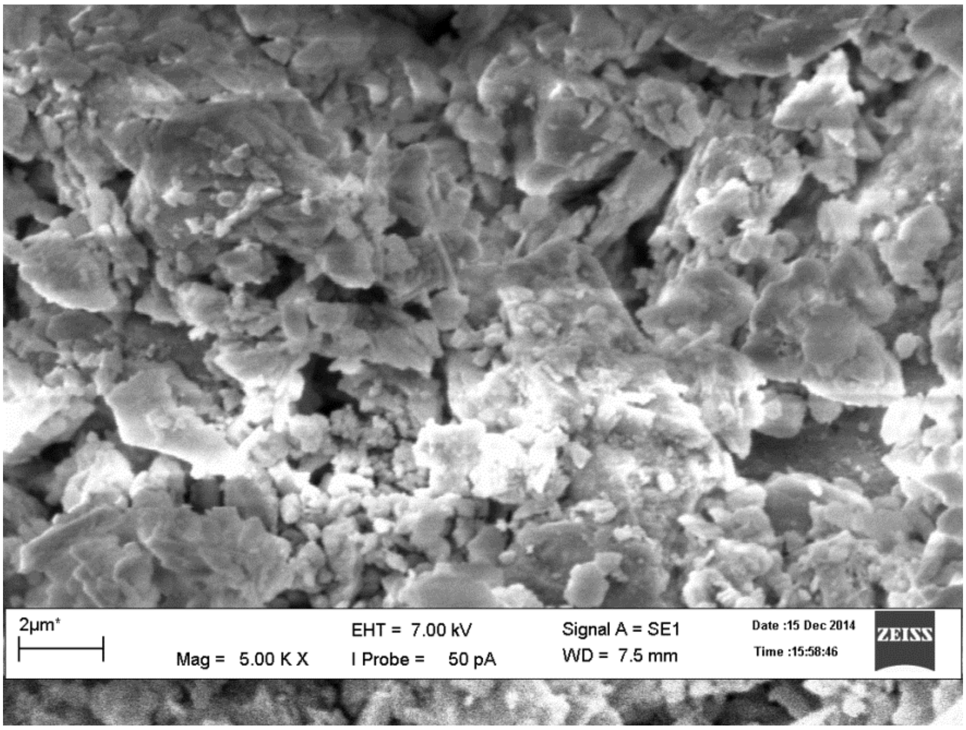


**Figure 4-12 : Figure 4-13 : SEM result 5 000 magnification 3%Ce-10%Ni/$Al_2O_3$.**

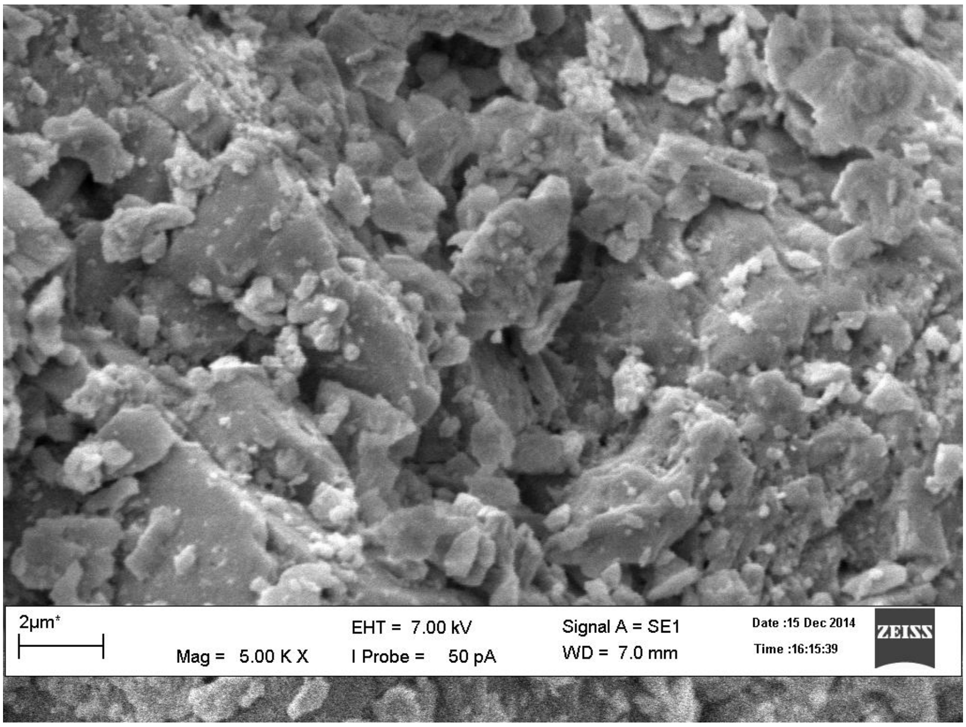


**Figure 4-14 : SEM result 5 000 magnification 10%Ni/$Al_2O_3$.**

Based on the first figure it can be seen that most of the catalyst have nearly the same morphology and particle size, which is round or sphere in shape. Apart from that alumina metal can be seen is enrich with Ni metals on its surface as in 3rd and last figures. There are a few cracks or pores can be seen in figure 4-10, this tells that the catalyst is a good absorption catalyst. The number of cracks or pores is directly proportional to catalyst efficiency. The presence of flakes also shows a good quality of the catalysts, as smaller flakes increases the surface area of contact between catalyst and reactants.

## *4.2 Reaction Study*

### *4.2.1* **Introduction**

The reactions was done by manipulating the feed ratio of ethanol to $CO_2$ from 1:1 to 1:2.5 (20 kPa to 50 kPa) at temperature of 973 K for 8 hours straight and for every 1 hour interval the product gas was collected and analysed using GC. Moreover to get a better overview of how the catalyst response during the reaction a control is run, whereby the control reaction run was conducted using unpromoted 10%Ni/$Al_2O_3$ catalyst at the same condition with feed ratio of 1:1 that is 20 kPa $CO_2$ flowrate. Based on illustrated curve in Figure 4-15 the highest conversion of $H_2$ and $CO_2$ is the feed ratio of 2.5:1 ethanol to carbon dioxide ($CO_2$). This tell that the addition of Ce metals increase the conversion of $H_2$ at 0.95. However at lower $CO_2$ partial pressure of 40 kPa below the conversion results show a lesser value compare to reaction run using unpromoted catalyst.

