

**Preparation and Characterization of Nickel and Limestone Based
Catalyst for Glycerol Dry Reforming**

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2014

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Bawadi Bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NURUL AMIRA AMZAH
910325-01-6346

ABSTRACT

This project aims to study the preparation and characterization of nickel and limestone based catalyst for glycerol dry reforming. This project comprises 2 parts. The first part is to synthesise and characterize the nickel based catalyst and the second part is to study effect of the different method of catalyst preparation of limestone based catalyst on the surface area. Three nickel based catalysts supported with different element which are Ni/CaO, Ni/Al₂O₃ and Ni/CeO₂ for 20wt% nickel has been synthesized. Besides that, limestone based catalyst also has been prepared by using loading and doping method. The comparison of surface area of limestone based catalyst; Ni/CaO has been done by characterized and analysed. All catalyst has undergone the characterization step by using TPR, SAP, TEM, FESEM and EDX. From the results, the reduction temperature of nickel oxide reduced to nickel is at 650 °C around 30 minutes. The BET surface area of NiO/Al₂O₃ are the highest followed by NiO/CaO and NiO/CeO₂. The TEM images of all three nickel based catalyst shows that the particle diameter of the catalyst is inversely proportional to the surface area. Thus, the particle diameter of Nickel supported with Alumina is 36.76nm, NiO/CaO is 42.5nm and NiO/CeO₂ is 48.33nm. Other than that, the surface area of limestone based catalyst using doping method in catalyst preparation increasing 87% compared to loading method. This proves that the limestone based catalyst is a promising candidate for dry reforming of glycerol.

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LIST OF ABBREVIATIONS

| | |
|-------|---|
| FYP | Final Year Project |
| SAP | Surface Area Analyzer & Porosimetry |
| TEM | Transmission Electron Microscopy |
| TPR | Temperature-Programmed Reduction |
| FESEM | Field-Emission Scanning Electron Microscopy |
| EDX | Electron Dispersed X-Ray |

CHAPTER 1

INTRODUCTION

1.1 Background Study

Nowadays, fossil fuels have become the most important energy in our daily life. The use of fossil fuels is not only limited to the certain industry but also the applications in the petroleum industry and chemical sectors. Fossil fuel is one of non-renewable sources that could not be regenerated or reproduced. Due to the reduction of fossil fuel day by day, developing alternative sources of energy become a considerable attention in the present scenario.

Recently, the production of biomass has become an intention and receives so much interest as a source of renewable energy. One of the methods is by producing hydrogen via biomass. Production of hydrogen via biomass has a potential to be alternative sources of renewable energy to replace the applications of fossil fuels in industry. During a bio-diesel production process, the significant amount of glycerol is produced as a by-product which has a high content of hydrogen. 10wt% of glycerol will be produced in the transesterification process of bio-diesel which means that every 1 tonne of manufactured bio-diesel, 100kg of glycerol are produced throughout the process (Grey, 2001). The utilization of glycerol to produce hydrogen or synthesis gas could potentially reduce the production costs of biodiesel (Hass et al, 2006).

Dry Reforming is one of the process for converting the glycerol to high value product which is hydrogen. It is also known as Carbon Dioxide reforming. Additionally, Carbon Dioxide involves in many hydrogen production technologies relying on renewable energy (Jankhah, 2008). Thus, glycerol reforming with Carbon Dioxide could be an attractive process. Since the bio-derived glycerol is considered to be renewable, carbon dioxide neutral and glycerol will not contribute to the

greenhouse effect (Behr, 2008). Secondly, glycerol dry reforming will convert Carbon dioxide into hydrogen or high value-added inert carbon and remove it from the carbon biosphere cycle.

In this research the nickel and limestone based catalyst will be prepared. Nickel Based catalyst is widely used in industry and has so much potential in producing hydrogen. Meanwhile, limestone based catalyst are basically has the lower surface area but according to Surahim et al (2012), limestone is a promising candidate of based catalyst for hydrogen production via biomass

1.2 Problem Statement

- There are only few studies about the catalyst used in glycerol dry reforming. Therefore, the nickel and limestone based catalyst will be synthesized and characterized perhaps can be useful in dry reforming of glycerol.
- The surface area of the limestone based catalyst is low. In order to increase the surface area of the catalyst, the doping method in catalyst preparation is introduced. There is less studies applied the doping method in catalyst preparation of hydrogen production via glycerol dry reforming. Usually, the current research used loading method which comprises 3 steps which are impregnation, calcination and reduction. In this project, the comparison of surface area of limestone based catalyst by using doping and loading method will be made.

1.3 Objectives

The main objective of this research is to carry out the study on preparation and characterization of nickel and limestone based catalyst.

The specific objectives are:

- To synthesize and characterize the nickel based catalyst.
- To study the effects of different method in catalyst preparation to the surface area of limestone based catalyst

1.4 Scope Of Work

The scope of work for this research are :

- Synthesize 20wt% of Nickel Based Catalyst by using three different support which is Alumina, Calcium Oxide and Ceria.
- Synthesize Limestone Based Catalyst by using two different methods in catalyst preparation which is Loading and Doping.
- Analyze and characterize the nickel and limestone based catalyst by using the analytical equipment such as Transmission Electron Microscopy (TEM), Field-Emission Scanning Electron Microscopy (FESEM), Surface Area Analyzer & Porosimetry (SAP), Temperature-Programmed Reduction (TPR) and Electron Dispersed X-ray (EDX) for catalyst morphology and surface area.
- Compare the surface area of limestone based catalyst on different method of catalyst preparation.

CHAPTER 2

LITERATURE REVIEW

2.1 Glycerol

Glycerol ($C_3H_5(OH)_3$) also refer as glycerin or 1,2,3 propanetriol is a colorless, odorless, viscous liquid with sweet taste. Glycerol is widely used in various applications such as pharmaceutical, cosmetics, toiletries, drugs and food products (Pagliaro & Rossi, 2010). Glycerol has a specific gravity of 1.261, a melting point of $18.2\text{ }^\circ\text{C}$ and a boiling point of $290\text{ }^\circ\text{C}$ under normal atmospheric pressure. Besides that, glycerol is a liquid organic compound of the alcohol family. Pagliaro and Rossi (2010) stated that glycerol has three hydrophilic alcoholic hydroxyl groups which are responsible for its solubility in water and its hygroscopic nature.

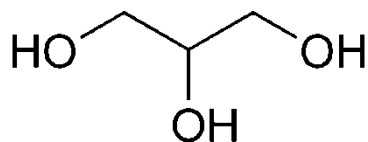


Figure 1 : Structure of glycerol. There is three hydroxyl group in glycerol

2.2 Nickel

Nickel is silvery-white, hard, malleable, and ductile metal. It is a good conductor of heat and electricity. In its familiar compounds nickel is bivalent, although it assumes other valences. It also forms a number of complex compounds. Most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen.

