CARBON DIOXIDE (CO_2) DRY REFORMING OF GLYCEROL FOR SYNGAS PRODUCTION OVER RHENIUM PROMOTED ON Ni-BASED CATALYST SUPPORTED ON SANTA BARBARA AMORPHOUS 15 (SBA15)

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ABSTRAK

Kekurangan sumber semula jadi adalah salah satu isu yang kritikal kerana ia adalah sumber mentah untuk menghasilkan tenaga oleh itu adalah penting untuk mencari jalan alternatif untuk menangani masalah kekurangan nya sumber semula jadi. Oleh itu, salah satu caranya adalah melalui penggunaan gliserol sebagai bahan mentah utama bagi pengeluaran hidrogen melalui proses (dry reforming). Kajian ke atas Ni/SBA-15 dan 3%Re_Ni/SBA-15 telah dijalankan bagi mempelajari sintesis, pencirian dan kajian mengenai prestasi gliserol (dry reforming). Ni / SBA-15 dan 3% Re_Ni / SBA-15 telah disintesis melalui teknik pengisitepuan basah. tindak balas telah dijalankan dalam keluli demgan pelbagai suhu (700C, 800C dan 900C) serta karbon dioksida kepada gliserol nisbah (0.5, 1 dan 3). Pencirian fizikokimia bagi Ni/SBA-15 dan 3%Re_Ni/SBA-15 dianalisis dengan menggunakan X-Ray Diffraction (XRD), Brunaeur-Emmett-Teller (BET) Berbilang analisis, Scanning Electron Microscopy (SEM), Thermogravimetric analysis (TGA), Temperature Programmed Oxidation (TPO- O_2) dan Field Emission Scanning Electron Microscope (FESEM). Berdasarkan kajian pencirian, didapati bahawa 3% Re_Ni/SBA-15 menunjukkan prestasi yang baik berbanding Ni / SBA-15. Oleh yang demikian, 3% Re_Ni/SBA-15 telah dipilih untuk kajian lanjut mengenai penukaran gliserol dan hasil hidrogen. Di samping itu, tindak balas telah dijalankan pada suhu tetap 700 ℃ dan karbon kepada nisbah gliserol (1: 1). 3% Re_Ni / SBA-15 memberikan penukaran gliserol dan hidrogen hasil yang tinggi sebanyak 57% dan 55%.

Kata kunci: Gliserol; Pengeringan pembaharuan; pemangkin -Ni

ABSTRACT

The depletion of natural resources is a critical issue as we are running out of raw resources to generate energy thus it is important for us to find alternative ways to replace these non-renewable sources. One of the ways is through the utilization of glycerol as a major feedstock for hydrogen production through dry reforming process. This work focused on the synthesis, characterization and studies on the performance of glycerol dry reforming over Ni-based catalyst supported on SBA-15 and promoted by rhenium (Re). The catalyst Ni/SBA-15 and 3%Re_Ni/SBA-15 were synthesized via wet impregnation technique. The reaction was conducted in stainless steel fixed bed reactor at various temperature (700˚C, 800˚C and 900˚C) and carbon dioxide to glycerol ratios (0.5, 1 and 3). The physicochemical characterizations of the catalysts were analyzed using X-Ray Diffraction (XRD), Brunaeur-Emmett-Teller (BET) multipoint analysis, Scanning Electron Microscopy (SEM), Thermogravimetric analysis (TGA)-Calcination studies, Temperature Programmed Oxidation (TPO-O_2) and Field Emission Scanning Electron Microscope (FESEM). Based on characterization studies, it was found that 3%Re_Ni/SBA-15 catalyst showed a good performance compared to non-promoted Ni/SBA-15 catalyst. As the result of XRD analysis show smaller crystallite size and indicate fine Ni dispersion on promoted catalyst. For BET analysis, promoted catalyst gave higher specific surface area, bigger pore volume as well as bigger average pore volume. Besides, SEM analysis show promoted catalyst has smooth and creates longitudinal surface which due to small cryrstallite size as depicted in XRD analysis. TGA analysis show that promoted catalyst need more higher temperature to eliminate water vapor in between 30 to 100 ℃. Moreover, 3%Re_Ni/SBA-15 catalyst has been chosen for further study on glycerol conversion and hydrogen yield. The reaction were carried out at fixed temperature 700℃ and carbon to glycerol ratio (1:1). It was found that 3%Re_Ni/SBA-15 catalyst gave higher glycerol conversion and hydrogen yield of 57% and 55% respectively meanwhile Ni/SBA-15 gave lower glycerol conversion and hydrogen yield of 20% and 18% respectively.

Keywords: Glycerol; Dry reforming; Ni-based catalyst

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Currently, one main environmental challenge is to avoid or reduce the impacts of global warming. Carbon dioxide (CO_2) is the main greenhouse gas and 70-75% of the CO_2 emission is originated from the combustion of fossil fuels (Halvorsen et al.,1989). The progressive depletion of conventional fossil fuels lead to increase in the utilization of renewable energy sources. Currently, many researchers focused on the development of sustainable and environmental friendly source of energy from biomass to replace conventional fossil fuels. Currently, the commercialize biomass especially glycerol has become one of the most considerable feedstock for the syngas production by researchers worldwide.

Glycerol by-product from the biodiesel production become a compressing alternative to the syngas production due to the cost and availability. Researchers showed a surge of interest in the use of glycerol as renewable feedstock to produce hydrogen and other functional chemicals. It was estimated that approximately 10% of crude glycerol will be produced from the transesterification process of biodiesel (Karinen and Krause, 2006; Fernandez et el., 2010; Huang et al., 2013). There are five types of processes that has been implemented to convert glycerol to syngas such as steam reforming, partial oxidation, autothermal reforming, aqueous phase reforming and supercritical reforming (Fan et al., 2010). The versatile new applications of glycerol in the everyday life and chemical industry will improve the economic viability of the biodiesel industry.

Synthesis gas or syngas is defined as a gas that contains hydrogen and carbon monoxide as the main combustible components. Raw syngas also contain considerable amounts of CO_2 and H_2O. Syngas is an important intermediate product in chemical industry. The world market for syngas (mainly from fossil energy sources like coal, natural gas and oil/residues) is dominated by the ammonia industry. Other main applications are the production of hydrogen for use in refineries, e.g. hydrogenation steps, and for the production of methanol. Figure 1.1 shows the percentage distribution of syngas consumption worldwide.

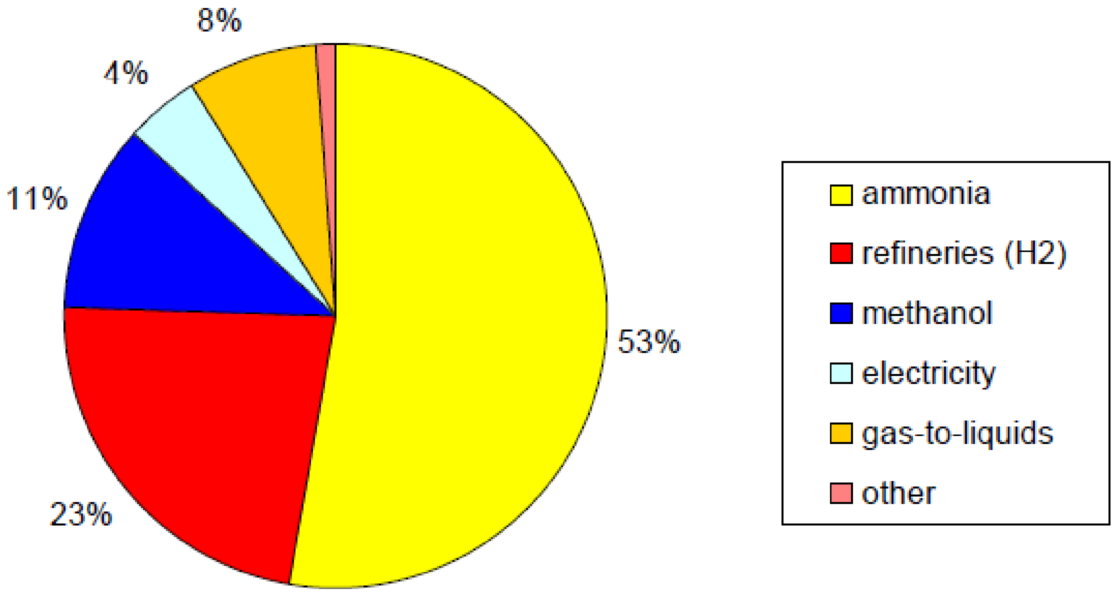

Figure 1.1. The percentage distribution of syngas consumption worldwide

In syngas technologies, Ni is commonly use as the based catalyst in reforming process due to its stability and high catalytic activity (Saad et al., 2015). The good selection of catalyst promoter can improve the catalyst stability in glycerol reforming process and the catalyst activity. Besides, it also help to maximize the hydrogen production.

1.2 Motivation

The depletion of natural resources is a critical issue as we are running out of raw resources to generate energy thus it is important for us to find alternative ways to replace these non-renewable sources. One of the ways is through the utilization of glycerol as a major feedstock for hydrogen production through dry reforming process. Glycerol is one of the by-product from the transesterification process of biodiesel. Exploiting glycerol as feedstock for the syngas will help to reduce the production of biodiesel and it will also added some values towards this waste product and directly resolved the environmental problems

1.3 Problem statement

Glycerol is one of the by-product produced from the transesterification process of biodiesel. Since depletion of fossil fuels and petroleum reserves will drive to energy crisis, the use of glycerol as raw material offers an economical and environmental friendly way to generate renewable hydrogen production. Besides, glycerol dry reforming provides a greener process since it utilizes waste products, glycerol and greenhouse gases CO_2 as the reactants. Nickel is used as a catalyst in syngas technology due to its viability and low cost. Moreover, SBA-15 also found to be a suitable supporter in dry reforming of glycerol since it can be used at higher reaction temperatures. The mesoporous structure of SBA-15 was not destroyed and the pore walls of SBA-15 could prevent the aggregation of the nickel species.

1.4 Objectives

The main objectives of this research is:

- To synthesize and characterize Ni/SBA-15 and 3%Re_Ni/SBA-15 catalysts using wet impregnation method.
- To study the performance of Ni/SBA-15 and 3%Re_Ni/SBA-15 catalysts in the glycerol dry reforming reaction.

1.5 Scopes of study

The scopes of this research are:

- To synthesis Ni/SBA-15 and 3%Re_Ni/SBA-15 catalysts via wet impregnation method.
- To characterize Ni/SBA-15 and 3%Re_Ni/SBA-15 catalysts using Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), Temperature-Programmed Oxidation (TPO- O_2), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM) and also Field Emission Scanning Electron Microscope(FESEM) to study on which catalysts that contribute better performance on producing higher hydrogen yield and glycerol conversion based on the crystallite size, surface area, cumulative pore volume, average pore size, morphology of catalyst surface, temperature to eliminate water vapor and also carbon deposition weight loss.
- To conduct reaction studies of glycerol dry reforming as well as investigate the effect of carbon to glycerol ratio (CGR) in 0.5,1 and 3 meanwhile effect of temperature in 700, 800 and 900˚C towards performance of catalyst in glycerol dry reforming.