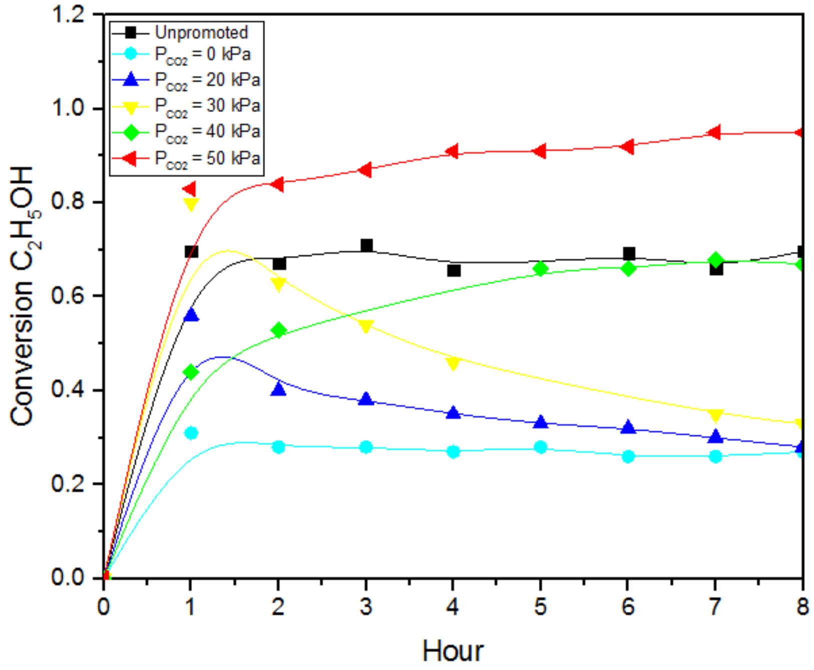


**Figure 4-15 : Conversion of $C_2H_5OH$**

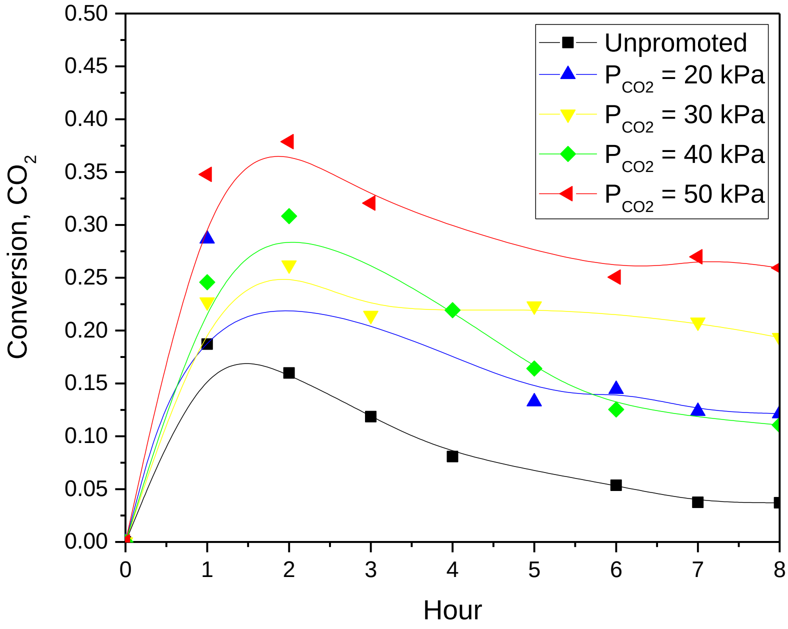


**Figure 4-16 : Conversion of $CO_2$**

The effect of higher amount of partial pressure flow rate influences the conversion of ethanol gas and carbon dioxide to be the highest at feed ratio ethanol to carbon dioxide of 2.5. Moreover the presence of Ce-promoted catalyst gives better conversion of $H_2$ compare to without promoter catalyst as high as 90 % conversion. When zero flow of carbon dioxide gas, based on Figure 4-16 there no $CO_2$ gas was formed hence there is no graph can be seen. The unpromoted catalyst also gives out the lowest conversion of $CO_2$ gas. Overall the trend shows that after the 2 hour the curve will start to decrease as more coking accumulated on the surface of the catalysts. The most severe coking suffered is with the unpromoted catalyst.

