METHANE DRY REFORMING OVER Ce-PROMOTED Ni/Al_2O_3 CATALYST: KINETIC STUDIES

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METHANE DRY REFORMING OVER Ce-PROMOTED Ni/Al_2O_3 CATALYST: KINETIC STUDIES

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
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SUPERVISOR’S DECLARATION

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

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STUDENT'S DECLARATION

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

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Dedication

To be who had given me dreams to look forward to.

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ABSTRACT

Syngas (or H_2 and CO mixture) production has received significant attention since it is the main feedstock of Fischer-Tropsch synthesis for synthetic fuel manufacture to replace petroleum-based energy. Dry reforming of methane (DRM) has been considered as an efficient and green approach for producing syngas due to greenhouse gas utilization and desired syngas composition. In this research, the objectives were to prepare 3%Ce-10%Ni/Al_2O_3, to investigate the physicochemical attributes of 3%Ce-10%Ni/Al_2O_3 catalyst and examine the effect of reactant partial pressure on DRM performance. XRD diffractograms indicated the formation of CeO_2, NiO and $NiAl_2O_4$ phases corroborated with temperature-programmed calcination (TPC) results. The complete thermal decomposition and oxidation of metal precursors were observed at 750 K during TPC measurement. DRM performance over 3%Ce-10%Ni/Al_2O_3 catalyst was stable with time-on-stream for all CO_2:CH_4 ratios. CH_4 and CO_2 reaction rates enhanced with growing CO_2 partial pressure (P_{CO2}) and exhibited a maximum at P_{CO2}=30 kPa. CH_4 conversion enhanced with growing CO_2 partial pressure (P_{CO2}) and exhibited a maximum at P_{CO2}=40 kPa and CO_2 conversion vice versa to the CH_4 conversion. H_2 , CO selectivity and yield enhanced with lessen CO_2 partial pressure (P_{CO2}) and exhibited a maximum at P_{CO2}=20 kPa. Interestingly, H_2/CO ratio also reduced with an increase in CO_2 partial pressure and the ratio of H_2/CO was always inferior to unity for all runs reasonably due to the reverse water-gas shift reaction.

ABSTRAK

Syngas (atau H_2 dan CO campuran) pengeluaran telah mendapat perhatian yang besar kerana ia adalah bahan mentah utama sintesis Fischer-Tropsch untuk pembuatan bahan api sintetik untuk menggantikan tenaga berasaskan petroleum. Keringkan pembaharuan metana (DRM) telah dianggap sebagai satu pendekatan yang cekap dan hijau untuk menghasilkan syngas disebabkan oleh penggunaan gas rumah hijau dan dikehendaki komposisi syngas. Dalam kajian ini, objektif adalah untuk menyediakan 3% Ce-10% Ni / Al_2O_3, untuk menyiasat sifat-sifat fizikokimia sebanyak 3% Ce-10% Ni / Al_2O_3 pemangkin dan memeriksa kesan tekanan separa bahan tindak balas terhadap prestasi DRM. Diffractograms XRD menunjukkan pembentukan CeO_2, NiO dan $NiAl_2O_4$ fasa disokong dengan pengkalsinan (TPC) Suhu yang diprogram. Penguraian terma lengkap dan pengoksidaan prekursor logam diperhatikan pada 750 K semasa pengukuran TPC. Prestasi DRM lebih 3% Ce-10% Ni / Al_2O_3 pemangkin stabil dengan masa-ke-aliran untuk semua CO_2: nisbah CH_4. CH_4 dan CO_2 kadar tindak balas dipertingkatkan dengan CO_2 yang semakin meningkat tekanan separa (PCO_2) dan dipamerkan maksimum di PCO_2 = 30 kPa. Menariknya, nisbah H_2 / CO juga dikurangkan dengan peningkatan CO2 tekanan separa dan nisbah H_2 / CO selalu kalah dengan perpaduan untuk semua berjalan dengan munasabah kerana sebaliknya air-gas peralihan tindak balas.

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LIST OF ABBREVIATIONS

α_0	Ratio of number of gas of inelastic collisions resulting in absorption to total number of collisions of gas molecules on the surface.
C	Constant value, characteristics of the adsorbate.
n	Number of adsorbed molecules desorbing in unit area of the surface.
θ	Fraction of surface of covered by adsorbed molecules.
P	Gas pressure.
P_s	Saturation pressure of adsorbed gas.
S_A	Surface area of solid.
μ	Number of molecules colliding in unit time with a unit area of the surface.
V	Volume of gas adsorbed.
V_M	Volume of gas adsorbed corresponding to monolayer coverage.

LIST OF ABBREVIATIONS

ATR	Autothermal reforming
BET	Brunauer, Emmett and Teller isotherm
DR	Dry reforming
DRM	Dry reforming of methane
DAE	Differential algebraic equation
POX	Partial oxidation
SR	Steam reforming
TGA	Thermogravimetry analysis
WGS	Water gas shift

1 INTRODUCTION

1.1 *Background of the Study*

Production of synthesis gas from natural gas have become very important in the chemical industries for reason related to the soaring petroleum price, depletion of oil reserves, and environmental problems with exhaust gas (K.Tomishige, 2007) (Liu et al.,2011) (Ki.Nakagawa, 2011). Natural gas is often found with or near the crude oil reserves. Methane constitutes majority of natural gas, with a fraction of 70 to 98 % depending on the location where it is obtained (Ross, 1996). Hence, natural gas could play a significant role as a carbon source for the world's supply of fuel and fuel-based chemicals in this century. It has been found that most of the world's natural gas reserved are situated in remote areas and are not easily accessible from the areas of high-energy consumption. Methane is also considered to be a major green-house gas and contribute to global warming. The other green-house gases are CO_2, water-vapor, and ozone (Fan, 2009). To maintain the greener environment, Methane and carbon dioxide should be eliminate by using methane dry (CO_2) reforming to produce a valuable gas is called synthetic gas.