CHAPTER 2

LITERATURE REVIEW

2.1 Energy

Sustainable energy development strategies typically involve three major technological changes: energy savings on the demand side, efficiency improvements in the energy production and replacement of fossil fuels by various sources of renewable energy. First, the major challenge is to expand the amount of renewable energy in the supply system. Renewable energy is considered as an important resource in many countries around the world. Renewable sources, such as wind and solar, only constitute a very small share of the total supply. In some regions and countries, the share of renewable energy has grown substantially during the last couple of decades. One of the challenges of renewable energy strategies for sustainable development is to integrate a high share of intermittent resources into the energy system, especially the electricity supply. In addition, Energy Information Administration (EIA) states that fossil fuels contribute about 86.4% to the sources of energy in the world for 2007 and followed by nuclear 8.5%, hydroelectric 6.3% and others like solar, waste and wind 0.9%. Globally, it is estimated that almost 80% of energy comes from fossil fuel (i.e. oil, natural gas and coal).

2.2 Fossil Fuels

Fossil fuels are hydrocarbons, primarily coal, fuel oil or natural gas, formed from the remains of dead plants and animals. In common dialogue, the term fossil fuel also includes hydrocarbon-containing natural resources that are not derived from animal or plant sources. These are sometimes known as mineral fuels. It is generated from buried combustible geologic deposits of organic materials, formed from decayed plants and animals that have been converted to crude oil, coal, natural gas, or heavy oils by exposure to heat and pressure in the earth's crust over hundreds of millions of years. The burning of fossil fuels by humans is the largest source of emissions of carbon dioxide, which is one of the greenhouse gases that allows radiative forcing and contributes to global warming. Concerns are grown among researches to replace fossil fuel and petroleum reserves in order to save the environment and preserve natural resources. Thus, synthesis gas becomes one of the alternatives energy that can be used in future. Syngas is a renewable source that predicted to become a primary energy for the future (Chheda et al., 2007;Saraswat & Pant, 2012).

2.3 Synthesis Gas

Synthesis gas or briefly, syngas is a mixture of carbon monoxide, carbon dioxide and hydrogen. Syngas can be produced from many sources, including natural gas, coal, biomass or virtually any hydrocarbon feedstock by reacting it with steam or oxygen. Syngas is a crucial intermediate resource for production of hydrogen, ammonia, methanol and synthetic hydrocarbon fuels. The formation of syngas is strongly endothermic and requires high temperatures. Syngas could be an alternative fuel for the non-renewable resources and it helps to reduce the environmental problem. The composition of raw syngas generally contain 25-30% hydrogen, 5-15% carbon dioxide, 30-60% carbon monoxide and 2-3% water (Gills,2006). Recently biomass has been touted as another optional feedstock for syngas production. Biomass is an organic material that comes from organic wastes, energy crops and agricultural residues and it by products (Muhammadi et al., 2011). The production of syngas by using biomass as a feedstock helps to reduce the depletion of fossil fuel and also petroleum reserves. Glycerol is one of the by-product of producing biodiesel through transesterification process that can be used to produce synthesis gas.

2.4 Glycerol as the by-product of biodiesel process

Most of the energy consumed worldwide comes from fossil sources. However, these sources are limited. Thus, the search for alternative is strategically important (Cruz et al., 2011). Biodiesel consists of alkyl esters derived from either the transesterification of triglycerides or the esterification of free fatty acids with low molecular weight alcohols (Melero et al., 2012; Morales et al., 2011). The transesterification process involve three steps reversible reaction of triglyceride (fat/oil) with an alcohol to form fatty acid methyl ester and glycerol.

The general equation of transesterification reaction is presented in Eq.(2-1):

$$\text{Triglycerides} + 3CH_3OH \leftrightarrow 3\text{R} - \text{C}(OCH_3)O + C_3H_8O_3 \qquad (2\text{-}1)$$

Vegetable oil + Methanol ↔ Methyl ester + Glycerol

The three consecutive reactions of triglycerides is presented in Eq.(2.2 – 2.4):

$$\text{Triglycerides} + \text{R'OH} \leftrightarrow \text{Diglycerides} + \text{R'COO}R_1 \qquad (2\text{-}2)$$

$$\text{Diglycerides} + \text{R'OH} \leftrightarrow \text{Monoglycerides} + \text{R'COO}R_2 \qquad (2\text{-}3)$$

$$\text{Monoglycerides} + \text{R'OH} \leftrightarrow \text{Glycerol} + \text{R'COO}R_3 \qquad (2\text{-}4)$$

Almost 10% of glycerol is produced from biodiesel production (Yang et al., 2012). By 2016 global biodiesel market estimated to produce about 4 billion gallons of crude glycerol from biodiesel plant worldwide (Wang et al., 2006) while year 2020, 3 megatons of crude glycerol will be produced (Lin et al., 2013). Glycerol can also be produced through hydrogenolysis of sorbitol (Stelmachowski,2011), glucose fermentation (Gong et al., 2000) and also lignocelluloses to ethanol conversion (Rogers et al., 2005). The over production of glycerol attracts the interest of researchers to utilize the waste of glycerol as raw material of chemical products. Glycerol (glycerin) is odorless, colourless and viscous liquid that has multiple uses in cosmetic, paint, chemical, pharmaceutical and food (Fan et al., 2013). Besides, glycerol also can be converted into fuels, chemicals and material (Fan and co worker, 2010). Recent years shows that syngas can be produced using crude glycerol as the feedstock.

2.5 Process for Glycerol dry reforming into syngas

Glycerol can be produced using several processes such as steam reforming, partial oxidation, autothermal reforming and dry reforming process (Lin et al., 2013). The composition and quantity of syngas is depend on the type and temperature of the reactor, characteristic of the feedstock, type of process and also the variation of reaction condition (i.e. pressure, temperature, residence time and reaction). Previous studies showed that the steam reforming and partial oxidation are widely used for the syngas production (Wang et al., 2009).

2.5.1 Glycerol Steam Reforming

The Glycerol Steam Reforming is a high temperature endothermic process which uses a catalyst to react with glycerol with water to produce hydrogen. The overall reaction of hydrogen production by steam reforming of glycerol ($C_3H_8O_3$) could be depicted as follows:

$$C_3H_8O_3\text{ (g)} + 3H_2O\text{(g)} \rightarrow 7H_2\text{(g)} + 3CO_2\text{ (g)} \tag{2-5}$$

Wang et al., (2009) studied thermodynamic properties of glycerol reforming using the Gibbs free energy minimization. They concluded that high temperature, low pressure and high water/glycerin ratio favor the hydrogen production. Optimal conditions for hydrogen production from glycerol were found to be at a temperature of 925-975 K and a water/glycerin ratio of 9-12 at atmospheric pressure. Similar results were reported by Adhikari et al., (2007) who concluded that the best condition for producing hydrogen were at >900 K temperature, atmospheric pressure, and 9/1 of water/glycerin molar ratio. They explained that under these conditions, methane production was minimized and the carbon formation is thermodynamically inhibited. The viability of using steam reforming to produce hydrogen from biodiesel by-product glycerol was also confirmed by Slinn et al., (2007). The authors used aluminum oxide supported platinum catalyst. Optimum reformer performance was reached at 880 ºC, flow rate of 0.12 mols/min (glycerol) per kg catalyst, and steam/carbon ratio of 2.5. However, under the same reaction conditions, the yield of by-product glycerol was 30% less than the pure glycerol. The researchers attributed this by the fact that the long chain fatty acid impurities are harder to reform and more likely to form carbon. Many researchers investigated the effects of catalysts on the steam reforming of glycerol for hydrogen production. Adhikari et al., (2007) focused on the study of nickel-based catalysts with magnesium oxide, cerium oxide and titanium oxide supports. They found that maximum hydrogen yield, 4 mol of hydrogen out of 7 mol of stoichiometric maximum, could be obtained at 650 ºC with MgO supported catalysts. Iriondo et al., (2007) modified alumina-supported nickel catalysts with Ce, Mg, Zr and La to produce hydrogen from glycerol. They found the use of Ce, La, Mg and Zr as promoters in Ni based catalysts increases the hydrogen selectivity. The authors further deduced that Ce and La can increased the stability of nickel phases under reaction conditions; Mg was able to enhance surface nickel concentration and Zr improved the capacity to activate steam. Besides nickel based catalysts, other types of catalysts were also evaluated for steam reforming of glycerol. Ceria supported with Ir, Co and Ni catalysts have been studied by Zhang et al., (2007). All the investigated ceria-based catalysts exhibited significant activity and selectivity since the dehydration of glycerol to ethylene or propylene didn't occur, which can cause coke formation and deactivate the catalysts. Among the ceria-supported metal catalysts examined, the ceria oxide supported iridium catalyst showed a promising catalytic performance with more than 85% hydrogen selectivity and 100% of glycerol conversion at 400 ºC. As comparison, Hirai et al., (2005) developed a novel efficient catalyst for steam reforming of glycerin. Ruthenium catalysts were preferred and high performance was observed for the yttrium (III) oxide supported ruthenium catalysts.

2.5.2 Partial Oxidation

Partial oxidation is the process where substoichiometric number of oxygen reacts with glycerol to produce syngas (Lin et al., 2013) .The process can be depicted as follows:

$$\text{Glycerol} + \text{air} \rightarrow \text{carbon oxides} + \text{hydrogen} + \text{nitrogen} \qquad (2\text{-}6)$$

The advantages of partial oxidation process compared to glycerol steam reforming is as chemical equation following has fast start up time due to exothermic nature of the oxidation reaction and more compact steam reformer design as it does not need indirect addition of heat through a heat exchanger (Wang et al., 2010).

2.5.3 Pyrolysis

According to Peres (2013) pyrolysis is the process that can be done in two conditions which are the catalyzed pyrolysis and fast pyrolysis. The glycerol pyrolysis reaction is shown in Eq.(2-7) :

$$C_3H_8O_3 \leftrightarrow 3CO + 4H_2 \qquad (2\text{-}7)$$

It is one of the cheapest method for energy conversion and also a simple process. The process is highly endothermic (Lin, 2012). Besides, pyrolysis has high thermal efficiency, low carbon dioxide emission and short residence time. Glycerol pyrolysis involved two pathways, with the presence of carrier gas or without carrier gas. The experiments were conducted in a fixed bed reactor to produce hydrogen. They concluded that both carbonaceous catalysts gave higher yield of hydrogen where the optimum temperature was at 800℃. According to Chaudhari and Bakhshi (2002), they ran the pyrolysis process at 400℃ and 500℃ with the flow rate approximately 2 g/h. It was reported that the operation was quite difficult without the use of carrier gas because of the disposable solid waste (char) formation in feed inlet.

2.5.4 Glycerol Dry Reforming

Glycerol dry reforming offer a better pathway for the production of hydrogen as it reported to have a greener process where it utilize waste products, glycerol and greenhouse gases (CO_2) as it feedstock. The glycerol dry reforming concentrating on the thermodynamic analysis and effect on different types of support and promoters over nickel (Ni) based catalyst (Wang et al.,2009; Lee et al.,2013; Siew et al.,2013). The equation of glycerol dry reforming :

$$C_3H_8O_3(g) + CO_2(g) \leftrightarrow 4CO(g) + 3H_2(g) \qquad (2\text{-}8)$$

Lee et al., (2013) reported the use of cement clinker as support for the Ni based where the reaction temperature was held at 1023 K (Wang and co workers., 2009). The carbon dioxide to glycerol ratio (CGR) was manipulated with the pressure of carbon dioxide. The results shows that higher pressure of carbon dioxide and CGR will favor the side reaction (i.e. hydrogenation, methanation) and it need to be control so that it can achieve least carbon deposition and higher glycerol conversion. Different type of support and addition of promoter will help in improving the catalyst activity (Ebshish et al., 2011). The main drawback for this process is related to the catalyst deactivation which due to the carbon depositions. It causes the catalyst to loss its effective surface area which simultaneously affect the purity of reforming products (Adhikari et al., 2007). Thus, suitable catalyst is needed to minimize the carbon deposition.