Nickel Based catalyst are widely been applied in industry and widely used in hydrogenation process to increase the reaction rate. The demands of nickel based catalyst are increasing day by day for the process efficiencies Metals like platinum and nickel make good catalysts because they adsorb strongly enough to hold and activate the reactant (Clark, 2002). However, the platinum is costly compared to nickel.

2.3 Limestone

Limestone is a sedimentary rock composed mainly calcium carbonate (CaCO_3) in the form of mineral calcite. Approximately 50% of weight composition in limestone is Calcium Carbonate. The other substance composed in the limestone including the small composition of clay minerals, quartz, pyrite, iron oxide and other minerals. There is abundance of limestone in Malaysia. Basically the large occurrences of limestone in Peninsular Malaysia are in the Klang Valley, Kinta Valley, Langkawi Island, Gua Musang area and Pahang (Tan, 1998). The wide occurrences of limestone make the substance easy to find and not much cost will be contributed.

Limestone will be used as based catalyst in this research. According to Surahim et al (2012), they stated that the calcined limestone is a promising candidate of based catalyst for hydrogen production process via biomass due to its availability and lower cost compared to synthetic catalyst.

2.4 Hydrogen Gas

Hydrogen is chemical element which consists of 2 mole of hydrogen atom, (H_2). It is the most important and abundant element in the universe (Sorensen, 2005). Hydrogen is the simplest molecules and it is incredibly light. Hydrogen is colorless and odorless gas with no taste.

Nowadays, the hydrogen gas is one of the most important base-chemicals and is mainly used in the production of ammonia based fertilizers (Hulteberg, 2011). Hydrogen is a renewable energy and has been suggested as promising alternatives to the fossil fuels. Currently, almost 95% of the world's hydrogen is being produced from fossil fuel based feedstock. The hydrogen productions are attractive options for the future due to the lesser effects to the environment. Thus, it is important to find an alternative way to regenerate hydrogen from biomass source as the hydrogen can be used in various applications and will replace fossil fuels someday.

2.5 Dry Reforming

Dry Reforming or also known as Carbon Dioxide Reforming is a method of producing synthesis gas from the reaction of carbon dioxide with hydrocarbon such as methane and glycerol. In recent years, most of the researchers have been studied about the dry reforming of methane and not much for dry reforming on glycerol. Xiaodong et al (2009) have carried out the study of thermodynamic analysis of glycerol dry reforming for syngas production. The objective is to understand the possibility of glycerol dry reforming for hydrogen and synthesis gas production by using Gibbs free energy minimization method. From the research, they can conclude that the optimum conditions for hydrogen production are the temperature above 975K and CO_2 to glycerol ratio of 1. Besides that, the production of synthesis gas can reached the maximum with a temperature 1000K and CO_2 to glycerol ratio of 1. 6.4 mol of syngas per one mole of glycerol will be produced with 33% conversion of carbon dioxide (CO_2) under that condition.

Basically, the moles of hydrogen increase as the temperature increase when CGR is less than 1. If the CGR is more than 1, the number of moles of hydrogen will increase with the increasing of temperature until it reaches the maximum conditions.

The suggestions of the main reaction for glycerol dry reforming by Xiaodong et al (2010) are as follows:



Do Minh Tuan (2013) have conducted the experiment of syngas production from glycerol via dry reforming method using limestone based catalyst. He used Gas Chromatograph (GC) to determine the proportion of hydrogen, carbon monoxide and unreacted carbon dioxide and hydrogen. From the result, the objective of experiment was achieved as Hydrogen and Carbon Monoxide are two major components in the gaseous product. Thus, we can conclude that, the dry reforming method for hydrogen production via glycerol is a potential technique to convert glycerol to hydrogen.

2.6 Potential of Limestone as Based Catalyst

Limestone has a potential as based catalyst for hydrogen production as Surahim et al (2012) used the limestone catalyst in hydrogen production from rice straw gasification. They modified the limestone with an addition of transition metal promoters such as Nickel, Ferum and Cobbalt. At the end of the research, Surahim et al (2012) conclude that the modified limestone catalyst with Nickel as the metal promoters gave the highest production of hydrogen with the favorable temperature around 250-550 °C. However, the activity of the catalyst is more depending on the promoters used rather than surface area of catalyst.

Other than that, the used of carbonaceous catalyst seems to be potentially ideal for producing hydrogen or synthesis gas as the H₂/CO ratio is close to 1 and the CO₂emission is at very minimum range (Fernandez et al, 2010). Fernandez et al (2010) compared three different methods in producing hydrogen which are pyrolysis, steam reforming and dry reforming. The steam reforming generated the highest production of hydrogen compared to the others method.

Moreover, the preparation of catalyst comprises of 3 major step which are impregnation, drying and calcination as have been applied by Chawalit et al (2011) in preparation of heterogeneous catalyst from limestone for transesterification of vegetable oils. Thus, to characterize and prepare the limestone based catalyst, all the step mention above will be done step by step.

In addition, the doping method will be added in catalyst preparation of limestone based catalyst in order to compare the surface area of the active site of this catalyst. The comparison either loading method or doping method give the higher surface area to the limestone based catalyst will be determine in this research. The effects of the catalyst preparation method also will be investigated. Do Minh Tuan (2013) used Calcium Oxide (CaO) and Calcium Carbonate (CaCO₃) as the based catalyst as limestone substance mainly consist of those element. During the preparation of catalyst, the highest BET surface area of CaO and CaCO₃is $11.529\frac{\text{m}^2}{\text{g}}$ and $4.623\frac{\text{m}^2}{\text{g}}$ respectively. Thus, the doping method of catalyst preparation should be done in order

to investigate the comparison in surface area of loading and doping method in catalyst preparation.

2.7 Catalyst Preparation

Methods of catalyst preparation are very diverse and each catalyst may be produced via different routes (Haber et al, 1995). Preparation usually involves continuous step. Three main steps in catalyst preparation are firstly, preparation of primary solid like impregnation and precipitation. Secondly the processing of primary solid to obtain catalyst precursor through heat treatment or calcination process and lastly the activation of catalyst by reduction of metal oxide. There are three types of methods in preparation of primary solid or supported catalyst which are impregnation, co-precipitation and sol-gel method.

2.7.1 Impregnation

Impregnation requires support is contacted with a certain amount of solution of the metal precursor then it is aged, dried and undergoes the calcination step (Pinna, 1998). In impregnation there are two methods of contacting which are incipient wetness and wet impregnation (LePage et al, 1987). In incipient wetness impregnation or known as 'dry' impregnation (Pinna, 1998) the volume of the solution containing the precursor is equal or slightly less than the pore volume of the support. For example, the impregnating solution which is salt is sprayed to the support which is under stirring. The maximum loading is limited by the solubility of the precursor in the solution.