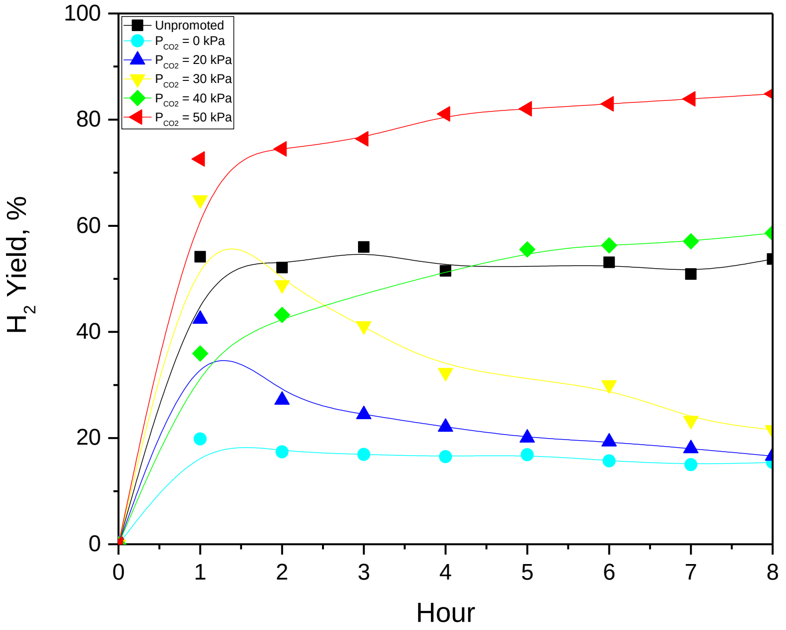


**Figure 4-17 : Yield profiles of $H_2$**

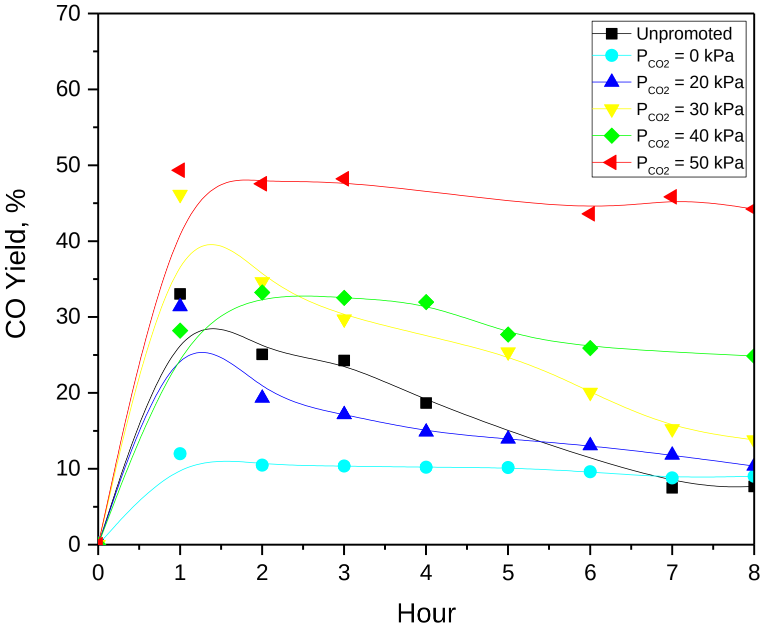


**Figure 4-18 : Yield profiles of CO**

Yield profiles results are based on Figure 4-17 and Figure 4-18 with the highest yield of $H_2$ 80 % and CO 50% gasses produce came from the reaction of promoted catalyst with the highest $CO_2$ feed ratio by the 8th hour period. Meanwhile the reaction without the flow of $CO_2$ gas emitted the lowest amount of $H_2$ and CO gasses yield when the reactions were conducted. From the Figure 4-18 yield graph can be seen that the yield of CO gas start to decrease as the reactions proceeds, this could possibly due to the deactivation of catalyst by coking or carbon deposition. On the other hand reaction at partial pressure of 50 kPa using promoted catalyst only showed a slighted decrease as the period of the reaction continue.