2.6 Catalyst

2.6.1 Based catalyst

Different types of catalyst with different supports and promoters have been used widely in the field of syngas reforming. Nickel (Ni) based catalyst and most VIII group metals especially noble metal that comprise of ruthenium (Ru), rhodium (Rh), palladium (Pd) and platinum (Pt) are widely used in reforming process (zhang et al., 2000). Studies on the methane reforming with Ni and Pt as metal based catalyst was conducted by (Pompeo et al., 2007). Both of the catalysts have good activities level but Ni has slightly more active than Pt. The reaction studies of glycerol dry reforming over Ni as based supported over calcium oxide (CaO) and zirconium oxide (ZrO_2) were conducted by Nabilah et al. (2016). The finding showed that through XRD analysis where the catalyst show low crystallinity and fine dispersion of Ni species resulted in high specific surface area which validated by BET analysis. Besides that, Hazimah et al conducted Silver (Ag) promoted Nickel (Ni) based catalyst supported on silicon oxide. It showed that the catalyst has the smaller particles which indicates the fine dispersion of NiO particles based on XRD analysis. Meanwhile, BET analysis reveals that the catalyst has the highest surface area. Noble metal catalyst shows less sensitivity to coke deposition comparing to Ni based catalyst (Rezaei et at., 2007 ; Pompeo et al ., 2007). However, noble metals are relatively more expensive to be consumed for the large scale processes. Thus, Ni is the most suitable catalyst in many gasification processes due to its economic feasibility and viability (Lee et al., 2014). Ni based catalyst is prove to be deactivated and more sensitive to the carbon deposition however with suitable choices of support material and excessive coke formation can be avoided (Gallo et al.,2012).

2.6.2 Catalyst Support

Type of catalyst, catalyst supports and catalyst promoters help to improve the catalyst activity (Ebshish et al., 2011). Based on Adhikari et al.(2009) research, titanium oxide, magnesium oxide and ceria oxide are used to support Ni in steam reforming process. The ceria oxide supported nickel catalyst was produced the highest conversion of hydrogen compared to magnesium oxide supported nickel catalyst and titanium oxide supported nickel catalyst. Hirai et al. (2005) reported on the effect of ruthenium on various supports such as yitrium oxide, zirconium oxide, cerium oxide, lanthanum oxide, silica oxide, magnesium oxide and aluminum oxide. It was found that up to 3wt% of Y_2O_3 has the highest yield of H_2 whilst MgO and Al_2O_3 show the low conversion of glycerine as it was difficult to reduce ruthenium oxide to metallic ruthenium. A series of Ni/SBA-15 catalysts with different Ni contents (2.5%–20%) were prepared using an incipient wet impregnation method. The catalyst preparation is similar to 15% nickel metal supported with Cao, $La_2O_{3,} and\ ZrO_2$ that conducted by (Nabilah et al., 2016). The catalytic properties of the catalysts for methane reforming with carbon dioxide were tested using a continuous-flow fixed-bed quartz reactor. The results indicated that the Ni/SBA-15 catalysts led to a higher conversion of CH_4 and CO_2 under the optimum reaction conditions. The 12.5% Ni/SBA-15 catalyst showed highly stable activity at 800°C for 600 h. However, after 710 h reaction the conversion of CH_4 and CO_2 decreased to 50% and 25% respectively. Coking was the main reason for the deactivation of the Ni/SBA-15 catalysts. At higher reaction temperatures, the mesoporous structure of SBA-15 was not destroyed and the pore walls of SBA-15 could prevent the aggregation of the nickel species. By inserting nickel into SBA-15, a small pore was formed besides the mesopores of SBA-15. Addition of promoters to a nickel based catalyst will improve the resistivity towards carbon formation (Seung-hoon et al., 2013).

2.6.3 Promoter of catalyst

Addition of promoter is one of the way to improve the stability and catalytic activity of Ni catalyst (Alipour et al., 2014). Ebshish et al .(2011) focus on the effect of promoter like cobalt (Co), sodium (Na), iron (Fe) and copper (Cu) to Ni/ Al_2O_3 and they concluded that Na has the best performance in hydrogen production because of the support reduction that avoid sintering of metal. Besides, Iriondo et al., (2007) reported the effect of promoter on alumina (Al_2O_3) for the steam reforming of ethanol lowered the rate of carbon deposition on the catalyst surface. Other than that, Nabilah et al., 2016 studied in glycerol dry reforming over 15% Ni catalyst supported on La_2O_3, CaO and ZrO_2 thus was found that 15% of Ni/CaO has the highest hydrogen and glycerol conversion with carbon to ratio 1 and temperature at 800˚C. From the work, it was observed that a good catalytic activity was achieved due to high Re content. Rosen et al. (2016) studied on the methane dry reforming where electrodeposition method is applied for the synthesis Re promoted on Ni foam. From the studies, it was found that there was no carbon accumulation on the catalyst and this suggested that the method is viable for this reforming process. Cook et al. (2014) studied the effect of different noble metal promoters (i.e. rhenium, platinum and ruthenium) towards cobalt (Co) supported on La/alumina support. It showed that Co/Re catalyst gave superior catalytic performance. Besides that, Hazimah et al conducted Silver (Ag) promoted Nickel (Ni) based catalyst supported on silicon oxide. It showed that the catalyst has the smaller particles which indicates the fine dispersion of NiO particles based on XRD analysis. Meanwhile, BET analysis reveals that the catalyst has the highest surface area. The SEM analysis gave the rougher surface which showed the formation of Ag particles and NiO. From the reaction study, it resulted that the glycerol conversion and hydrogen yield accounted for 32.6% and 24.7% respectively.

CHAPTER 3

METHODOLOGY

3.1 Chemicals

Glycerol (Fisher Scientific, 99.95 % purity), nickel (II) nitrate hexahydrate (Acros Organics , 99 %), hydrochloric acid(37wt %),Triblock copolymer poly (ethylene glycol) – poly(propylene glycol) – poly(ethylene glycol) (PEO –PPO- PEO/ P123) and tetraethylorthosilicate (Merck , TEOS) were used for this experiment. Glycerol was used as the feedstock for the dry reforming process. Carbon dioxide was used as reactant and nitrogen gas was used as the carrier gas for this reaction.

3.2 Catalyst Characterization

3.2.1 Scanning Electron Microscopy (SEM)

In this analysis, SEM (Carl Zeiss, OEL.JSM-7800F model) at Central Lab, UMP was used to study the morphology and structure of synthesized catalyst. Firstly, sample catalyst was first mounted on top of copper stub and covered by double side carbon tap before it was coated with gold using splutter coater machine. The sample images were produced based on the scan captured at different angle. This analysis was conducted at 10 – 15 kV of speed voltage with 155 eV resolutions.

3.2.2 X-Ray Diffraction (XRD)

XRD analysis was conducted using Rigaku Miniflex II at FIST Lab, UMP to obtain the crystalline structure of the catalyst. It was carried out using CuKα radiation ($\lambda = 1542$ Å) at 15 mA and 30kV. The scan rate was $1^{\circ}\ min^{-1}$ for values between 2Θ (10˚ to 80˚). The crystalline size was determined using Scherrer equation as shown in Equation 2.1.

$$d = \frac{K\lambda}{ß COS \Theta} \qquad 2.1$$

where d is the crystallite size, K is the shape factor (K= 0.94), λ is the X-ray radiation (λ = 0.154 nm), ß is the full width at half maximum (FHWM) and Ɵ is half of diffraction angle.

3.2.3 Brunauer-Emmett-Teller (BET) multipoint

In this analysis, liquid nitrogen was used as the adsorbate and the sample was degassed at 300˚C for 12 h to remove other adsorbed species attached to the catalyst. Data on the Barrett- Joyner-Halenda (BJH) method was employed to calculate the specific surface area, cumulative pore volume and average pore size.

3.2.4 Thermogravimetric Analysis (TGA)

TA instrument

The thermogravimetric analysis is conducted using (TGA Q-500 model) at CARIFF Lab, UMP to determine the temperature degradation and measure the amount and rate of change of a material as a function of temperature. There were two analyses conducted using the same instrument which is the temperature programmed calcination (TPC) and temperature programmed oxidation (TPO). Both analyses used the same ramping rate 10 Kmin^{-1}. From the analyses the weight percentage and derivative weight percentage versus temperature were plotted.

(a) Temperature Programmed Calcination (TPC)

For the fresh catalyst, temperature programmed calcination (TPC) was conducted to determine the thermal stability and the phase transition of the synthesized catalyst. 10mg of catalyst was filled in ceramic pan and heated at ramping rate of 10 Kmin^{-1} from room temperature up to 1173K in air.

(b) Temperature Programmed Oxidation (TPO)

For the spent catalyst, TPO analysis was conducted under O_2 blanket. The ramping rate was set at 10Kmin^{-1} starting from room temperature to 1173K with one hour holding period. From the analysis, the profile on the amount of carbon formed was recorded by calculating the weight loss in catalyst during the analysis.

3.2.5 Field Emission Scanning Electron Microscope (FESEM)

FESEM is utilized to produce high resolution image for the solid sample at magnification more than 500,000 times. The analysis conducted by using JEOL/JSM-7800F brand at Central Lab, UMP. The catalyst were mounted on top of copper stub and covered by double side carbon tape before it was coated with gold using splutter coater machine. For this analysis, the accelerating voltage employed for the experiment was in the range of 5 to 15 kV.

3.3 Dry Reforming Experimental Work

The glycerol dry reforming was carried out in a stainless steel fixed bed reactor (ID= 0.95 cm ; length 40 cm) under a pressure of 1 bar as shown in Figure 3.1. The reactor was loaded with 0.2 g of catalyst. Molar ratio of CO_2 to glycerol was fixed at 1:1. Glycerol was delivered to the reactor using the HPLC pump via the downward flow motion. The reaction temperature was fixed at 973 K. Before experiment started, hydrogen was flow into the reactor for catalyst reduction. Flow of nitrogen gas to the reactor was set at 0.1 L/min at 1 bar while flow of carbon dioxide gas to the reactor was set at 9.9 ml/min at 1 bar. The outlet gases were passed through a gas wash bottle which consists of silica gel flask to absorb moisture. The exit gas flowrate was measured using a bubble meter and finally collected into a gas sampling bag. The composition of syngas produced was determined using online Agilent gas chromatography (GC) with TCD capillary columns, HP – MOLSIV (30.0 m × 520µm × 40.0µm).