The second method of impregnation is wet or known as soaking impregnation. Wet impregnation requires the excess use of salt solution or metal precursor. After a certain time the solid is separated and the excess solvent is removed by drying. For both methods the operating variable is the temperature, which influences both the precursor solubility and the solution viscosity and as a consequence the wetting time (Campanati et al, 2003). The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying.

2.7.2 Co-Precipitation

Co-precipitation method requires the solutions containing metal salt and a salt of a compound that will be converted into the support. In order to get the hydroxide or carbonate precipitate, the solution is contacted under stirring with a base (Pinna, 1998). After washing, these can be transformed to oxides by heating in calcination step. This method usually used in large scale of production such as steam reforming. The typical catalysts prepared by using this method are Ni/Al₂O₃ and Cu-Zn Oxide/Alumina. By co-precipitation a uniform distribution on a molecular scale of the different active species in the final catalyst could be attained. During the preparation, many variables have to be controlled; efficient mixing, temperature, order of addition solutions and ageing time of catalyst precipitate (Pinna, 1998). All of these factors must take into account in order to get more appropriate catalyst.

2.7.3 Sol-gel

The sol-gel method or known as gelation route is a homogeneous process which results in a continuous transformation of a solution into a hydrated solid precursor which known as hydrogel. Sol-gel methods have several promising advantages over precipitation. In general, sol-gel syntheses have been recognized for their flexibility which allows better control of the texture, composition, homogeneity and also structural properties of the final solids. The nanoscale chemistry involved in sol-gel methods is a more direct way to prepare highly divided materials (Perego & Villa, 1997). During sol-gel preparation, four main steps may be identified in taking a precursor to a particular product which are formation of a hydrogel, its ageing, removal of solvent and heat treatment in calcination process.

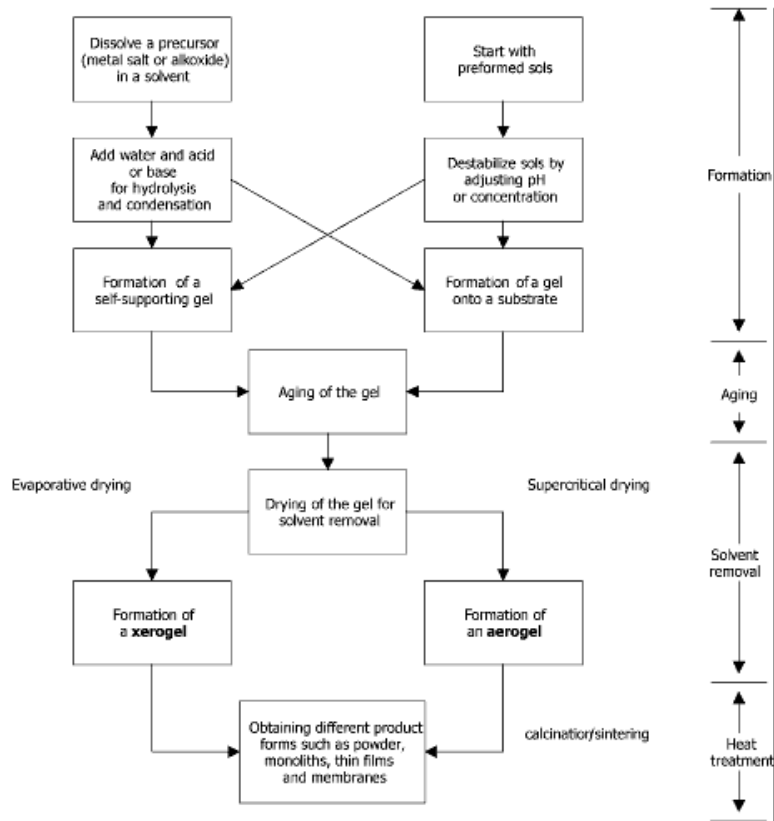


Figure 2 : Schematic diagram of different step in sol-gel precipitate.

(Source : Handbook of Heterogeneous Catalysis, vol 1

CHAPTER 3

METHODOLOGY

3.1 Process Flowchart

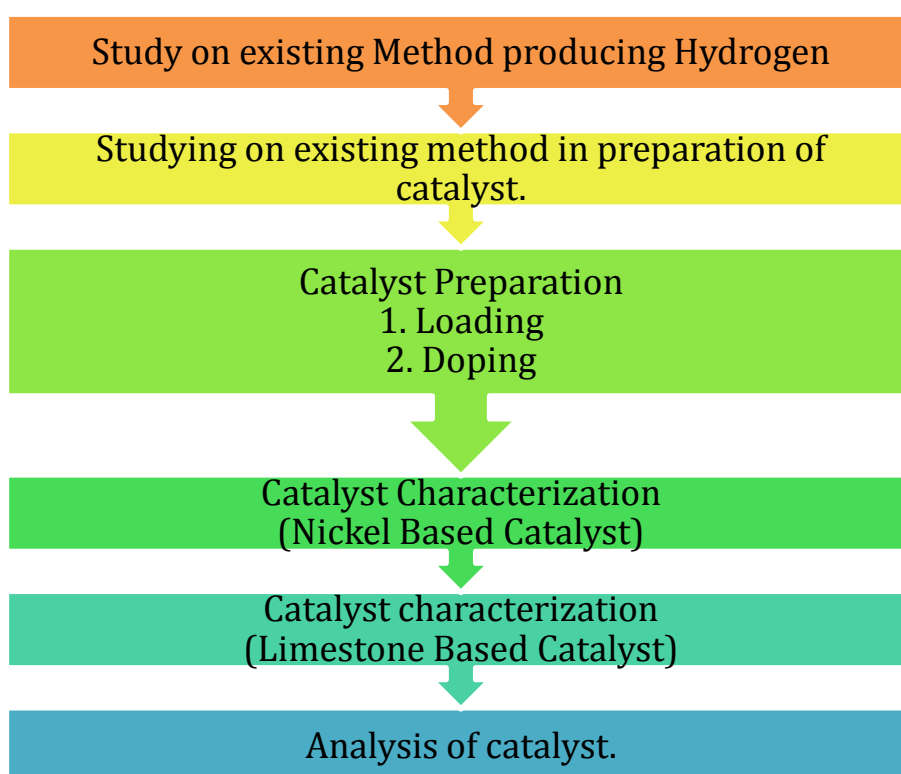


Figure 3: Process Flowchart

Three (3) types of nickel based catalyst will be prepared to carry out these experiments which are Ni/ Al_2O_3 , Ni/ CeO_2 and Ni/ CaO . In addition, the Alumina (Al) support will be the reference for this experiment. As mention in above section, there will be 2 methods in catalyst preparation which are loading technique and doping technique. Only limestone based catalyst will be applied on doping technique. Another 2 catalyst will be prepared for doping method which are NiO/ CaO contain 4wt% of nickel. After the preparation of catalyst, all five catalysts will be characterized by using the following method:

- i) **BET Analysis** – to determine the surface area of the catalyst
- ii) **Transmission Electron Microscopy (TEM)** – to examine the pore size of the catalyst.
- iii) **Field-Emission Scanning Electron Microscope (FESEM)**- to determine the morphology of the catalyst.