To improve the viability of methane conversion, research has been carried out into the conversion of methane to liquids or higher hydrocarbons. There are studies on direct oxidative conversions of methane into methanol, formaldehyde, propanal, benzene and other aromatics (Claridge, 1998), also direct oxidative coupling of methane to ethane and ethylene. But all these processes either demonstrate low yields or are not economically viable, not able to meet industrial requirements at the existing price of crude oil (Claridge, 1998). Existing industrial processes make use of methane as a primary feedstock for conversion to a mixture of carbon monoxide and hydrogen (synthesis gas or syngas). In fact, the cost of syngas production in converting natural gas to liquid fuels can be more than 60 % of the total cost. Hence, reducing the cost of syngas would play a significant role in the economics of the gas-to-liquids process (Rostrup-Nielsen, 1993) (Ross, 1996). The syngas produced serves as the feedstock in a variety of downstream processes, such as methanol synthesis, Fischer-Tropsch synthesis or ammonia synthesis.

1.2 Motivational and statement of problem

The production of syngas (CO and H_2) by CO2(dry) reforming of methane over a heterogeneous catalyst is one of the attractive routes for the utilization of the methane and CO_2 resources (Richardson 1990) (Ashcroft, 1991) (Edwards, 1995) (Wang, 1996). The product mixture of this reaction form a stoichiometric (1:1) feed has a low H_2/CO ratio (1:1) that is desirable for direct use as feedstock. This reaction also has important environmental implications as two greenhouse gases are converted into a valuable feedstock (Seshan, 1994).

Currently, significant interests have been registered for renewable and environmental friendly energy conversion technology such as fuel cell technology application since 18th century; fossil fuels in the form of coal, oil and natural gas have powered the technology and transportation networks that develop the society. This too over-dependence on fossil fuels has endanger the supply of energy and causes massive strains to the environment. Nowadays, the production of syngas, which is a mixture of hydrogen and carbon monoxide, has preferred natural gases as the sources (Ahmed, 2001). Hydrogen is expected to become an important energy carrier for sustained energy consumption with reduced impact on the environment.

In industry, hydrogen is practically produced form natural gas and mainly used for the ammonia synthesis (Penà, 1996) (Armor, 1999) (Rostrup-Nielsen, 2002). A hydrogen-based energy system is regarded as a viable and advantageous option for delivering high-quality energy services. Hydrogen should be used as a fuel for fuel cells because of the high efficiency of hydrogen energy to electricity as well as no emission of any pollutant gases (S.Takenaka, 2003).

Hydrogen based fuel cells are an attractive alternative to conventional combustion engines because of their better efficiency leading in turn to a reduction of CO_2 emission. Due to the progress in fuel cell technology the demand for new catalyst to produce hydrogen increases (Armor, 1999). One of the potential H_2 supplying is through methane dry reforming. Methane dry reforming is a catalytic process which produces useful value-added products and gives significant interest due to potential environmental benefits by utilising CO_2 and also increased demand for syngas (H_2 and CO) as the reaction as follow:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^o_{298} = 247 \frac{kJ}{mol} \qquad (1.1)$$

Carbon dioxide (CO_2) has been identified as the most significant greenhouse gas arising from anthropogenic activities**.** Anthropogenic emission of CO_2 has to be reduced to counteract global warming (Amin, 2012). Although noble metal based catalyst is highly activity, it has higher cost and might be limited in availability. Therefore, Ni catalyst has been chosen instead of noble metal. This is because it both to achieve activity and selectivity. In addition, Ni can undergo deactivation via carbon deposition and sintering (Liu, 2009) (Z.Meili, 2006) (Sun, 2010) (Wang, 2012) (A.Albarazi, 2013).

In order to achieve improvement in the activity, better support and promoters have been chosen which are aluminium oxide, Al_2O_3 and Lanthanide oxide. There are several positive effects of Lanthanide oxide which are high oxygen storage capacity (Yang, 2010), improved dispersion of Ni metal (Yang, 2010), promotion of the CO_2 adsorption on the surface of the catalyst and reduction of the chemical interaction between nickel and the support resulting in an increase in the extent to which Ni is formed.

Dry reforming of methane is currently widely used in industrial as a secondary reformer to reduce H_2:CO ratios produced by steam reforming. By replacing steam with CO_2, there is no drastic effect on the mechanism. However, like steam reforming, it suffers from deactivation of the supported metal catalyst via carbon formation. Besides that, it is an endothermic process with high energy requirements (Hou, 2003) (Gadalla, 1988) (Souza, 2004). As a standalone process, dry reforming would not contribute to a net decrease in CO_2 emissions, it may increase CO_2 emissions since energy required to sustain the reaction is likely to be derived from fossil fuels.

In efforts to reduce energy consumption of synthetic gas production, the catalytic partial oxidation process has attracted significant amounts of interest. Since the oxidation of hydrocarbons to synthesis gas mixtures is exothermic, this process is much more energy efficient than both the steam and dry reforming processes. However, direct oxidation has not been applied industrially, because it involves co-feeding of hydrocarbon-oxygen mixtures under flammable or explosive conditions since this process using oxygen gas. Flames in the reaction zone may also lead to local hot spots which may damage active catalyst. Instead, the applications of partial oxidation have almost always been in combination with steam reforming to give auto-thermal reforming.

1.3 Objectives

The objectives of this research are:

1. To prepare 3%Ce-10%Ni/Al_2O_3 catalyst and study the physiochemical properties of the catalyst for dry reforming of methane.
2. To investigate kinetics of methane dry reforming over 3%Ce-10%Ni/Al_2O_3 catalyst.