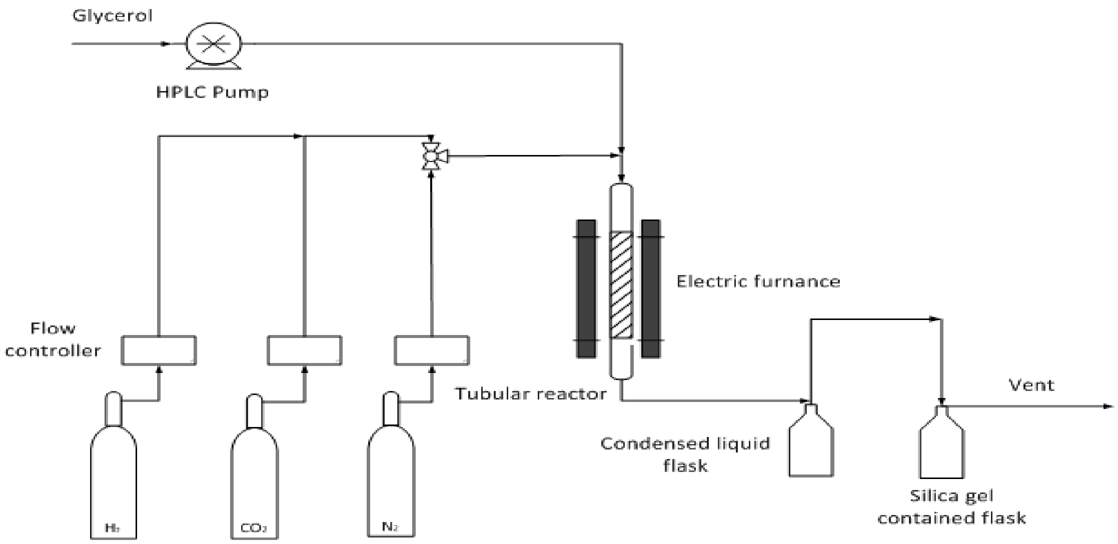

Figure 3.1 Experiment setup for the glycerol dry reforming

The catalyst performance was evaluated in terms of the glycerol conversion and hydrogen yield. The glycerol conversion to gaseous products was determined based on the atomic H-balance and defined as :

$$X_G = \frac{2F_{H_2} \times 4F_{CH_4}}{8F_{C_3H_8O_3}} \tag{3- 2}$$

The yield of hydrogen is expressed as :

$$Y_{H_2} = \frac{2F_{H_2}}{8F_{C_3H_8O_3}} \times 100 \tag{3- 3}$$

Where F_{H_2} and F_{CH_4} represents the molar flow rate of hydrogen and methane product respectively while $F_{C_3H_8O_3}$refers to the molar flow rate of the inlet glycerol.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter focuses on the physicochemical characterization of the promoted (3%Re_Ni/SBA15) and non-promoted (Ni/SBA15) catalyst. The physicochemical characterization performed using SEM, FESEM, BET, XRD, TGA and TPO. In the second section, the catalyst were subjected to the glycerol reforming reaction studies where the effects of temperature and carbon glycerol ratio (CGR) is monitored and evaluated.

4.2 Physicochemical Characterization of 3%Re_Ni/SBA15 and Ni/SBA15 catalyst

(a) X-Ray Diffraction (XRD)

The XRD technique was used to determine the crystalline phase and particle size of the catalyst and recorded in the 2Ө range of 10˚ to 80˚. All the peak phase for Ni/SBA-15 and 3%Re_Ni/SBA-15 existed in the diffractogram are shown in Figure 4.1 and Figure 4.2 respectively. The phase of NiO were detected at 2Ө of 37.26˚, 43.268˚, 62.822˚, 75.44˚, 75.83˚ and 79.392˚ for Ni/SBA-15. It produced sharp and longer peaks with the presence of crystallite size from 8.14nm to 12.25nm based on Table 4.1. On the other hand, the phase of NiO were detected at 2Ө of 3%Re_Ni/SBA-15 are 37.286 ˚, 43.235˚, 62.88˚ and 75.26˚. For Re species was undetectable by XRD pattern as it most likely due to well dispersion of metal (siew et al., 2014). It shows a broader and shorter peak compared to Ni/SBA-15. Besides, it crystallite size was smaller with 3.85nm to 4.78nm compared to the non-promoted catalyst. According to Razaei et al. (2007), bigger crystallite size causes higher crystallinity and leads to less nickel dispersion contributing to low surface area.

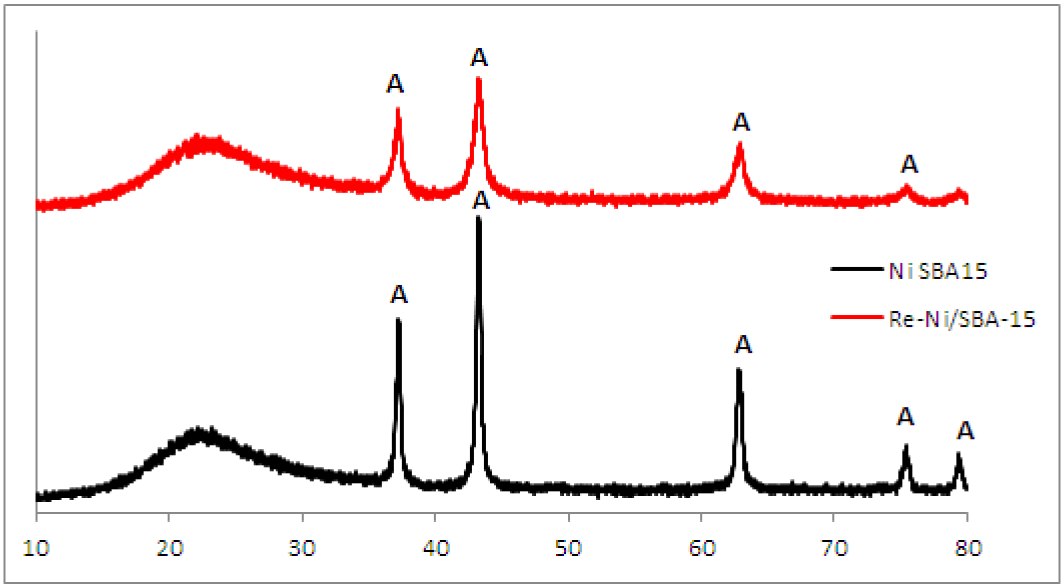

Figure 4.1 XRD pattern of Ni/SBA-15 and 3%Re_Ni/SBA-15 where (A)NiO

Table 4.1 Crystallite diameter for Ni/SBA-15 from XRD analysis

Catalyst : Ni/SBA-15						
2Θ	37.260	43.268	62.822	75.4	75.83	79.392
FWHM	0.328	0.346	0.415	0.45	0.3	0.43
Crystalline Size (nm)	9.33	9.01	8.18	8.14	12.25	8.76

Table 4.2 Crystallite diameter for 3%Re_Ni/SBA-15 from XRD analysis

Catalyst : 3%Re_Ni/SBA-15				
2Θ	37.286	43.235	62.88	75.26
FWHM	0.64	0.706	0.88	0.95
Crystalline Size (nm)	4.78	4.42	3.86	3.85

(b)Brunaeur-Emmett-Teller (BET) multipoint analysis

The N_2 physisorption properties of Ni/SBA-15 and 3%Re_Ni/SBA-15 are shown in Table 4.3. From the BET analysis, it shows that the non-promoted catalyst has lower specific surface area, pore volume and average pore diameter compared to the promoted catalyst. Moreover, the 3%Re_Ni/SBA-15 gave higher surface area with 295.3397 m^2g^{-1} compared to Ni/SBA-15 with 221.5249 m^2g^{-1} due to the presence of smaller nickel crystallite size as depicted from the XRD analysis. Re promoter lessen the carbon deposition on the surface of the catalyst which improve the catalytic activity as the active site of the catalyst is not accumulated by carbon. Cook et al. (2014) studied the effect of different noble metal promoters (i.e. rhenium, platinum and ruthenium) towards cobalt (Co) supported on La/alumina support. It showed that Co/Re gave superior catalytic performance. Besides that, according to Siew et al. (2014) the non-promoted Ni/Al_2O_3 catalyst exhibited the lowest BET surface area while the optimum surface area belong to 3%La_Ni/$\mathrm{Al_2O_3}$ catalyst that gave the highest BET surface area which is similar to this work.

Table 4.3 BET Surface area for Ni/SBA-15 and 3%Re_Ni/SBA-15 catalyst

Catalyst	Ni/SBA-15	3%Re_Ni/SBA-15
BET surface area, m^2g^{-1}	221.5249	295.3397
Cumulative Pore Volume, cm^3g^{-1}	0.326218	0.559401
Average Pore Size, nm	52.631	70.803

(c) Scanning Electron Microscopy (SEM)

SEM is used to observe the morphology of Ni/SBA-15 and 3%Re_Ni/SBA-15. Figure 4.3 shows the SEM results on both catalysts and comparison took place at 5000x magnification. The structure of Ni/SBA-15 was found to be rough and creates bulky surface resulting from the presence of large crystalline size as depicted in XRD analysis. On the other hand, 3%Re_Ni/SBA-15 has smooth and longitudinal surface due to smaller crystallite size in XRD analysis which indicates fine dispersion of nickel and contributed to less agglomeration compared to Ni/SBA-15. This is due to the addition of 3% Re as promoter. According to Seung hoon et al. (2013), addition of promoters to a nickel based catalyst will improve the resistivity towards carbon formation.