3.2 Catalyst Preparation Procedure

3.2.1 Loading Method

This procedure is for 20wt% of Nickel.

1. The 100ml of 0.2g/ml of standard solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was prepared by using 99.08g $\text{Ni}(\text{NO}_3)_2$. (Figure 4)
2. By using 10g basis, 8g of Al_2O_3 / CaO / CeO_2 powder was put in the beaker.
3. 10ml of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was added on the powdered Al_2O_3 / CaO / CeO_2 by using pipette/burette. The solution was stirred at the same time. (Figure 5)
4. 20ml of deionized water was added to the solution and the solution was stirred for 1 hour with magnetic stirrer at 300rpm at room temperature. The function of deionized water is to facilitate the stirring process. (Figure 6)
5. The pH of the solution was checked by using pH meter in the laboratory.
6. The catalyst was dried in oven at 90°C for 20hours. (Figure 7)
7. The catalyst was calcined at 800°C for 5hours with heating rate of $5^\circ\text{C}/\text{min}$. (Figure 8)
8. The catalyst was stored in desiccator and will be used in the experiment.
9. The procedure was repeated for 4wt% of Nickel for limestone based catalyst.



Figure 4 Preparation of 0.2g/ml Nickel Nitrate Hexahydrate standard solution.

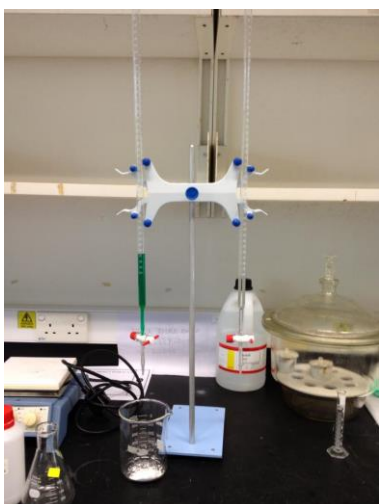


Figure 5 Impregnation method



Figure 6 The solution was stirred for 1 hour with magnetic stirrer



Figure 7 Catalyst after dried in oven.



Figure 8 : Catalyst was calcined in the furnace at 800C



Figure 9 Catalyst after 5 hours of calcination

3.2.2 Doping Method

4 wt% of CaO will be used in this doping method in order to compare with loading method. Here are the procedure :

1. 1.92g of Calcium Oxide (CaO) was mixed with 40ml of deionized water to the Teflon autoclave.
2. The solution was stirred for 1 hour by using magnetic stirrer.
3. The pH of the solution was checked by using pH meter. The pH must be greater than 6.75. If not, the solution will be adjusted by using dropwise addition of sodium hydroxide or aqueous ammonia solution.
4. 0.638g of nickel nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to the Teflon autoclave and stirred it for 3 hours at room temperature.
5. The Teflon autoclave was sealed and kept in oven for 24 hours at 100°C.
6. Collect the precipitate from autoclave after cool it to room temperature.
7. The product was recovered by filtration, washes the precipitate with deionized water and dried at room temperature for 12 hours.
8. The Ni-doped will be obtained by calcining the catalyst at 600°C for 5 hours at 5°C/min.

3.3 Procedure For Standard Solution Preparation

1. Weighted the amount of chemicals $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ needed and dissolved with deionized water.
2. Sample calculation for amount of chemicals needed:-

(a) Preparation 0.2g/ml of Ni

MW of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 290.79 \text{ g/mol}$

MW of Ni = 58.6934g/mol

For 100ml of solution, need 20g of Ni

$$\begin{aligned} \text{Amount of } \text{Ni}(\text{NO}_3)_2 \text{ needed} &= \frac{20\text{gNi}}{58.6934\text{gNi/mol}} \times 290.79 \frac{\text{g Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}}{\text{mol}} \\ &= \underline{99.09 \text{ g Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}} \end{aligned}$$

(b) 20 wt% of Ni

MW of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 290.79 \text{ g/mol}$

MW of Ni = 58.6934g/mol

For 10g basis, mass of Ni= 2 g, $\text{Al}_2\text{O}_3 = 8 \text{ g}$

$$0.2\text{g/ml} \times \text{amount of } \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} = 4 \text{ g Ni}$$

$$\begin{aligned} \text{Amount of } \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} &= \frac{2 \text{ g}}{0.2 \text{ g/ml}} \\ &= \underline{10 \text{ ml for 20wt\% of Ni}} \end{aligned}$$

3.4 Tools And Equipment

3.4.1 Chemical Used

Below are the raw materials and chemicals that are required in this experiment

1. Nickel Nitrate Hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$)
2. Calcium Oxide (CaO)
3. Aluminium Oxide (Al_2O_3)
4. Deionized Water
5. Carbon Dioxide (CO_2)
6. Hydrogen (H_2)
7. Nitrogen (N_2)

3.4.2 Analytical Equipment Used

There are five equipment required to analyze the catalyst and gas produce throughout the experiment. Below are the analytical equipment used in this project :

1. Temperature-Programmed Reduction (TPR)
2. Surface Area Analyzer & Porosimetry (SAP)
3. Transmission Electron Microscope (TEM)
4. Field Emission Scanning Electron Microscope (FESEM)
5. Electron Dispersed X-Ray (EDX)

3.5 Gantt Chart And Key Milestone

| Project activities | Week No | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|------------------------------------|---------|---|---|------|---|---|---|------|---|----|----|----|-----|----|---|------|---|---|-----|---|---|-----|---|----|---------|----|----|----|----|--|
| | MAY | | | JUNE | | | | JULY | | | | | AUG | | | SEPT | | | OCT | | | NOV | | | DEC/JAN | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | |
| Selection of project topic | █ | █ | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Preliminary research work | █ | █ | █ | █ | █ | | | | | | | | | | | | | | | | | | | | | | | | | |
| Submission of extended proposal | | | | | | • | | | | | | | | | | | | | | | | | | | | | | | | |
| Proposal defence | | | | | | | █ | █ | █ | | | | | | | | | | | | | | | | | | | | | |
| Fine-tuning research methodology | | | | | | | | | █ | █ | █ | █ | | | | | | | | | | | | | | | | | | |
| Submission of interim draft report | | | | | | | | | | | | • | | | | | | | | | | | | | | | | | | |
| Submission of interim report | | | | | | | | | | | | | • | | | | | | | | | | | | | | | | | |
| Arrival of experimental apparatus | | | | | | | | | | | | | | • | | | | | | | | | | | | | | | | |
| Catalyst Preparation | | | | | | | | | | | | | | █ | █ | █ | █ | █ | █ | █ | █ | █ | █ | | | | | | | |
| Submission of progress report | | | | | | | | | | | | | | | | | | | | | | • | | | | | | | | |
| Data post-processing | | | | | | | | | | | | | | | | | | | | | | █ | █ | █ | | | | | | |
| Data analysis and documentation | | | | | | | | | | | | | | | | | | | | | | | █ | █ | █ | | | | | |
| Pre-SEDEX | | | | | | | | | | | | | | | | | | | | | | | | • | | | | | | |
| Submission of draft report | | | | | | | | | | | | | | | | | | | | | | | | | • | | | | | |
| Submission of dissertation | | | | | | | | | | | | | | | | | | | | | | | | | | • | | | | |
| Submission of technical paper | | | | | | | | | | | | | | | | | | | | | | | | | | | • | | | |
| Oral presentation | | | | | | | | | | | | | | | | | | | | | | | | | | | | | • | |
| Submission of project dissertation | | | | | | | | | | | | | | | | | | | | | | | | | | | | | × | |