1.4 Scope of this research

In order to achieve the objectives, several scopes have been identified. Firstly, the process of pre-treatment of the support had done. The support, alumina, Al_2O_3, was calcined from room temperature, 300 K to 973 K and was held constant for 5 hours. Then, the wet-impregnation process also has been taken. The catalyst, were nickel(II) nitrate, $Ni(NO_3)_2$ and cerium (III) nitrate, $Ce(NO_3)_3$ has been stirred continuously for 3 hours and directly put into the oven for the drying process at 383 K and left overnight. After that, the sample had undergone calcination process at 973 K for 5 hours. The samples then underwent catalyst characterization were Brunauer-Emmett-Teller (BET), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Temperature-Gravimetric Analysis (TGA). Lastly, the sample tested on the process of methane dry reforming using in a conventional vertical fixed-bed tubular reactor.

1.5 Main contribution of this work

Carbon dioxide (CO_2) has been identified as the most significant greenhouse gas arising from anthropogenic activities. It is of great importance to reduce anthropogenic CO_2 emissions in order to counteract global warming. One such method, which is presently being extensively investigated, is the sequestration of CO_2 produced by concentrated sources (such as industrial plants and power stations). However, no one can be sure of the potential influence of CO_2 buried on the ecosystem in the long term. Conversion of CO_2 instead of its sequestration is presently being explored as one potential alternative solution. Production of useful value-added products such as chemicals products, fuels by dry reforming of methane appears to be an interesting method. The dry reforming of methane produces an equimolar synthesis gas (syngas) which is a mixture of hydrogen (H_2) and carbon monoxide (CO), from carbon dioxide and methane (CH_4), according to equation below.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (1.2)$$

Furthermore, dry reforming can be viably used as a method of CO_2 mitigation for the production of hydrogen or of synthetic fuels. This work assesses whether monometallic catalyst can be replaced by bimetallic catalyst and used in dry reforming reaction to give a promising conversion of syngas from CO_2 utilisation. First, a comparison between the monometallic catalystt and bimetallic catalyst is performed as well as a study of the production of hydrogen from the dry reforming of methane. Furthermore, a thermodynamic analysis is carried out by the method of equilibrium constants defining the thermodynamic limit and the optimum conditions.

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 provides the introduction of research, objectives and scopes of the research. Chapter 2 also provides a literature review of the applications of catalytic steam reforming, CO_2 reforming and catalytic partial oxidation. A general description on the flow characteristics of the system, as well as the advantages and disadvantages are presented. This chapter also provides a brief discussion of applications and limitations for reforming process as well as the catalyst deactivation.

Chapter 3 gives a flow chart of preparing catalyst by using wetness impregnation method, followed by mixing slurry and lastly drying and calcination process. The other sections give detailed explanations about the preparation procedures and reaction run.

Chapter 4 is devoted to reaction work and the result of the reaction has been done within this semester. In this chapter, the detailed descriptions about the result of characterization by using advanced technologies are discussed. Chapter 5 provides the conclusion and recommendation the research.

2 LITERATURE REVIEW

2.1 Introduction

Production of synthesis gas from natural gas and Fisher-Tropsch synthesis from the synthesis gas have become very important in the chemical industry for reasons related to the soaring petroleum price, depletion of oil reserves, and environmental problems with exhaust gases (K.Tomishige, 2007) (Liu, 2011) (Li, 2011). Partial Oxidation (H_2/CO = 2) and dry reforming (H_2/CO = 1) have been proposed as alternatives methods to achieve a high CO selectivity and a more appropriate H_2/CO ratio for downstream synthesis. Initially, dry reforming has not been widely used due to the high level of carbon formation from methane and CO. However nowadays, dry reforming of methane has gained interest from both industrial and environmental aspects due to increased interest in the effective utilisation of CO_2 which is a green-house gas arising from anthropogenic activities. Since dry reforming is highly endothermic and reversible reaction, therefore it needs to operate at high temperature to achieve equilibrium between methane, water, carbon monoxide, and carbon dioxide. Today's energy, which is mainly depends on fossil energy carriers, can in no way be evaluated as sustainable. Regarding to the progressive industrialization of developing nations and growth in the world's population from time to time, especially those countries in Asia as well as South

Syngas can be used for production of various chemicals such as methanol, ammonia, oxo chemicals, and their individual derivatives such as formaldehyde, urea, butanol, dimethyl ether (DME), and others. Simultaneously, Fisher Tropsch synthesis (FT–synthesis) can be used for the production of hydrocarbon fuels such as diesel and gasoline. Two or more derivatives can also be produced at the same time, which enables polygeneration. Hence, chemicals, fuels, or power can be produced depending upon the requirement as well as changes in the domestic energy markets or global economic conditions.

The major opportunity in the syngas market is removing dependency on conventional natural resources for the production of chemicals and fuels. Undeniably, gradual depletion of the world's oil reserves enable a growing recognition of the potential of world natural gas reserves have led to an increased interest in more efficient utilization of methane (CH_4). Today natural gas is the preferred source for production of syngas, a mixture of hydrogen and carbon monoxide, from which purified hydrogen can be obtained. There are several different catalytic processes for producing syngas from natural gas (Armor, 2005).

In fact, the conventional method to produce syngas can be major classified into two, steam reforming of natural gas and the CO_2 (or dry) reforming process. Indeed, CO_2 (or dry) reforming process has attracted significant interest due to increased interest in the effective utilization of CO_2 from the environmental perspective compared to the steam reforming technology. Actually, many natural gas fields contain copious amounts of CO_2, natural gas dry reforming may be readily carried out without pre-separation of CO_2 from the natural gas. In some situation, combination of steam and CO_2 reforming may be advantageous. Undeniably, utilization of the CO_2-CH_4 reforming reaction is already employed in some industrial processes. However, there is always a question whether transformation of CH_4 and CO_2 into other chemicals could have a significant impact on the concentration of these gases in the atmosphere.