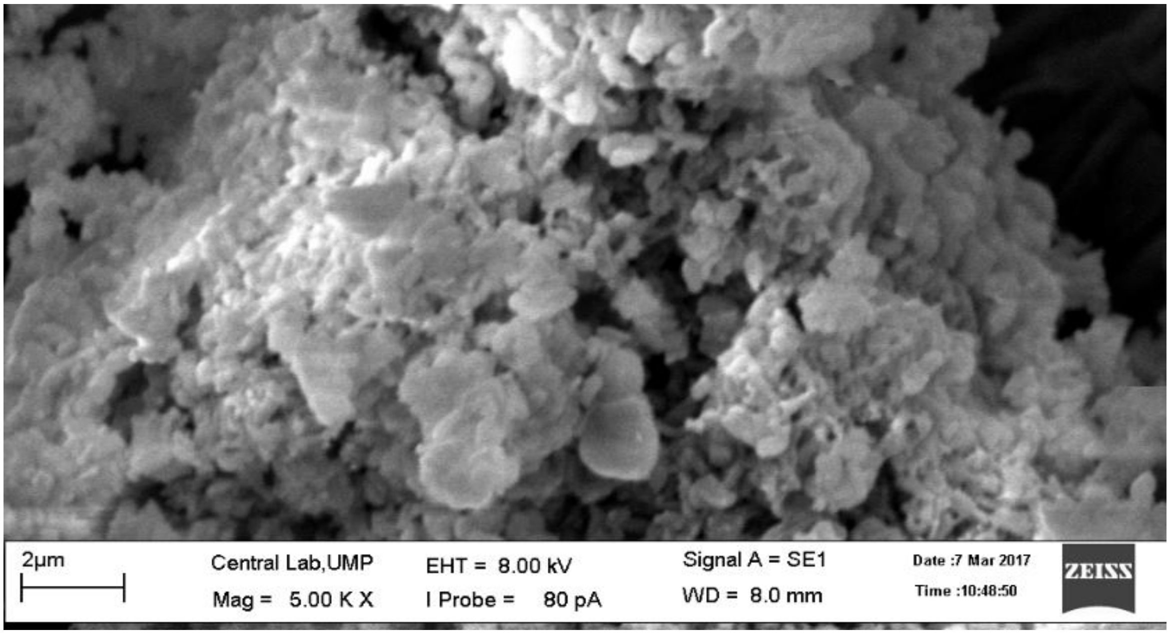

Figure 4.2 Morphology structure of Ni/SBA-15 at 5000x magnification

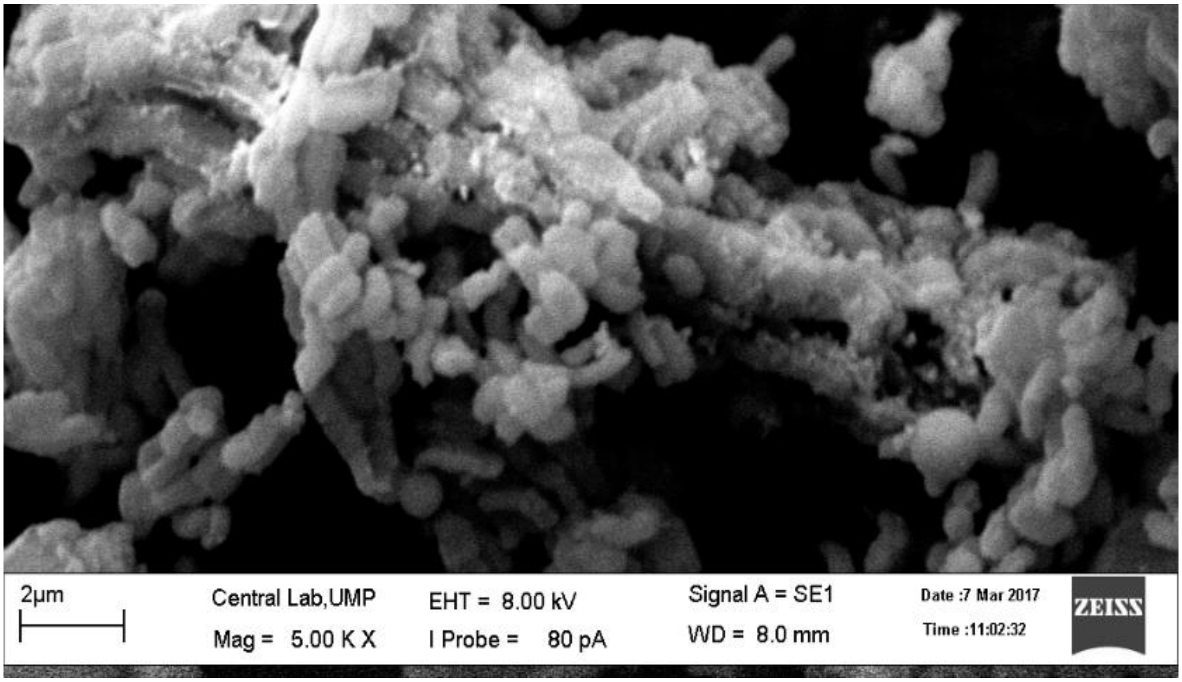

Figure 4.3 Morphology structure of 3%Re_Ni/SBA-15 catalyst at 5000x magnification

(d) Thermogravimetric analysis (TGA) – Calcination studies

The aim of studying TGA is to determine the thermal decomposition of both catalyst on Ni/SBA-15 and 3%Re_Ni/SBA-15. Figure 4.4 and Figure 4.5 shows the TGA analysis at 10 kmin^{-1}. For both catalyst peaks that presence before 227˚C which indicates the elimination of water vapors from the catalyst. It suggested that from the graph, promoted catalyst has higher peak in between 30 to 100 ˚C as it has more water vapor to eliminate compared to non-promoted catalyst. Meanwhile, there was few peaks formed between 100˚C and 300˚C were resulted from the complete transformation of $Ni_3(NO_3)_2 6H_2O$ into NiO (Estelle, 2003; Lee et al. 2013). The decomposition steps of $Ni_3(NO_3)_2 6H_2O$ proposed by Estelle et al. (2003) is shown in equation

$Ni(NO_3)_2 \cdot 6H_2O \rightarrow Ni(NO_3)_2 \cdot 4H_2O \rightarrow Ni(NO_3)_2 \cdot 2H_2O$ 4.1

$Ni(NO_3)_2 \cdot 2H_2O \rightarrow \mathrm{Ni}(NO_3)_2 (OH)_2 \cdot 2H_2O \rightarrow \mathrm{Ni}\ (NO_3)_2 (OH)_4$ 4.2

$\mathrm{Ni}\ (NO_3)_2 (OH)_4 \rightarrow Ni(NO_3)_2 \rightarrow \mathrm{NiO}$ 4.3

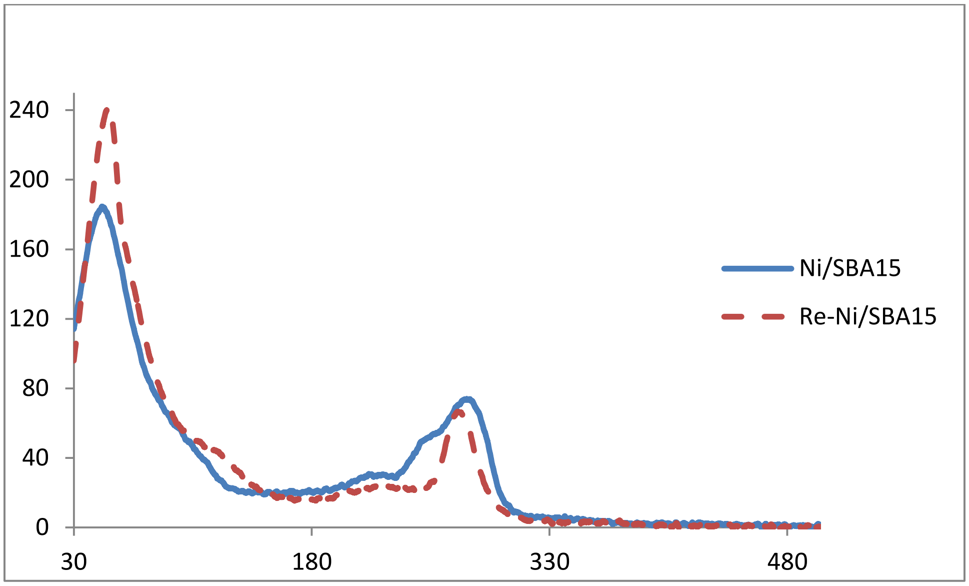

Figure 4.4 TGA analysis of Ni/SBA-15 and 3%Re_Ni/SBA-15 at 10 kmin^{-1} from 30˚C to 900˚C

Chapter 5

Effect of Reaction Parameters towards Glycerol Dry Reforming

5.1 Introduction

This chapter discuss the effect of reaction parameters towards glycerol dry reforming over 3%Re_Ni/SBA-15 catalyst. The conversion of glycerol and hydrogen yield were studied by manipulating the temperature and carbon to glycerol ratio (CGR). The discussion started with elaboration on the effect of CGR at fix temperature at (700˚C) towards the glycerol conversion and hydrogen yield. It was followed with studies on the effect of temperature at fix CGR(1:1) towards the glycerol conversion and hydrogen yield. Lastly, the performance of both catalysts Ni/SBA-15 and 3%Re_Ni/SBA-15 on the glycerol conversion and hydrogen yield were compared.

5.2 The effect of carbon to glycerol ratio (CGR) in glycerol dry reforming

In this experiment, the value of CGR was manipulated by varying the partial pressure of CO_2 and the temperature was fixed at 700℃.

Figure 5.1 shows the glycerol conversion against time for 3 different CGR using 3%Re_Ni/SBA-15 catalyst. On the other hand, Figure 5.2 shows the trend of glycerol equilibrium conversion for 3 CGR. From the results, it shows that the highest glycerol conversion is at CGR 1:1 with almost 50% conversion and CGR 1:3 resulted in the lowest glycerol conversion with about only 21% conversion.

Figure 5.3 shows that the yield of hydrogen obtained at 3 different CGR using 3%Re_Ni/SBS-15 catalyst. The graph shows that starting from the 120 mins, the amount of hydrogen for 3 different CGR started to stabilize and CGR1:1 gave the highest hydrogen yield. Meanwhile, Figure 5.4 shows the trend of 3 different CGR versus hydrogen yield. As resulted, the highest hydrogen yield is at CGR 1:1 with almost 57% and the lowest hydrogen yield is at CGR1:3 with only 25% yield.

From these result, it can be concluded that the glycerol conversion and hydrogen yield for CGR 1:0.5, CGR1:1 and CGR1:3 were inversely proportional to carbon glycerol ratio. As in Figure 5.2 and Figure 5.4 were resulted that the higher the CGR the lower the glycerol conversion and hydrogen yield. According to Lee et al. (2014), the CO_2 did not participate in the production of hydrogen as it was contributed by the glycerol decomposition.

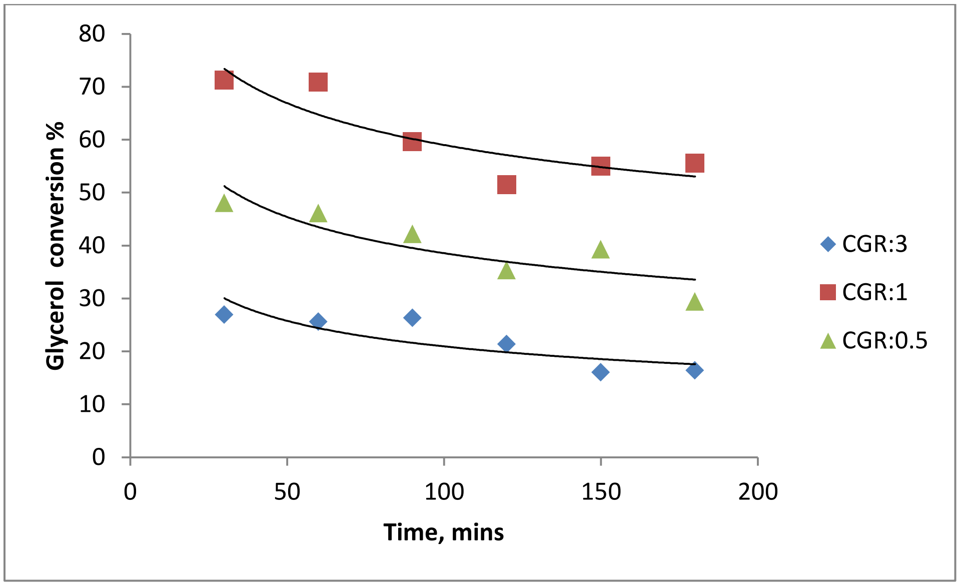

Figure 5.1 The glycerol conversion of 3%Re_Ni/SBA-15 at different CGR [Reaction conditions: T= 973K, Time= 180mins]

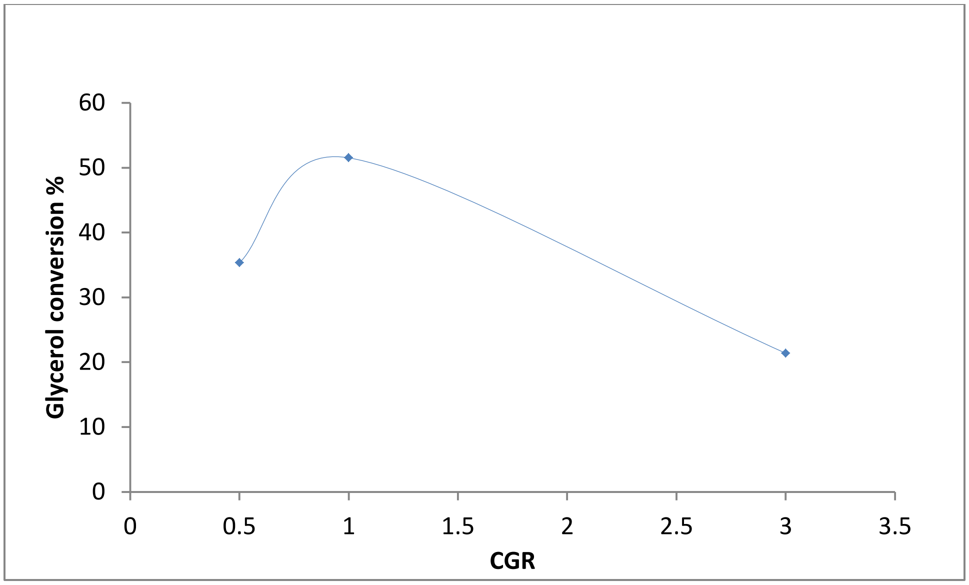

Figure 5.2 The trend of different CGR versus glycerol conversion [Reaction conditions: T= 973K, Time= 180mins]