Figure 10: Gantt Chart of final year projec

CHAPTER 4

RESULT AND DISCUSSION

4.1 Catalyst Characterization

At the beginning of November, 5 sample of catalyst have been prepared successfully until calcination step. There are 2 method in preparing the catalyst which is loading method and doping method. The catalyst prepared is as below with its simplified name:

1. Nickel Oxide supported with Aluminum Oxide 20wt% (NiO/Al₂O₃)
2. Nickel Oxide supported with Calcium Oxide 20wt% (NiO/CaO)
3. Nickel Oxide supported with Cerium Oxide 20wt% (NiO/CeO₂)
4. Nickel Oxide supported with Calcium Oxide 4 wt% (NiO/CaO Loading)
5. Nickel Oxide supported with Calcium Oxide 4 wt% (NiO/CaO Doping)

The results were obtained with Temperature-Programmed Reduction (TPR), Surface Area and Porosimetry (SAP) Analyzer, Transmission Electron Microscopy (TEM) analysis, and Field-Emission Scanning Electron Microscopy (FESEM) analysis.

In this section, the morphologies of catalyst will be discussed based on the analysis results of FESEM and TEM. SAP analysis give the information on the BET surface area, pore size, pore volume and particle diameter which will be useful in analyzing the catalytic activity of catalyst in dry reforming of glycerol. Other than that, the TPR analysis will give the information on reduction temperature as well as the time to reduce oxide from the precursor that will be useful while doing the dry reforming application.

4.1.1 Nickel Based Catalyst

(a) PH Value

At the beginning of November, 3 samples of Nickel Based catalyst have been prepared successfully until the calcination step. The pH value of each catalyst was measured during the preparation of catalyst which is before the drying process.

Here are the summarized of pH value for 3 samples of catalyst.

Table 1 :pH value of catalyst

| Catalyst | Composition (wt%) | pH Measured |
|------------------------------------|----------------------|-------------|
| NiO/CaO | 20 | 8.80 |
| NiO/CeO ₂ | 20 | 6.18 |
| NiO/Al ₂ O ₃ | 20 | 6.29 |

Table 1 shows that the pH value of each catalyst. The purpose of pH checking is to determine whether the surface of the catalyst support will adsorb anions or cations during the catalyst preparation process. The pH of NiO/CaO for 20wt% is 8.80. The NiO/CeO₂ has the pH value 6.18 for 20wt% respectively. The pH value for NiO/Al₂O₃ is 6.29 for 20wt%. Furthermore, the pH measured can conclude that the catalyst is positively charge or negatively charge based on the zero point of charge (PSZ) of Nickel Oxide. Basically the zero point of charge (PSZ) of NiO is around 10-11pH. Most of pH values of the catalyst were lower than PSZ value, which means that it is positively polarized. It will adsorbed and cover with anions.

(b) Temperature-Programmed Reduction

TPR measurement were carried out in a conventional flow system with a moisture trap connected to a Thermal Conductivity Detector (TCD) at temperature ranging from room temperature until 900°C. A mixed stream of Hydrogen and Nitrogen was used. For this project, the temperature was raised up to 800°C with heating rate of 20°C/min. The holding time was set for 30min. Table below are the summarized of the report of the TPR measurement for 20wt% of nickel.

Table 2: Analysis of Temperature-Reduction Programmed Reduction

| Type of Catalyst | Mass (g) | Amount Gas absorbed ($\mu\text{mol/g}$) | Total Metal Surface (m^2) | Dispersion Degree (%) | Mean Particle Diameter (nm) |
|------------------------------------|----------|---|--------------------------------------|-----------------------|-----------------------------|
| NiO/Al ₂ O ₃ | 0.0542 | 1848.31 | 3.921 | 54.248 | 1.864 |
| NiO/CaO | 0.0433 | 1854.97 | 3.144 | 54.443 | 1.857 |
| NiO/CeO ₂ | 0.0993 | 2600.09 | 10.107 | 76.313 | 1.325 |

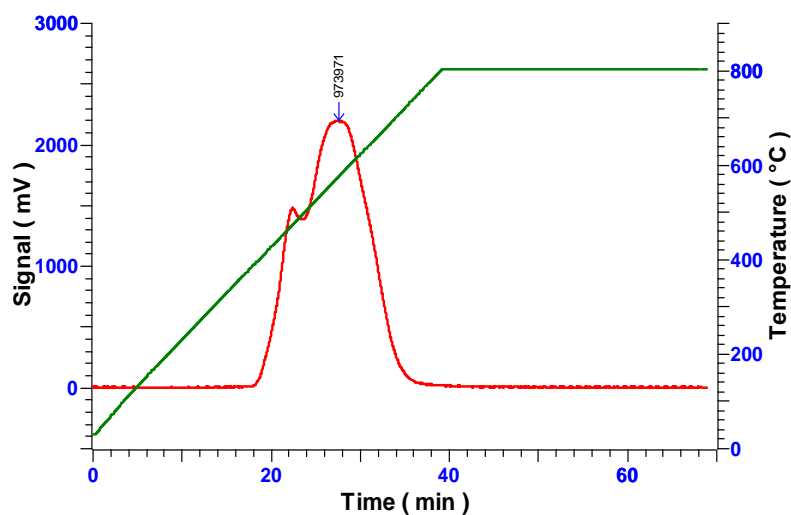


Figure 11 : TPR profile for NiO/Al₂O₃.

Figure 11 shows that the signal indicates the hydrogen uptake or absorption by the catalyst. There are 2 peaks that can be seen in the above figure which occur at 500°C and 700°C for 1500mV and 2500mV hydrogen uptake respectively. At minutes of 20, the temperature starts to increase until it reaches 600°C and decreases after minutes of 30. The hydrogen uptake is directly proportional to the temperature. As the temperature increases, the absorption of hydrogen to the catalyst also will increase. Besides that, the first peak occurs around 500°C possibly because the nickel oxide is not completely reduced to the nickel metal. Therefore, the reduction temperature for NiO/Al₂O₃ is at 650°C and for 30 minutes.