2.2 Hydrogen production from methane

2.2.1 Steam Reforming

$$CH_4 + H_2O \leftrightarrow CO + 3\ H_2 \quad (\Delta H = 206\ kJ/mol) \tag{2.1}$$

The process of methane steam reforming produce syngas with a ratio H_2/CO equals to three, usually this process within the presence of nickel catalyst, methane will reacts with water steam (steam to carbon ratio of between 2 to 4) at temperature greater than 1073 K (Reyes, 2003) which is an endothermic process. Consequently, this process is relatively energy and cost intensive. B.Gaudernack reported in 1998 that catalytic steam reforming accounts for more than 48% of the global production. In 1984, Rostrup-Nielsen stated that catalytic steam produced over 80% of ammonia and has been the first developed by BASF in 1926 (Peña, 1996) (Marschner, 2005).

The use of steam has brought several disadvantages, which are endothermic reactions, high product H_2:CO ratio of 3 or more (which is unsuitable for downstream processing, steam corrosion problem, cost in handling excess steam and the occurrence of the water-gas shift reaction which produces significant amounts of CO_2 in the product (Bharadwaj, 1995). Therefore, research on alternative processes of methane reforming with economic viability prospect is gaining interest.

Since the overall reaction is endothermic, it is necessary to supply the needed heat to the reaction throughout the whole process. In steam reforming, this is accomplished by combustion of a part of the fuel in a direct-fired or indirectly fired furnace. According to Le Chatelier’s principle, equilibrium concentrations for reaction are shifted to the right at high temperature and low pressure. In order to achieve a highly conversion of the methane, a very high temperature and long residence time at this high temperature is required, meaning that an overall energy loss and a huge size for the methane reforming reactor. Nevertheless, by using catalysts it is possible to reduce the temperature necessary for total conversion of the methane to below 1000 °C within considerable short residence time. In Table 2-1, the advantages and disadvantages of steam reforming are listed.

Table 2-1: Advantages and Disadvantages of Steam Reforming.

Characteristic	**Advantage**	**Disadvantage**
Hydrogen Yield	Higher than 50% at T > 600 °C.	Potential high level of carbonaceous material formation.
Heat Requirement	Heat generated from combustion can be used to drive steam reforming reaction with overall higher system efficiency.	Potential higher cost.
Startup/ transients	Relative stable during transition operation.	Still needs external igniter to start up although the catalyst bed can be used for catalyst combustion tentatively. Heat transfer efficiency and higher volume makes the start-up slow

2.2.2 Partial Oxidation

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \quad (\Delta H = -38\ kJ/mol) \tag{2.2}$$

(Liander, 2006) was the first suggested the production of synthesis gas by catalytic partial oxidation due to interest in ammonia process. The partial oxidation process is a catalytic process that involves partial oxidation of the methane and product of this reaction is syngas with a good H_2/CO ratio (Fathi, 2000). Methane partial oxidation may occur in non-catalytic homogenous conditions at very high temperatures (York, 2007). In 1946 the partial oxidation of methane was investigated over refractory-supported Ni catalyst in temperatures between 973 to 1173 K (Prettre, 1946). This process is an exothermic process and considered as an expensive process because it requires a flow of pure oxygen as a feed. Therefore, there is a warning danger that exists in this process since the reagents can cause flammable or explosion if the process is not handled with care (Pena, 1996).

The partial oxidation of methane is an exothermic process and, thus from economic perspective, it can be considered more economic than the processes of steam reforming or dry reforming, because, being an exothermic reaction, it requires a lower amount of thermal energy compared to others. Generally, reaction times are very short (in milliseconds) and occur at high temperatures of 850 to 1200 ^{0}C. The product mixtures have a lower H_2: CO ratio of 2, which is ideal for the Fischer-Tropsch synthesis from synthesis gas (Foo, 2012). The advantages and disadvantages of catalytic partial oxidation are listed in Table 2-2 below.

Table 2-2: Advantages and Disadvantages of Catalytic Partial Oxidation

Characteristic	**Advantage**	**Disadvantage**
Hydrogen Yield	None.	Relatively low yield can be tuned by improving catalyst and convert some CO back to H_2.
Heat Requirement	The system is exothermic.	The heat generated from the reaction needs to removed or utilized in the system.
Startup/ transients	Startup is fast. Transient test is relatively easy to control.	High temperature startup/shutdowns may cause catalyst degradation.

2.2.3 Auto-Thermal Reforming

$$2CH_4 + \frac{1}{2}O_2 + H_2O \leftrightarrow 2CO + 4H_2 \ (\Delta H = -36 \text{ kJ/mol}) \qquad (2.3)$$

The auto-thermal reforming (ATR) of methane is a combination of both steam reforming and partial oxidation in the presence of a catalyst. Therefore, this process involves three reactants, which are CH_4, H_2O, and O_2. This process is designed to save energy, because the thermal energy required is generated in the partial oxidation of the methane. It is called auto-thermal since it consumes the thermal energy that it produces. Similar to other reforming processes of methane, the main purpose of auto-thermal reforming is the production of syngas. The value of the H_2/CO ratio of the syngas obtained in this process is the function of the gases reactant fractions introduced in the process input. Typically, the value of H_2/CO ratio range is in between 1 and 2 (Palm, 2002). In Table 2-3 below, the advantages and disadvantages are shown.

Table 2-3: Advantages and Disadvantages of Autothermal Reforming.

Characteristic	Advantage	Disadvantage
Hydrogen Yield	About 50% yield of the product.	Lower hydrogen yield than steam reforming.
Heat Requirement	None.	May need startup heat, and control systems to switch between lean burning and autothermal reforming regimes.
Startup / transients	Moderate.	Transient fluctuations for load matching may be as much as 110 per second.

2.3 Dry Reforming of Methane (DRM)

$$CH_4 + CO_2 \leftrightarrow 2\ CO + 2\ H_2 \qquad (\Delta H = 247\ \text{kJ/mol}) \qquad (2.4)$$

Methane dry reforming (DRM) is a catalytic reaction between methane and carbon dioxide to produce synthesis gas (a mixture of hydrogen and carbon monoxide) that can be used for chemical processes like Fischer-Tropsch or synthesis of various chemicals. Similar to steam reforming reaction, the product equilibrium is influenced by the water-gas shift reaction, except this case it is the reverse reaction (RWGS) which is influential (Bradford, 1999). Recent days, production of syngas through methane dry reforming process has been attracted intense interest due to concerns over global warming and anthropogenic green-house gas concentration. The advantage of this process compared to steam reforming is that the dry methane reforming produce low H/CO ratio which is 1 and suitable for the downstream activities such as synthesis of alcohols (Cheng, 2005) (Hou, 2003). Since CO_2 is present in many natural gas fields, CO_2 reforming may be carried out without pre-separation of CO_2 from natural gas (Hu, 2004).