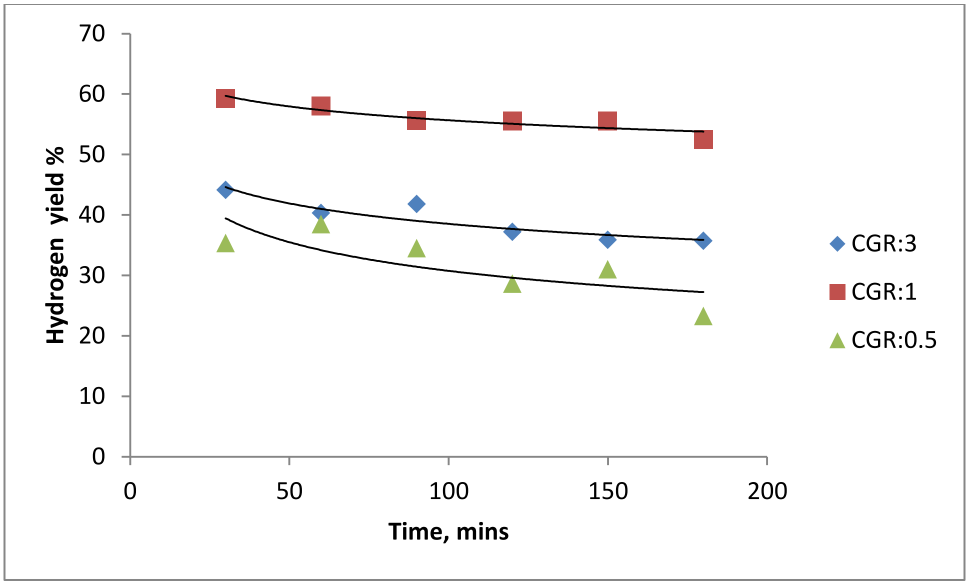

Figure 5.3 The hydrogen yield of 3%Re_Ni/SBA-15 at different CGR [Reaction conditions: T= 973K, Time= 180mins]

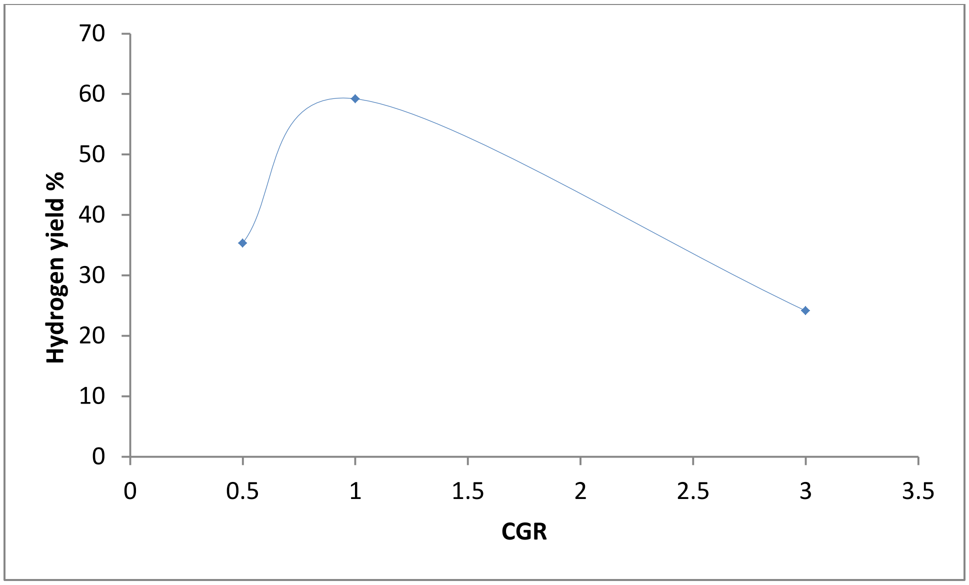

Figure 5.4 The trend of different CGR versus hydrogen yield [Reaction conditions: T= 973K, Time= 180mins]

5.3 The effect of reaction temperature in glycerol dry reforming

The effect of temperature towards glycerol conversion and hydrogen yield were carried out at fixed CGR (CO_2 to $C_2H_8O_3$) which is at 1:1 for 3%Re_Ni/SBA-15 catalyst. The temperature was manipulated at 3 different points starting from 700˚C, 800˚C and 900˚C.

The results of glycerol conversion and hydrogen yield were tabulated in Table 5.1 and Table 5.2 meanwhile the trend of the results were presented in Figure 5.5, Figure 5.6, Figure 5.7 and Figure 5.8. At fix CGR 1:1, 700˚C gave the highest for both glycerol conversion and hydrogen yield respectively. Moreover, according to the Figure 5.6 and Figure 5.8 for the glycerol conversion at 700˚C gave the highest value which is almost 57% and the glycerol conversion which was dropped to 48% when the temperature reached 800˚C which contributed as the lowest glycerol conversion. Meanwhile, for hydrogen yield (Figure 5.5 and Figure 5.7), 700˚C resulted as the highest hydrogen yield with almost 55% yield and the lowest hydrogen yield was obtained at 800˚C with approximate 38% yield.

As a conclusion, at fix CGR 1:1 with 700˚C gave the highest results for both glycerol conversion and also hydrogen yield respectively. When the temperature increase to 800˚C the glycerol conversion and hydrogen yield started to drop drastically as it is due to carbon laydown which mean as the temperature increase the rate of formation of CH_4 and CO also increaseAccording to Nabilah et al. (2016), at 900°C the carbon formation started to exist slowly as the glycerol conversion and hydrogen yield started to decrease.

Table 5.1 Glycerol conversion of 3%Re_Ni/SBA-15 at different range of temperature [Reaction condition: CGR 1:1 and Time= 180 mins]

Glycerol conversion for 3%Re_Ni/SBA-15			
Temperature	700˚C	800˚C	900˚C
% Conversion	57	48	54

Table 5.2 Hydrogen yield of 3%Re_Ni/SBA-15 catalyst at different range of temperature [Reaction condition: CGR 1:1 and Time= 180 mins]

Hydrogen yield for 3%Re_Ni/SBA-15			
Temperature	700˚C	800˚C	900˚C
% Yield	55	38	50

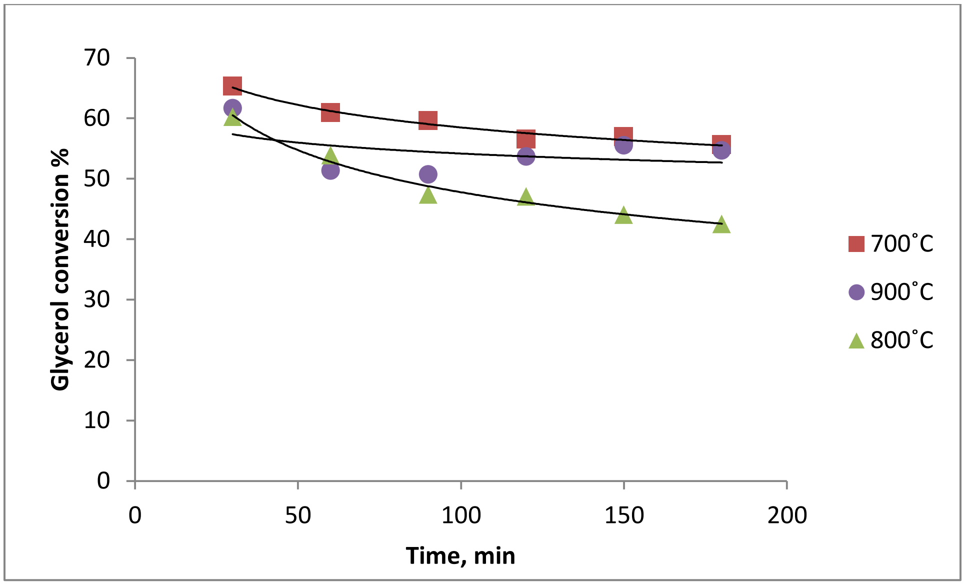

Figure 5.5 The glycerol conversion of 3%Re_Ni/SBA-15 at different range of temperature [Reaction condition: CGR 1:1 and Time= 180mins]

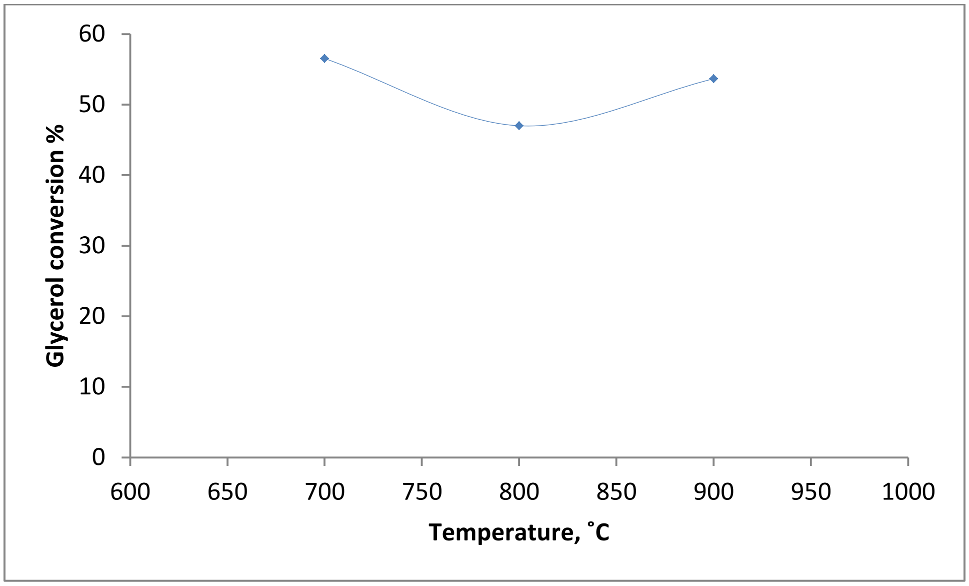

Figure 5.6 The trend of glycerol conversion of 3%Re_Ni/SBA-15 at different range of temperature [Reaction condition; CGR 1:1 and Time= 180mins]