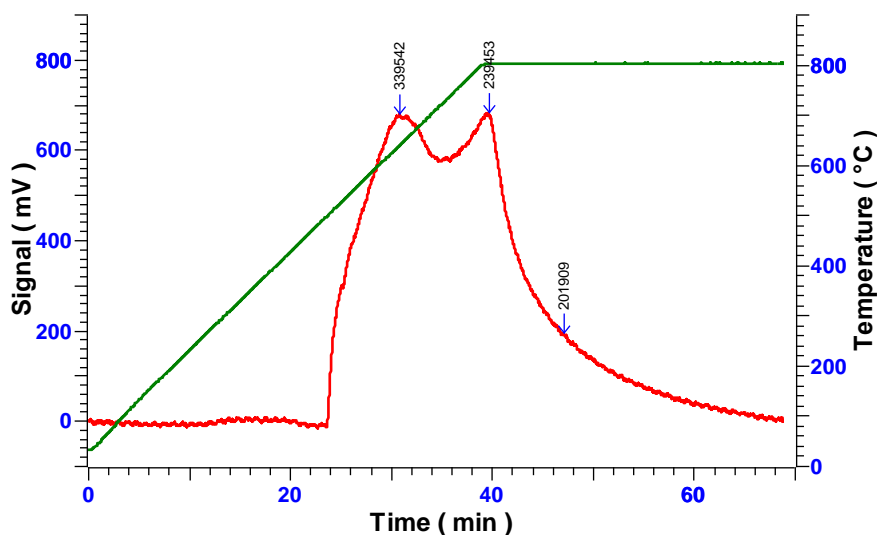


Figure 12 : TPR Profile for NiO/CaO

Figure 12 shows the Temperature-Programmed Reduction graph for NiO/CaO catalyst. There are two peaks that appear during the process. Both peaks occurred when the absorption of hydrogen at 700mV which arises at minutes of 31 and 40. The first peak indicates that the nickel oxide is reduced to the nickel metal by absorption of hydrogen. Meanwhile, at the second peak there are two possibilities that occur in the process. The first possibility is that the nickel oxide is not completely changed to the nickel metal and the second is that the peak indicates that the calcium oxide is reduced to calcium.

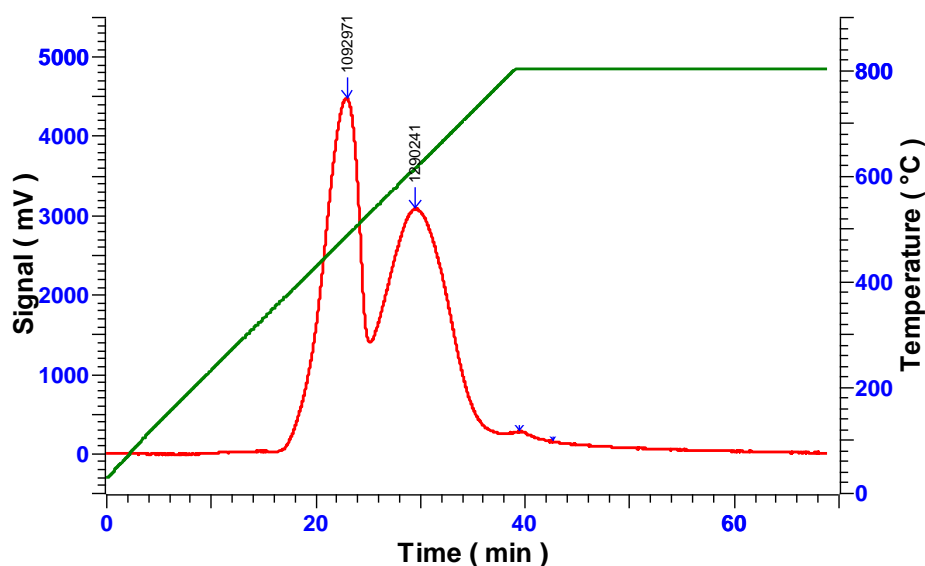


Figure 13 : TPR profile for NiO/CeO₂

Figure 13 shows that the highest hydrogen uptake for NiO/CeO₂ catalyst is 4500mV at 25 minutes. the NiO/CeO₂ shows two clear peak. The first peak occurs at 450°C and second peak at 600°C. The oxide from Ceria may reduce to be Ce₂O₃ during the first peak. In order to prevent this from happen, the nickel supported with ceria must be promoted to more active metal such as copper in order to lower the reduction temperature. Otherwise, the ceria is not a good support for nickel based catalyst.

Basically from the TPR analysis, we can conclude that the reduction temperature for Nickel based catalyst is at 650°C for 30minutes. This analysis is very crucial in order to determine the temperature of reduction before doing the dry reforming experiment. This is important because the nickel must be reduce to nickel metal for catalytic reaction and by knowing the reduction temperature it will prevents the other metal oxides in the catalyst from being reduced.

(c) Surface Area Analyzer & Porosimetry (SAP) Analysis

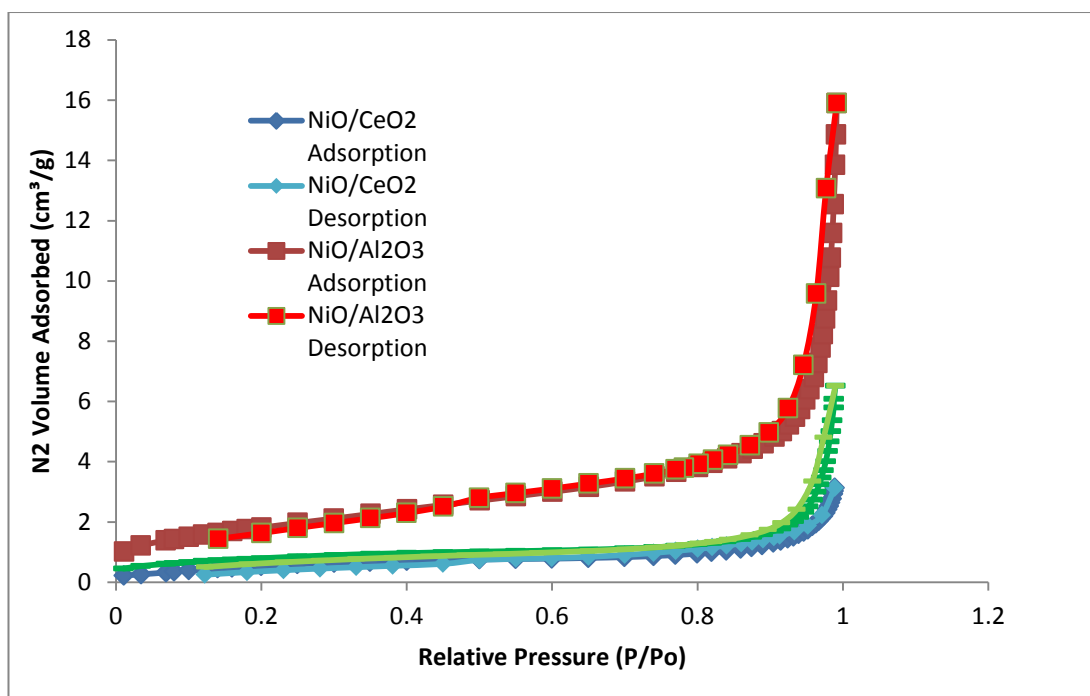


Figure 14 : Adsorption isotherm comparison for all three catalyst.