Another advantage of this process is due to its potentially friendly effect on the environment by reducing greenhouse gas emissions. Furthermore, dry reforming of methane may be used to convert biogas form landfills, sewage processing or anaerobic fermentation due to their suitable composition of CH_4 and CO_2. (Cheng, 2001) reported that, the value of the H_2/CO ratio obtained in the dry reforming of methane is considered the best product of reforming process when it comes to use the syngas produce as a raw material for the synthesis of chemical. On the other hand, this type of reforming process is considered relatively expensive because, being an endothermic process consumes a great amount of energy. But from the industrial point of view, it will be more practical to develop Ni based catalyst because of their low price, high activity at elevated temperature, excellent thermal stability and wide availability (Kim, 2000).

2.4 *Current Challenges with Dry Reforming of Methane (DRM)*

The main disadvantage of DRM is the high thermodynamic potential to coke formation of the catalyst (Gadalla, 1988) (Hou, 2003) (Souza, 2004). The deposition of coke on the surface of the catalyst contributes to the reduction of its longitivity. (Ding, 2001) suggested that carbon deposition was inevitable in the temperature range 300 ^{o}C to 1000 ^{o}C from the thermodynamics analysis. Process of DRM is often challenged by many factors. This reaction is characterized by several aspects such as carbon deposition leading to rapid catalyst deactivation (Olsbye, 1997) (Batiot-Dupeyrat, 2008) and severe temperature gradients at high conversions due to the highly endothermic nature of the raction (Daza, 2010). It has been reported that there are various type of carbon formation on Ni-based catalyst during DRM process at least some of which may also be produced on noble metal catalysts. Carbon deposition on catalysts results primarily from the following reactions (Gallego, 2008) (Xu, 2009):

Methane decomposition:

$$CH_4 \rightarrow C_{(C\ )} + 2H_2 \quad (\Delta H = 75 \text{ kJ/mol}) \tag{2.5}$$

CO disproportionation (Boudouard reaction):

$$2CO \rightarrow C_{(C\ )} + CO_2 \quad (\Delta H = 205 \text{ kJ/mol}) \tag{2.6}$$

Methane decomposition is favoured at high temperature, meaning that there is a need to optimize the temperature to minimize the thermodynamic driving force for carbon deposition from these two reactions. Catalyst can inhibit carbon formation kinetically at condition where carbon formation is thermodynamically favourable as desirable.

2.5 Catalyst

Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst. With a catalyst, reactions occur faster and with less energy. The behaviour of supported metallic catalyst in the CH_4 reforming with CO_2 depends on several interrelated factors such as the nature of the metal, the support type, the metallic particle size and the characteristics of the metal-support interface (Zhang, 1996) (Bitter, 1997) (Tsipouriari, 1994) (Ricchardson, 1990) (Qin, 1994). Group VIII metals, usually base metal catalyst (Ni, Co and Fe) as well as noble metal catalysts (Pt, Ru, Rh, and Pd) are active for the dry reforming reaction. These are usually dispersed on various oxide supports. In the reforming reaction, the catalysts contain one or more metallic active species deposited on a support material.

The metals species interact with the support to form of metal-support interaction. Alumina (γ-Alumina, α-Alumina) are widely used as support or as bi-supports in the form of magnesium aluminate or calcium aluminate. In addition, ceria, magnesia, pervoskites, and zirconia are also commonly employed as support materials. The selection support plays the important role in determining the activity and stability of a catalytic material. The main function of the support metal is to increase the surface area of the active component. Catalytic activities generally increase with increasing catalyst surface area, but a linear relationship cannot be expected since the reaction is often strongly dependent on structure of the catalyst surface. The modification of metal-based catalyst by promoters in dry reforming will also be examined along with their application in the improvement of catalyst deactivation.

2.5.1 Base Metal Catalyst

(Li, 2005) showed the superiority of Ni over Pt and Pd in alumina-supported systems for dry reforming of methane. Other studies undertaken by Rostrup-Nielsen (1973), Engler et al. (1991), and Murata et al. (2004) revealed that Ru and Re exhibited activity comparable to Pt, Pd and Rh during reforming of methane. Interestingly, Wang et al. (2004) also suggested that Ni and Re give higher conversions than Ru and Rh in dry reforming of methane. Significantly, for dry reforming of methane, there is a clear indication that Ni is indeed the most active species, whilst Pd and Pt also give good conversions (Souza, 2004) (Fidalgo, 2010). Nickel catalysts is an important class of catalytic materials and are widely applied in many important reactions, such as hydrogenations (Aderson, 1994), natural gas reforming for syngas production (Ruckenstein, 1996), dealkylation (Coughlan, 1992). The good performance of nickel-containing materials in oxidative dehydrogenation and also have high activity and selectivity in the reforming of hydrocarbons to syngas and also have low cost (Rostrup-Nielsen, 1993) (Tsang, 1995) (Bhardwaj, 1995). Hence,these catalysts are commonly used in the syngas production processess.