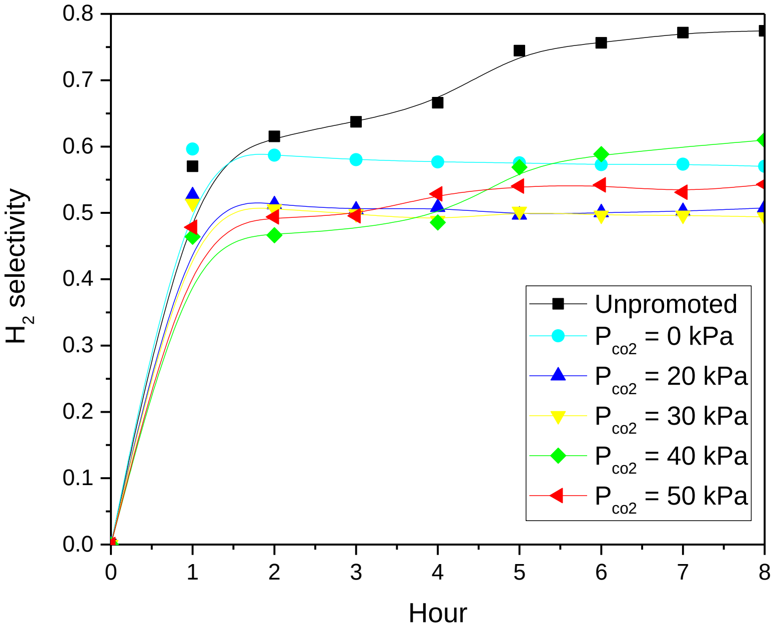


**Figure 4-19 : Selectivity profile of $H_2$**

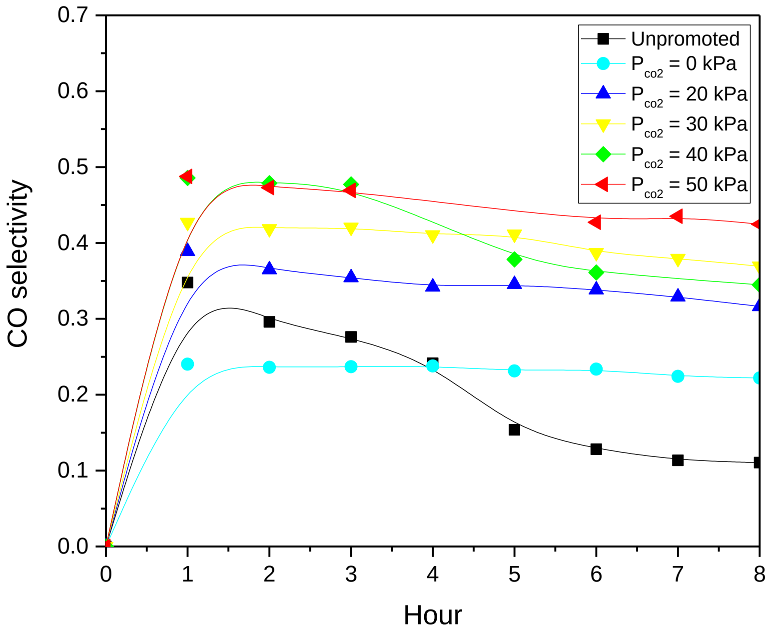


**Figure 4-20 : Selectivity profile of CO**

Overall the highest CO selectivity is for reaction conducted using promoted catalyst. Despite that the reaction with unpromoted catalyst gives the highest $H_2$ selectivity follow by reaction run with the flow rate of $CO_2$. The lowest result for CO selectivity for unpromoted catalyst and the values continues to decreases until 0.1 at the last hour.