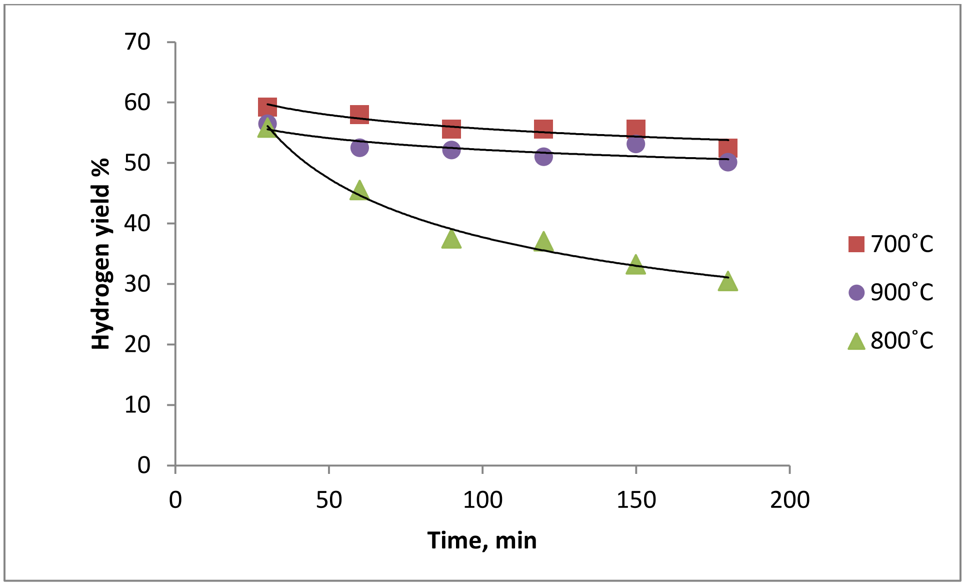

Figure 5.7 The hydrogen yield of 3%Re_Ni/SBA-15 at different range of temperature [Reaction condition: CGR 1:1 and Time= 180mins]

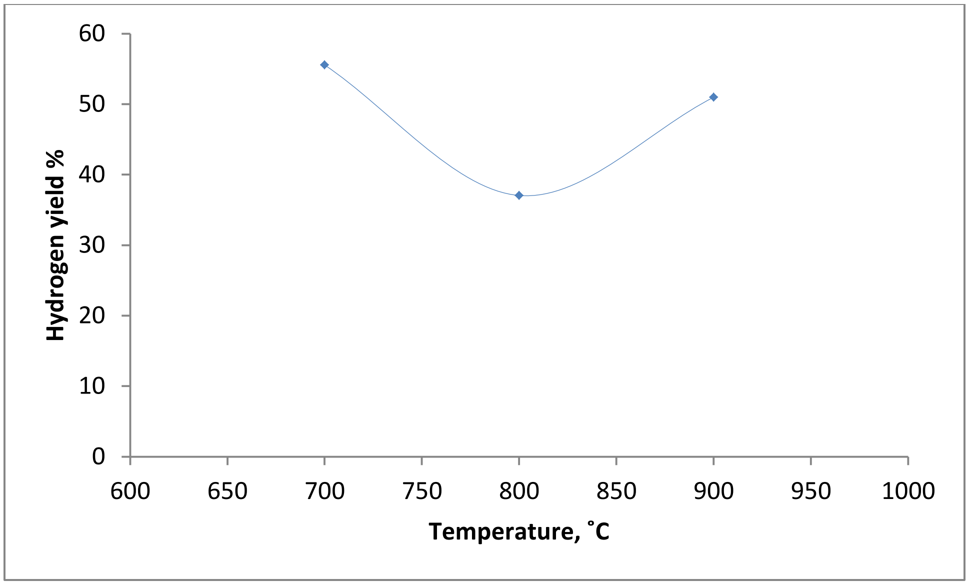

Figure 5.8 The trend of hydrogen yield of 3%Re_Ni/SBA-15 at different range of temperature [Reaction condition; CGR 1:1 and Time= 180mins]

5.4 The comparison of Ni/SBA15 and 3%Ni/SBA15 catalyst

The comparison of both Ni/SBA-15 and 3%Ni/SBA-15 catalyst has been conducted at CGR 1:1 and 700˚C. The aim is to compare the performance of both catalysts and the influence of promoter to the catalytic activities. The results for glycerol conversion and hydrogen yield were plotted in Figure 5.9 and Figure 5.10.

From the result, 3%Re_Ni/SBA-15 gave higher value for both glycerol conversion and hydrogen yield which are almost 57% and 55% respectively according to Figure 5.9 and Figure 5.10. Meanwhile, Ni/SBA-15 gave lower glycerol conversion with around 20% and hydrogen yield with around 18% only. Moreover, 3%Re_Ni/SBA-15 has better catalytic activity compared to Ni/SBA-15, this is due to the addition of Re promoter that lessen the carbon deposition. Less carbon deposited on the surface of catalyst will improved the catalytic activity of catalyst as the active site of catalyst is not accumulated by carbon (Bahari et al., 2015).

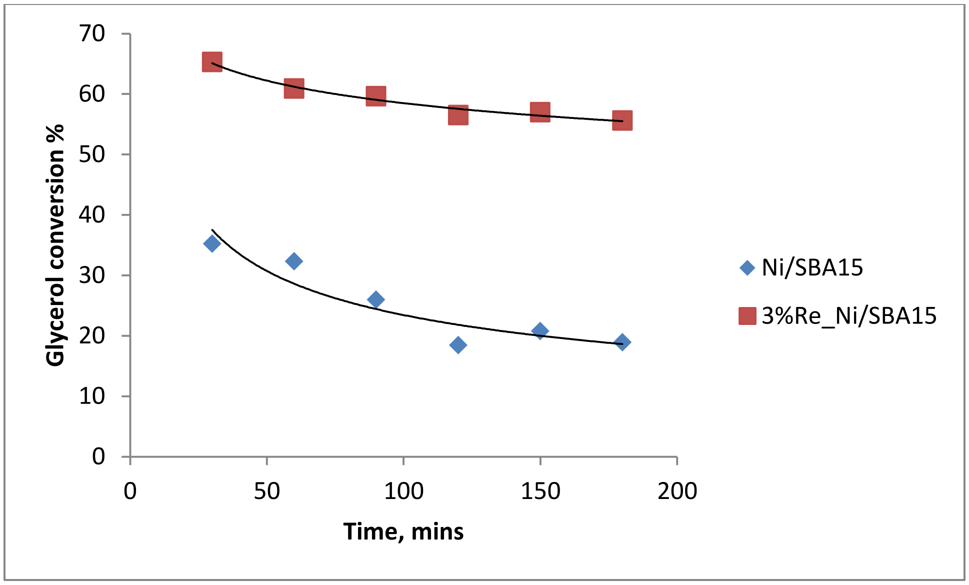

Figure 5.9 The glycerol conversion of Ni/SBA-15 and 3%Re_Ni/SBA-15 catalyst [Reaction condition: CGR1:1 , T= 700˚C and Time= 180mins]

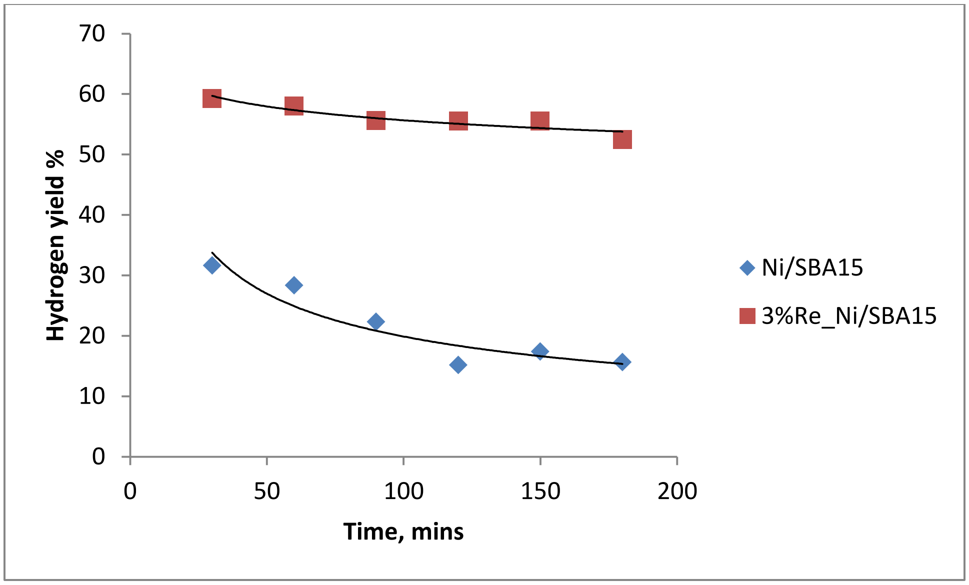

Figure 5.10 The hydrogen yield of Ni/SBA-15 and 3%Re_Ni/SBA-15 catalyst [Reaction condition: CGR1:1 , T= 700˚C and Time= 180mins]

In addition, the existence of carbon can be proved by the field emission scanning electron microscope (FESEM) analysis as shown in Figure 4.7. The surface morphology resulted by FESEM imaging shows that the carbon structure of 3%Re_Ni/SBA-15 catalyst has smooth and longitudinal surface which it gave higher BET surface area as resulted in Table 4.3 compared to non-promoted Ni/SBA-15 catalyst. Based on the image, the morphology imaging show filamentous-type as the particle has longitudinal surface. Meanwhile, according to Bartholomew et al. (2001), filament-type carbon structure can be categorized as vermicular carbon C_v which is formed by the dissolved carbidic carbon C_α in Ni-surface layers at high reaction temperature (773-1173K). Besides that, for Temperature Programmed Oxidation (TPO - O_2) analysis in Figure 4.6 shows the non-isothermal profiles of weight percentage reduction with gasification temperature under oxygen with heating ramping of 10 kmin^{-1}. It shows that started 30˚C the weight loss occurred it is mainly due to the elimination of carbon upon oxidation with excess oxygen. The sample amount of carbon deposition weight loss is 3.51wt%. Meanwhile, the TPO curve show that the addition of Re as a promoter has lessen the carbon deposition. Less carbon deposited on the surface of catalyst will improved the catalytic activity of catalyst as the active site of catalyst is not accumulated by carbon (Bahari et al., 2015). Besides that, a similar group of Re such as La-metal promotion has increase the basicity of the catalyst and reduced carbon formation by (Kumar P et al. 2008).