2.5.2 Effect of Support

The nickel-based catalyst the use of Al_2O_3 as a support appeared in general to give higher activity during methane dry reforming over other unmodified, single-component supports. For lower temperature range (<600 ^oC), Matsumura et al. (2004) and Kusakabe et al. (2004) however reported that Ni/ZrO_2 showed better activity and stability than both Ni/Al_2O_3 and Ni/SiO_2. In an effort to improve the performance of ZrO_2, several researchers have added cerium oxide (CeO_2) to this support. The accompanying enhancement were credited to the role of the CeO_2 in stabilizing metal dispersion (Kusakabe et al., 2004). In contrast, Laosiripojana and Assabumrungrat (2005) found lower conversion in Ni/Al_2O_3, although accompanied with less carbon deposition, compared to $Ni/CeZrO_2$. They argued that dry reforming activity of Ni/Al_2O_3 is strongly inhibited by high hydrogen presence. Nakagawa et al. (2003) studied the effect of support material in nickel-based catalysts for dry reforming of methane.

2.5.3 *Effect of Promoter on Ni-Based Catalyst*

In order to improve the stability and the carbon resistance of nickel-based catalysts, the supports metal have been modified by adding the promoter, mainly by addition of alkali and alkaline earth metal oxides as well as rare earth oxides (Wang, 2001) (Dong, 2002) (Takeguchi, 2003). The rare earth oxides have a high oxygen storages capacity and can absorb or release oxygen reversibly in responding to the oxygen concentration in the gas-phase. Their presence shows advantage effects on the catalyst performance, such as improving the dispersion of the active species and delaying the transition of alumina support (Soria, 1996) (Morterra, 1996). It has been demonstrated that the addition of ceria as a promoter in the Ni/ Al_2O_3 catalyst can enhance the activity, stability and resistance of carbon deposition in methane reforming with CO_2 (Wang, 1998) (Cheng, 2001). Further studies by Zhang et al. (1994), Cheng et al. (1996), and Choudhary et al. (1996) found that Ni supported on CaO-Al_2O_3 exhibited higher reforming activity rather than Ni/Al_2O_3, while Lodeng et al. (1997) and Lu et al. (1999) found the addition of CaO increased the coke formation of Ni/ Al_2O_3. But Horiuchi et al. (1996) indicated that excess impregnated Ca reduced the activity of Ni/ γ- Al_2O_3. Hou et al. (2003) reported that, the Ca-promoted Ni/ α- Al_2O_3 the reforming activity was increased greatly and the coke formation rate changed slightly compared with pure Ni/ α- Al_2O_3.

They also found that the coke formation rate decreased when the Ca/Ni reached at $\leq$ 0.08, mol ratio. They reported, the Ca/Ni at $\geq$ 0.1, mol ratio resulted in higher coke formation. So, the influence of Ca on the activity of Ni/ α- Al_2O_3 changed with the amount of Ca added. Yang et al. (2010) studies the promotional effect of La_2O_3 and CeO_2 on Ni/ γ- Al_2O_3 catalysts for CO_2 reforming of methane. They reported that the CH_4, CO_2 and total carbon conversion decreased with La loading increasing from 0 to 3 %, and did not clearly changed with La loading increasing from 3% to 9%. However, the carbon deposition on the 10% Ni/La_2O_3- γ-Al_2O_3 catalyst decreased with increased La loading, while the carbon deposition did not clearly changed with La loading increasing from 3 to 9 %.

2.6 *Catalyst Deactivation*

In reality, catalysts in chemical processes, especially in hydrocarbon processes, lose their activity over time due to different reasons and conditions. Unfortunately, this decline in activity is unavoidable except in limited cases but it can be slowed and kept to an insignificant level. Table 2-4 provides a summary of the major mechanisms of catalyst deactivation (Bartholomew, 2001). There are three main mechanisms of deactivation that cause the loss of catalyst activity: sintering or aging, coking or fouling, and poisoning.

Table 2-4: Mechanisms of catalyst deactivation (Bartholomew, 2001).

Mechanism	Type	Description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites resulting in blocked sites.
Fouling	Mechanical	Physical deposition of species from fluid phase onto catalytic surface and pores.
Thermal degradation	Thermal	Thermally-induced loss of catalytic surface area, support area and active phase-support reactions.
Vapour formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound.
Vapour-solid and solid-solid reactions	Chemical	Reaction of fluid, support or promoter with catalytic phase to produce inactive phase.
Attrition/crushing	Mechanical	Loss of catalytic material from abrasion Loss of internal surface area from mechanical-induced crushing of catalyst.

2.6.1 Sintering (Aging)

Sintering is one of the catalyst deactivation types, it is refers to the loss of catalyst activity due to structural changes in the crystals on the catalyst surface and stemming from high temperature exposure. It is caused by excessive temperatures, and is an irreversible process in which more stable crystal structures with lower surface areas are formed (Di Marcoberardino et al, 2014). Sometimes the main stream gas concentration can be a cause of the sintering deactivation. In supported metal catalysts, sintering mainly occurs due to the loss of active surface area caused by crystal agglomeration and growth of the metals deposited on the support or by pore blockage inside the catalyst pellet.

There are two main theories to descript the sintering mechanism, namely he atomic migration and the crystallites migration models. As shown in Figure 2-1, in crystallite migration, entire crystallites migrate over the support surface before colliding and coalescing, while in atomic migration, atoms which migrate over the surface are captured by larger crystallites (Bartholomew, 2001).

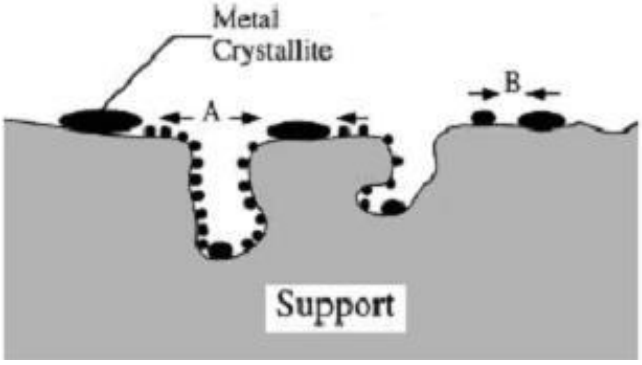


Figure 2-1: Conceptual models for crystallite growth due to sintering: (A) atomic migration, and (B) crystallite migration (Bartholomew, 2001).