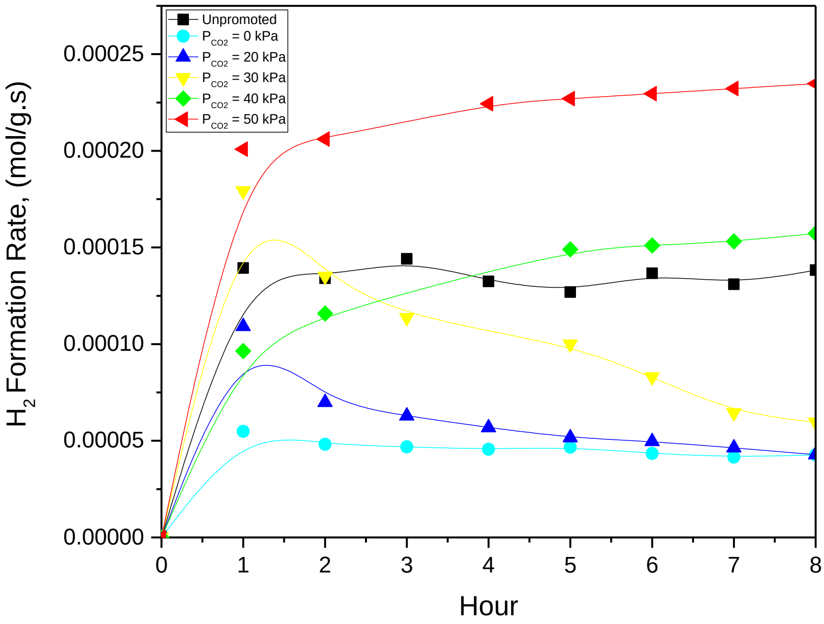


**Figure 4-21 : Formation rate of $H_2$**

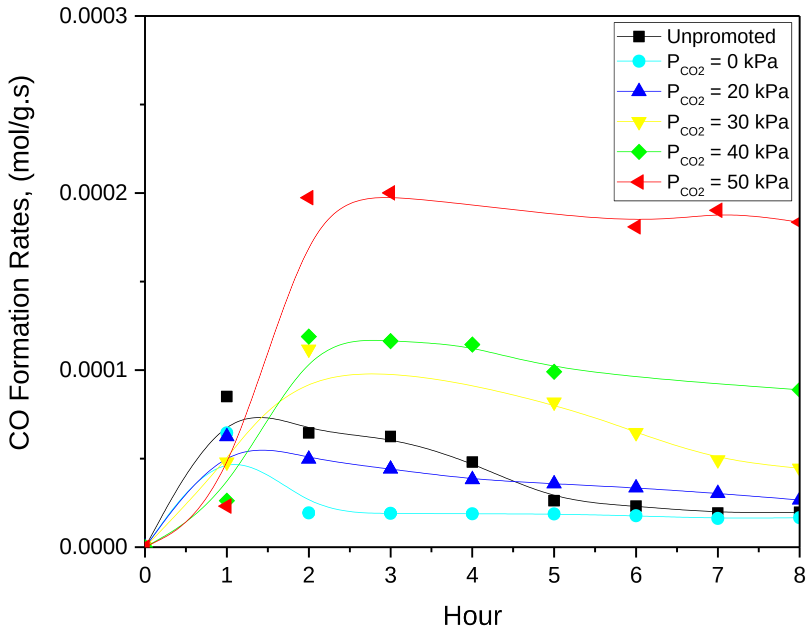


**Figure 4-22 : Formation rate of CO**

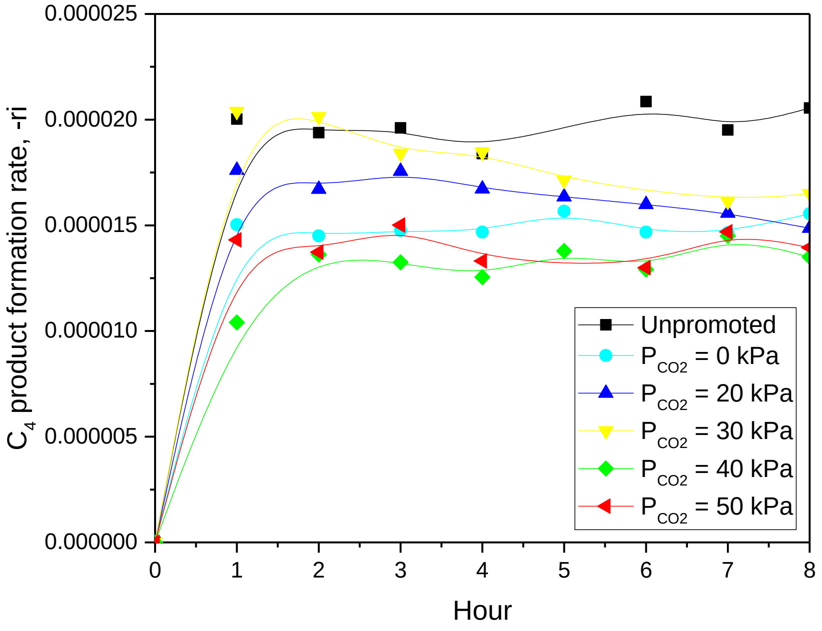


**Figure 4-23 : Formation rate of $CH_4$**

Based on the results portrayed by Figures 4-21, 4-22 and 4-23 the reactions with promoted catalyst with the highest $CO_2$ partial pressure of 50 kPa continue to produce the highest amount of formation of $H_2$ and CO gasses. However the reaction with zero carbon dioxide partial pressure emits the lowest formation of the two gasses but formed the highest amount of $CH_4$ gas.