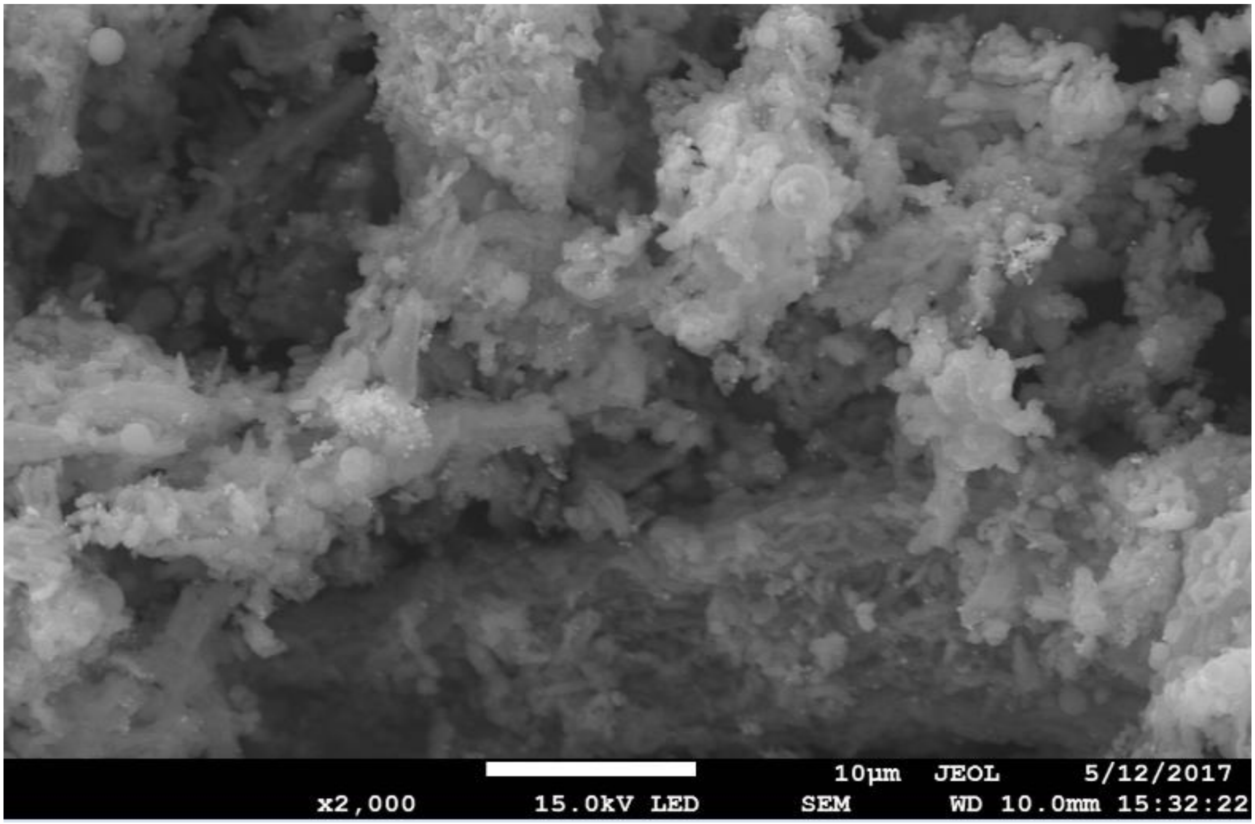

Figure 5.11 FESEM image of spent Re-promoted Ni/SBA-15 catalyst at 2000x magnification

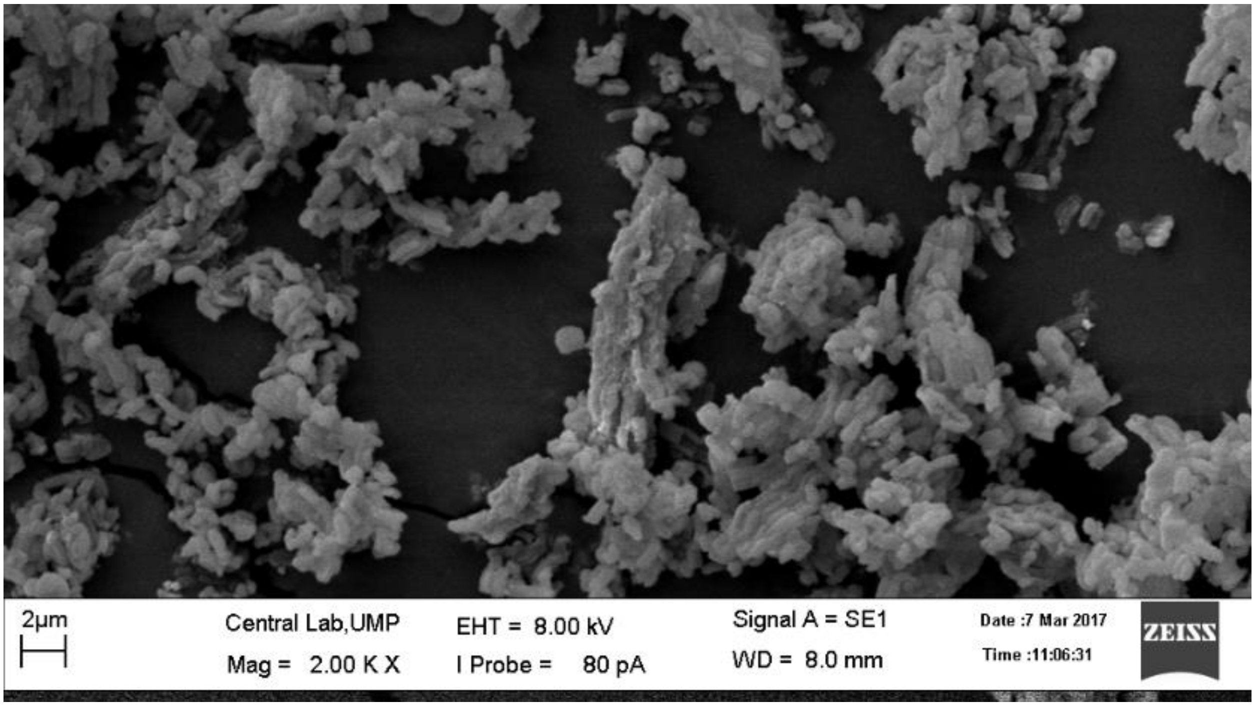

Figure 5.12 FESEM image of fresh Re-promoted Ni/SBA-15 catalyst at 2000x magnification

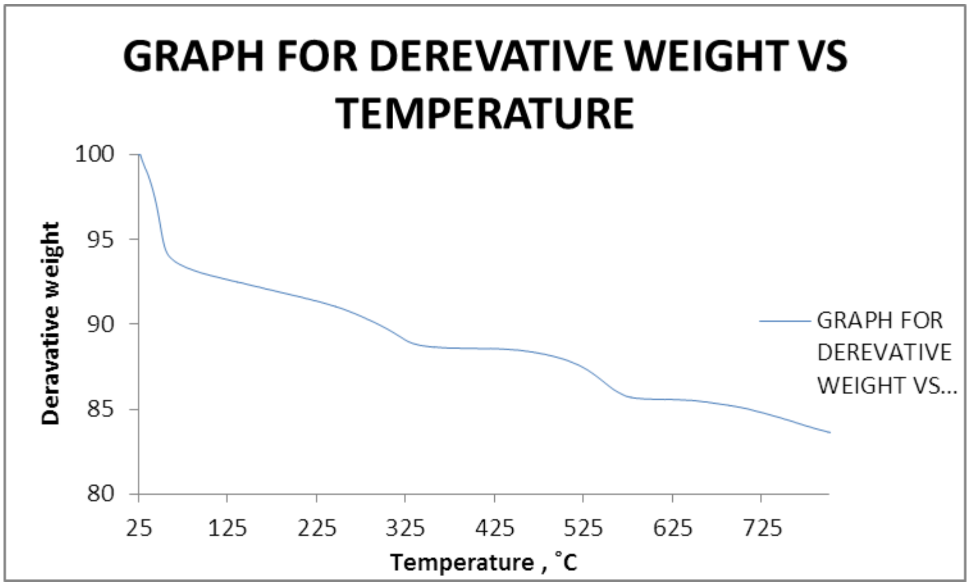

Figure 5.13 TPO curve for the spent catalyst of 3%Re_Ni/SBA-15 at 10 $kmin^{-1}$ from 25˚C to 900˚

CHAPTER 6

CONCLUSION

6.1 Conclusion

Chapter 6 summarize the important findings from the compilation on chapter 4 and chapter 5 results on characterization and reaction studies.

In chapter 4, the characterization catalyst of both 3%Re_Ni/SBA-15 and Ni/SBA-15 catalysts were discussed by using XRD, BET, SEM, FESEM, TGA and TPO analyses. In XRD analysis, it showed that Ni/SBA-15 produced sharp and longer peaks with the presence of large crystallite size from 8.14nm to 12.25nm, while 3%Re_Ni/SBA-15 gave broader and shorter peaks with smaller crystallite size with 3.85nm to 4.78nm. For BET analysis, Ni/SBA-15 has smaller surface area with 221.5249 m^2g^{-1} while 3%Re_Ni/SBA-15 has bigger surface area with 295.3397 m^2g^{-1} it is due to the presence of smaller nickel crystallite size as depicted from the XRD analysis. The SEM analysis observed that the structure of Ni/SBA-15 was found to be rough and creates bulky surface resulting from the presence of large crystalline size as depicted in XRD analysis. On the other hand, 3%Re_Ni/SBA-15 has smooth and longitudinal surface due to smaller crystallite size in XRD analysis which indicates fine dispersion of nickel and contributed less agglomeration compared to Ni/SBA-15. This is due to the addition of Re as the promoter. Furthermore, TGA analysis showed that for both catalysts peak that presence before 227˚C which indicates the elimination of water vapors from the catalyst. It suggested that from the graph, promoted catalyst has higher peak in between 30 to 100 ˚C as it has more water vapor to eliminate compared to non-promoted catalyst. Meanwhile, there was few peaks formed between 100˚C and 300˚C were resulted from the complete transformation of $Ni_3(NO_3)_2 6H_2O$ into NiO (Estelle, 2003; Lee et al. 2013).

In the other hand, chapter 5 is the study of effect of carbon to ratio and temperature at fixed carbon to ratio (1). From the studies of catalyst characterization, 3%Re_Ni/SBA-15 has been chose for further studies in reaction studies as it shows the best catalyst for glycerol dry reforming reaction. It was found that 3%Re_Ni/SBA-15 produced the highest percentage for both glycerol conversion and hydrogen yield with 57% and 55% respectively under the condition of 700 ℃ and CGR (1:1). Moreover, the higher the CGR the lower the glycerol conversion and hydrogen yield. According to Lee et al. (2014), the CO_2 did not participate in the production of hydrogen as it was contributed by the glycerol decomposition. Other than that, when the temperature increase the glycerol conversion and hydrogen yield started to drop drastically as it is due to carbon laydown which mean as the temperature increase the rate of formation of CH_4 and CO also increase. Lee et al. (2014), both the CH_4 and CO production rates positively correlated with the temperature which is consistent with the Arrhenius characteristic. According to Nabilah et al. (2016), at 900℃ the carbon formation started to exist slowly as the glycerol conversion and hydrogen yield started to decrease.

Furthermore, for both comparison on Ni/SBA-15 and 3%Re_Ni/SBA-15 catalysts has been conducted at CGR 1:1 and 700˚C. From the result, 3%Re_Ni/SBA-15 gave higher value for both glycerol conversion and hydrogen yield which are almost 57% and 55% respectively. Meanwhile, Ni/SBA-15 gave lower glycerol conversion with around 20% and hydrogen yield with around 18% only. Moreover, 3%Re_Ni/SBA-15 has better catalytic activity compared to Ni/SBA-15, this is due to the addition of Re promoter that lessen the carbon deposition. Less carbon deposited on the surface of catalyst will improved the catalytic activity of catalyst as the active site of catalyst is not accumulated by carbon.

For spent catalyst of 3%Re_Ni/SBA-15 also being conducted by using FESEM and TPO analyses. The surface morphology resulted by FESEM imaging shows that the carbon structure of 3%Re_Ni/SBA-15 catalyst has smooth and longitudinal surface which it gave higher BET surface area. Based on the image, the morphology imaging show filamentous-type as the particle has longitudinal surface. Besides that, for Temperature Programmed Oxidation (TPO - O_2) analysis shows the non-isothermal profiles of weight percentage reduction with gasification temperature under oxygen with heating ramping of 10 kmin^{-1}. It shows that started 30˚C the weight loss occurred it is mainly due to the elimination of carbon upon oxidation with excess oxygen. The sample amount of carbon deposition weight loss is 3.51wt%. Meanwhile, the TPO curve show that the addition of Re as a promoter has lessen the carbon deposition. Less carbon deposited on the surface of catalyst will improved the catalytic activity of catalyst as the active site of catalyst is not accumulated by carbon.

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