Prolonged exposure of the catalyst to high temperatures is the common cause of occurrence of sintering since the sintering rates are being exponentially function of temperature. The effects of sintering are irreversible or difficult to reverse. Consequently, minimise sintering by selecting a suitable temperature for the process is the important element to be considered (Kim, 1985). Additionally, Moulijn, van Diepen & Kapteijn (2001) proposed that the temperatures applied do not exceed 0.3 to 0.5 times of the melting point of the catalyst, respectively known as the temperatures melting. The temperature is the point at which atoms at defects become mobile whereas the bulk atoms become mobile. Table 2-9 shows melting temperature for some metals and support that are frequently used in hydrocarbon conversion processes (Moulijn et al,2001).

Table 2-5: Melting temperatures (K) of common compounds in heterogenous catalysis (Moulijn et al, 2001).

Compound	**Temperature Melting**
Pt	2028
PtO	823
Pd	1828
PdO	1023
Rh	2258
Ru	2723
Fe	1808
Co	1753
Ni	1725
NiO	2228
Ag	1233
Cu	1356
CuO	1599
Mo	2883
Zn	2248
Al_2O_3	2318
SiO_2	1986

2.6.2 Coking (Fouling)

Coking is a physical type of deactivation and reflects the loss of the catalyst active surface area due to deposition of species obtained from the fluid phase causing blockage of sites and/or pores (Furimsky, 1999). Coke deposition is a major problem for the methane reforming reactions, and occurs via methane cracking and/or the Boudouard reaction, leading to loss of adsorption sites for the reactants. Carbon lay-down is the main complexity that prevented dry reforming from commercial operation. As described in Figure 2-2, carbon chemi- or physi-sorbed leading to encapsulating the metallic active sites with subsequent plugging for microand mesopores of the support. Eventually, production loss and pressure build-up in the plugged reactor and subsequently, a costly shutdown is only the solution to resolve the crisis.

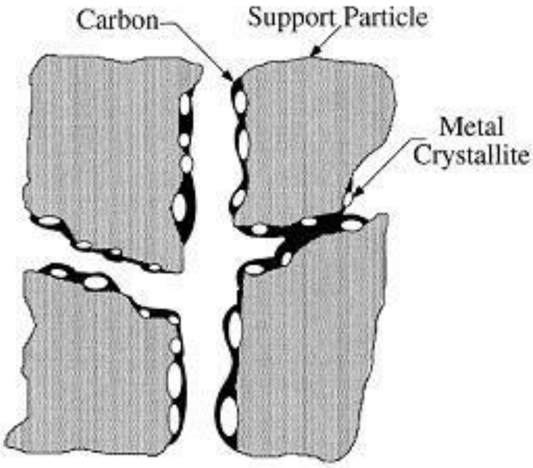


Figure 2-2: Visual illustration for fouling, crystallite encapsulation and pore plugging of a supported metal catalyst due to carbon deposition (Bartholomew, 2001).

Bartholomew (2001) provided detailed insights into nature of carbon deposits and the mechanisms of their formation. According to the thermodynamic analysis, it is suggested that prevention of carbon deposition could be realised at high CO_2/CH_4 ratios and high temperatures (Gadalla & Bower, 1988). However, industrially it is preferable to operate close to stoichiometric ratios and at low temperatures. Hence, development of advanced carbonresistant catalysts is important and necessary, as well as the understanding of the carbon formation mechanisms. In the methane dry reforming reaction, the main sources of carbon deposition ars attributed to CO disproportionation reaction and CH_4 decomposition.

2.6.3 Poisoining

Poisoning is the loss of activity due to impurities from the feed depositing on the active portion leading to a decline in the existing active sites for the main reaction. In industrial application, the main cause for poisoning over Ni-based catalyst surface is the adsorption of H_2S during methane dry reforming process (Sivasanker, 2004). Generally, poison adsorption is a fast process and the influence depends on the nature of the poison and its amount in the feed. Bartholomew (2001) proposed that pre-treatment for the feed is a feasible option may decrease the concentration of the poison to an acceptable level, resulting the adsorption strength between catalyst surface and poison molecule require a higher to crack the interaction.

Furthermore, under the exploration for an active catalyst, the tolerance of the metallic active sites for these poisons should be taken into consideration. Figure 2-3 exhibits a great tolerance for these catalysts against sulphur among some of the transition metals such as Ru, Co, Fe under the methanation process (Bartholomew, 2001).

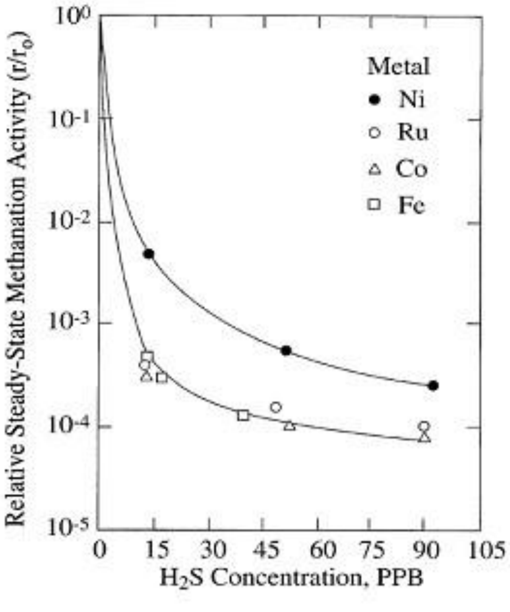


Figure 2-3: Relative steady-state methanation activity profiles for some of the transition metals as a function of gas phase H_2S concentration (Bartholomew, 2001).

3 MATERIALS AND METHODS

3.1 Introduction

This chapter provides a detailed description of the materials such as chemical, chemical formula, purity of the chemical and application. As well as provides the equipment for characterising the catalyst and the experimental procedures and reaction runs. This information includes the grade of chemicals and gases, equipment information and supplier. Theoretical outlines and operational aspects of the various catalyst characterization instruments are also prepared.