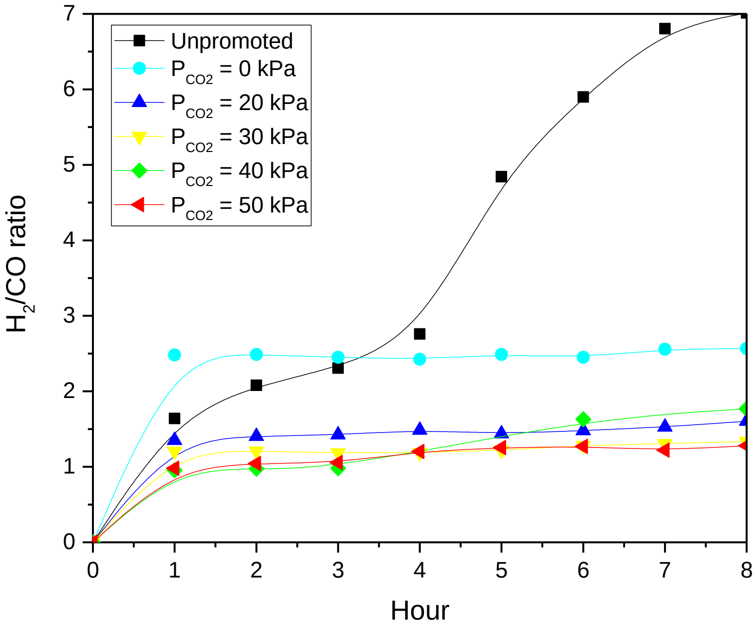


**Figure 4-24 : $H_2$/CO ratio graph**

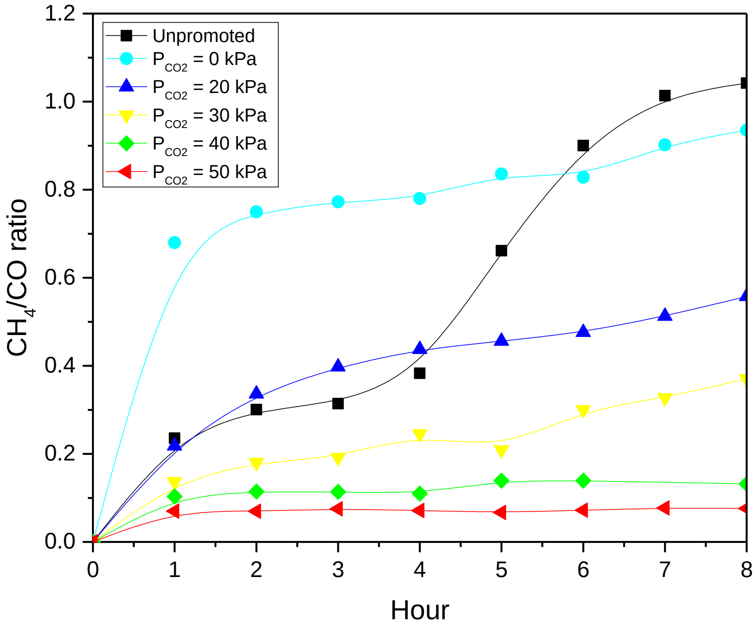


**Figure 4-25 : $CH_4$/CO ratio graph**

Figure 4-24 and Figure 4-25 shows reaction without promoted gives highest amount $H_2$/CO and $CH_4$/CO. Vice versa to reaction of promoted with 50 kPa partial pressure $CO_2$ ratio that show the lowest trend compare to other reactions of $H_2$/CO 1.5 and $CH_4$/CO 0.005.

# 5 CONCLUSIONS AND RECOMENDATION

## *5.1 Conclusions*

As conclusion the comparison between catalysts on ethanol dry reforming that were synthesized via wet impregnation with promoter 3%Ce-10%Ni/$Al_2O_3$ and without promoter 10%Ni/$Al_2O_3$ at different feed composition from 0 to 2.5 feed ratio ( 0 to 50 kPa ) of $CO_2$ : $C_2H_5OH$ at fixed temperature 973 K and 1 atm ambient pressure. Overall the best results are obtained from reaction using promoted catalyst at 50 kPa. This is because by supplying sufficient amount of $CO_2$ allow the $CH_4$ produced to further decompose into more $H_2$ gases. The addition of Ce promoter metal significantly enhances the catalytic activity of the reaction act as accelerator to catalysis, this results also show consistence outcome as stated in some of related journals.

Through temperature-programmed reduction the results for the reduction process was conducted with addition of Cerium promoted catalyst, stronger metal-support interaction was recorded for Ce-promoted catalyst. Calcination with air process for $Ce(NO_3)_3$ and $Ni(NO_3)_2$ metal precursors were completely decomposed and oxidized to $CeO_2$ and NiO phases.