Nitrogen adsorption-desorption isotherm of the NiO/Al₂O₃, NiO/CaO and NiO/CeO₂ have an adsorption branch that shows an uptake of adsorbed volume at high relative pressure. All three catalyst exhibits the type-IV isotherm with H1 type of hysteresis. The type-IV isotherm indicates the mesoporous materials with a relative narrow loop at 0.8 to 1.0 of relative pressure (Instrument Q, n.d). H1-type of hysteresis has been associated with porous material exhibiting a narrow distribution of relatively uniform cylindrical pores. Based on figure 17 the NiO/ Al₂O₃ catalyst has the higher nitrogen adsorption compared to the NiO/CaO and NiO/CeO₂.

Table 3 summarized the pore volume, pore diameter, pore size and BET surface area information from ASAP analysis.

Table 3 : Summary of ASAP analysis for nickel based catalyst.

| Type of Catalyst | BET Surface Area (m ² /g) | Pore Size (Å) | Pore Volume (cm ³ /g) |
|------------------------------------|--------------------------------------|---------------|----------------------------------|
| NiO/Al ₂ O ₃ | 6.4205 | 107.1435 | 0.017928 |
| NiO/CaO | 2.8960 | 107.0998 | 0.007754 |
| NiO/CeO ₂ | 2.2476 | 72.5813 | 0.004078 |

The BET surface area, Pore size and pore volume of the nickel based catalyst are shown as in table 3. Nickel based catalyst supported with alumina has the highest surface area, pore size and pore volume among all followed by calcium and ceria. This proves that the alumina is the good support which gives higher surface area to the catalyst.

(d) Transmission Electron Microscopy (TEM) Analysis

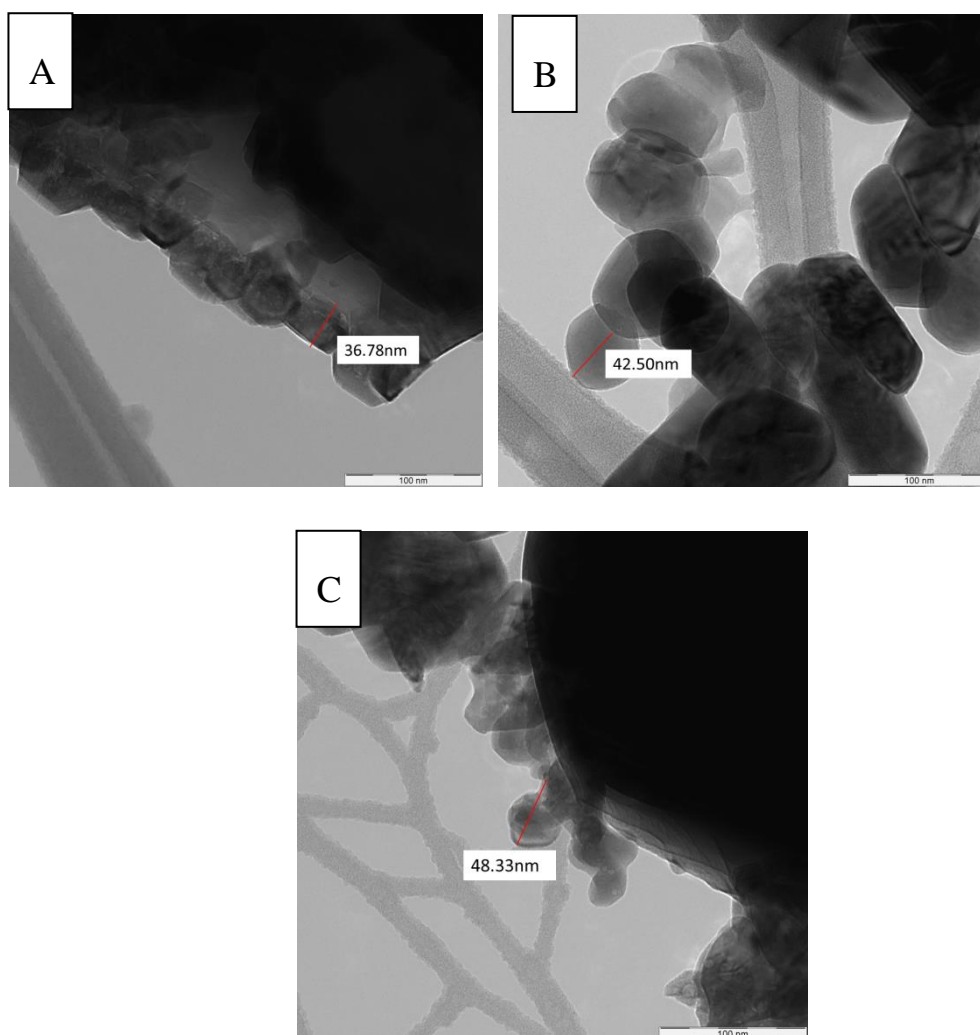
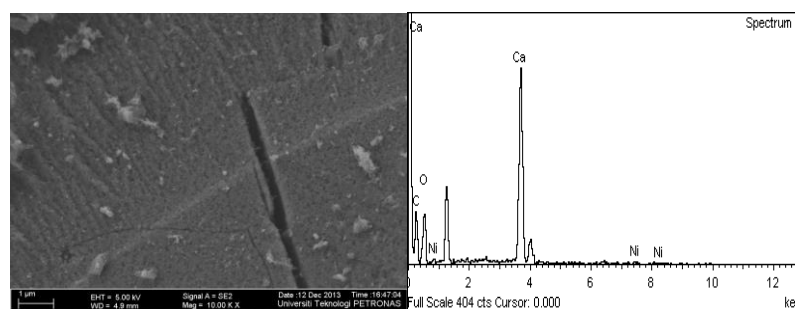


Figure 15 : TEM images under 100nm magnification. (a) NiO/Al₂O₃ (b) NiO/CaO (c) NiO/CeO₂