On the other hand the result of the reactions shows a good performance during dry reforming reaction and as illustrated from the graphs obtained almost all of the reactions achieved steady state after the first hour and from 5 to 7 hour most reactions shows stable results. The best result is from reaction with Ce promoter metal for feed ratio of 2.5 (50 kPa) which give highest conversion, yield and formation rate. The addition of higher partial pressure of $CO_2$ does increase the reaction rate, despite that at lower partial pressure of 40 kPa result in negative outcome to the reactions. The possible reason could be due to the addition of Ce metal deposited unto the pores of the catalyst therefore restricted the reaction activity and less products yield can be seen from the graphs obtained.

## *5.2 Recommendation*

For future study the following remarks can be considered to further develop and improvement of performance of ethanol dries reforming:

- Further investigation of higher partial pressure of carbon dioxide should be done so that better comparison of reaction results can be seen.
- Better study of cerium promoter with different loading as this could be the key to have higher conversion rate of hydrogen gas produce.
- SEM analysis also could be done for the spend catalyst to get a better overview of catalyst coking effect of different $CO_2$ partial pressure feed.
- The effect of different catalyst preparation could help to improve the reforming reaction as catalyst synthesizing method influence the dispersion of active site.

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# APPENDIX

Catalyst preparation for 3%Ce-10%Ni/$Al_2O_3$ catalyst, calculation procedure shown below.

Mass of $Al_2O_3$ = 0.87 × 20 g = 7.4 g

Mass of desired Ni metal = 0.1 × 20 g = 2.0 g

Mass of desired Ce metal = 0.03 × 15 g = 0.6 g

The required Ce metal = ( $Ce(NO_3)2.6H_2O$ × 0.6 g ) / $Ce(NO_3)2.6H_2O$

$$= \frac{434.22\ g \times 2\ g}{58.69\ g} = 9.90895\ g$$