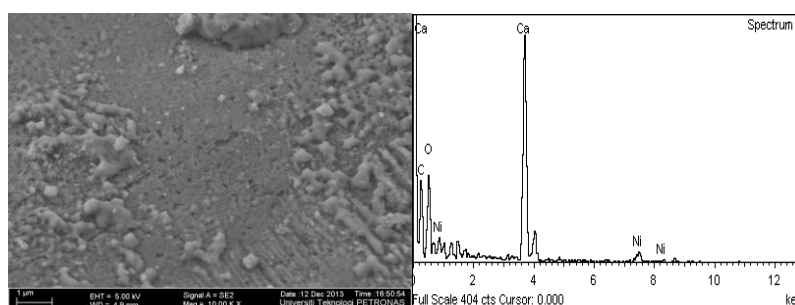
Figure 15 above shows that the TEM images for all three catalysts captured under 100nm magnifications. The images shows the morphology of the catalyst. From calculation, the particle size for NiO/Al₂O₃ is 36.76nm, NiO/CaO is 42.5nm and NiO/CeO₂ is 48.33nm. Low particle size gives the higher surface area of the catalyst. The BET surface area of NiO/Al₂O₃ is the highest among all three catalysts. The diameter of catalyst particle is inversely proportional to the surface area.

4.1.2 Limestone Based Catalyst

(a) Field-Emission Scanning Electron and Microscopy (FESEM)



(a)



(b)

Figure 16: FESEM images and EDX patterns for (a) NiO/CaO loading method. (b) NiO/CaO Doping Method

FESEM analysis in Figure 16 showed the surface structure of the NiO/CaO catalyst by using impregnation method or known as loading method and doping method to prepare the catalyst. The images show that the structures of catalyst are porous for both. The FESEM analysis cannot indicate the rate of porosity of the catalyst but it can be measured by using SAP analysis which can be discussed in below section. Other than that, EDX spectrum confirms the existed element in the catalyst. In figure 4, it shows that there are Calcium, Oxygen and Nickel element in the materials as the prepared in catalyst preparation. However, there are formation of Carbon existed in the patterns, 30.16 wt% in loading method and 29.75 wt% in doping method. The formation of carbon perhaps happen during the calcination process where there are air purging in high temperature. The deposited of Carbon may deactivate the active sites of the catalyst during the reaction application or adsorption (Bartholomew, 2001)

(b) Surface Area Analyzer and Porosimetry (SAP)

Table 4: Summary of SAP analysis for Limestone Based Catalyst

| Type of Catalyst | BET Surface Area (m ² /g) | Pore Size (Å) | Pore Volume (cm ³ /g) |
|------------------|--------------------------------------|---------------|----------------------------------|
| NiO/CaO Loading | 8.0105 | 225.696 | 0.048289 |
| NiO/CaO Doping | 15.0155 | 161.230 | 0.053932 |

Table 2 shows the summary of SAP analysis for Limestone Based Catalyst. From the table, it shows that the doping method of catalyst preparation give higher surface area and pore volume compared to loading method. The BET surface area of the doping method is 15.0155 and for loading method is 8.0155. There is 87% of increasing in surface area for the doping method. Thus, it confirms that the doping method can give higher surface area to the catalyst based on the SAP analysis and Nitrogen adsorption-desorption graph in figure 5 below.

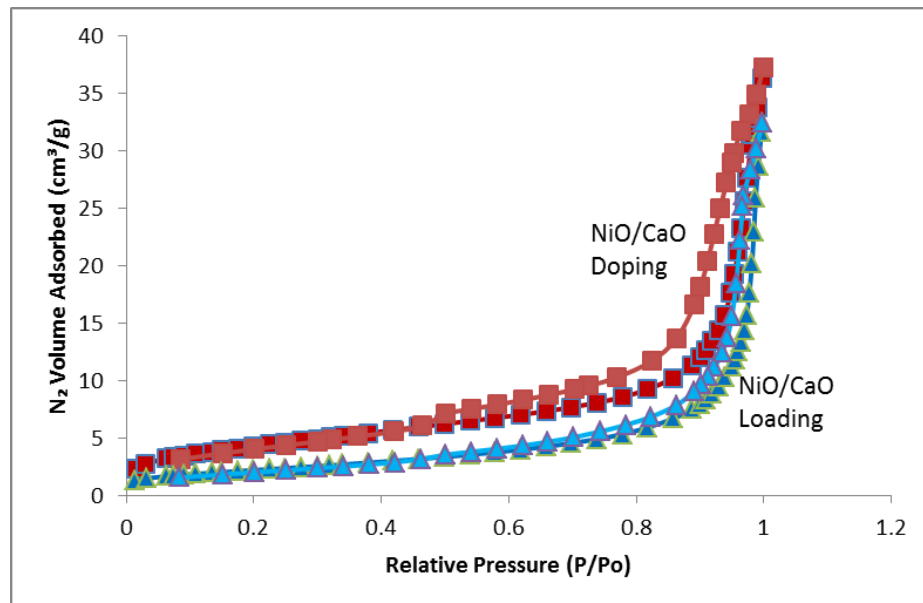


Figure 17: Adsorption isotherm comparison for limestone based catalyst.

From figure 17, it shows that this is the Type IV isotherm with hysteresis Type I which associated with porous material (Instrument, n.d) for both catalyst. The limestone cased catalyst NiO/CaO doping method absorbs more nitrogen compared to the loading method. The absorption of Nitrogen in catalyst is directly proportional to the BET surface area. Therefore, higher surface area will absorb more nitrogen and it can be confirmed that the doping method has higher surface area compared to the loading method.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The Nickel-based catalysts which are Nickel supported with Alumina ($\text{NiO}/\text{Al}_2\text{O}_3$), Nickel supported with Calcium Oxide (NiO/CaO) and Nickel supported with Ceria (NiO/CeO_2) has the potential in producing hydrogen from dry reforming glycerol based on the morphology and analysis by using TPR, TEM and SAP. Besides that, the SAP analysis and FESEM images confirm that the doping method of catalyst preparation gives higher surface area compared to the one that using impregnation method which is loading method. 87% increasing in BET surface area for doping method. The different method in preparation of catalyst surely gives an impact to the surface area of the catalyst. The limestone based catalyst had higher potential to be the lowest price in the industry because of the abundance in Malaysia. The utilization of the limestone can be done by commercialized it in industry. Both nickel and limestone based catalyst is the promising candidate of based catalyst for hydrogen production. The objectives of this project have been achieved.

As a recommendation, the continuation of this project should be done by using the real limestone as the based catalyst so that more appropriate results can be seen. Moreover, the different method in catalyst preparation or pre-treatment of the catalyst can be done in order to increase more in surface area of the catalyst. The doping method also can be improvised for the future works. Besides that, for future work, focus more to the limestone based catalyst compared to nickel. This is because, nickel based catalyst has been widely used in industry but the limestone based catalyst only few studies doing the research about it. Other than that, to test the performance of the catalyst in producing hydrogen, the experimental work using hydrocracker equipment for glycerol dry reforming need to be done in the future.

CHAPTER 6

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