3.2 Chemicals

A list of chemicals used in this work is provided in Table 3-1. Chemicals were obtained from source named Sigma-Aldrich (Cerium (III) Nitrate Hexahydrate 99.9%trace metal basis, Nickel (II) Nitrate Hexahydrate crystallizes ≥ 97.0%, Aluminium Oxide).

Table 3-1: List of chemicals used

Chemical	Formula	Purity/Concentration	Application
Aluminium Oxide	Al_2O_3	99%	Catalyst synthesis
Nickel(II) Nitrate	$Ni(NO_3)_2.6H_2O$	>99.9%	Catalyst synthesis
Cerium(III) Nitrate	$Ce(NO_3)_3.6H_2O$	>97.0 %	Catalyst synthesis

3.3 Catalyst Preparation

This section presents the details of the catalyst preparation procedures. Figure 3-1 shows the entire catalyst preparation procedure:

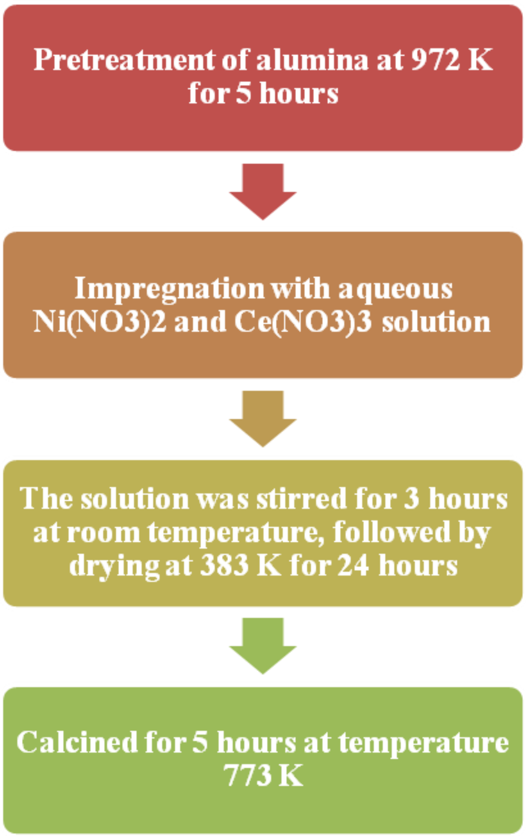


Figure 3-1: Catalyst preparation flowchart.

3.3.1 Support Preparation

The use of catalyst supports may improve mechanical strength; reduce cost of the catalyst through dilution of the expensive active material with cheaper support materials (Hardiman, 2007). Alumina is the most popular support in hydrocarbon-mediated reactions due to its low cost and excellent thermal and mechanical properties. Therefore, it has been chosen as the support for this experiment. The support, aluminium oxide, Al_2O_3which is obtained from Sigma-Aldrich has firstly being calcined in air from room temperature, 300 K to 973 K (as shown in Figure 3-2) and is held constantly for 5 hours in order to ensure the prevention of phase transformations during the high temperature catalyst preparation processes and subsequent reaction runs.

Figure 3-2: Calcination of the support

3.3.2 *Catalyst Impregnation*

All catalyst in this study was prepared through the wet impregnation method. This method includes the addition of an aqueous metal precursor solution to the support material, followed by stirring of the slurry, drying and finally calcinations which is to decompose the metal precursor compounds to metal oxides. The total volume of liquid added is depending on the solubility of the metal. There is main advantage by using the wet impregnation method, which is that catalyst with pre-determined metal loadings maybe prepared (Huang & Schwarz, 1987). The nickel (II) nitrate, Ni $(NO_3)_2$ and cerium nitrate $CeNO_3$ are both obtained from Sigma-Aldrich. Firstly, the wet impregnation process is being done. The catalysts are both being weighed by 7.43 g for nickel (II) nitrate and 4.3 g for cerium nitrate. Then, the catalyst is being put in the 100 ml of beaker and 10ml of distilled water is poured in it.

The amount of distilled water to be put was firstly being identified from the solubility graph of the sample. After that, the solution is being stirred continously for 3 hours by using magnetic stirrer (Figure 3-3). Then, the solution has being dried for 24 hours at temperature 383 K. After drying process is finished, the catalyst is then calcined for 5 hours for temperature at 773 K (Figure 3-4). Later, the process of reduction of H_2 has being done for both of the catalyst at the temperature of 773 K for 5 hours process.

Activation of the catalyst wil be conducted via in situ reduction in the fixed bed reactor during the main reaction.

Figure 3-3: Stirring process of the slurry

Figure 3-4: Impregnated, uncalcined 3%Ce-10%Ni/Al_2O_3

Figure 3-5: Impregnated, calcined and uncalcined 3%Ce-10%Ni/Al_2O_3

3.4 Catalyst Characterization

Catalyst characterization provides useful information on the physiochemical attributes of the catalyst. Analytical techniques such as spectroscopic, microscopic, diffraction or chemical analysis can be effectively used to investigate the catalyst surface and bulk properties. This section describes the fundamental concepts of various characterization methods employed for this study. Most substances used as catalysts supports are porous in nature. These materials contain deep and complicated network of pores accountable for internal surface area. Surface area is obviously a key property of a porous material. Despite the fact that support surface are not uniform in nature, higher surface area is often a good indication of a more active catalyst. In such a case, metal crystallites can be more homogeneously distributed on the maximum possible surface and hence, an increase in adsorption sites for reactant molecules.

3.4.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most commonly technique in catalyst characterization which is used to identify the crystalline phases in catalysts through the elastic scattering of X-ray photons in a periodic lattice (Chorkendorff, 2003). Mean crystallite size of less than 10 mm may also be estimated through the elastic scattering. In XRD analysis, an X-ray source is bombarded with high energy electrons which then emit X-rays as shown in Figure 3-5. Consequently, the angle at which constructive interference may be measured, and the lattice spacing can be evaluated from the Bragg equation (Cullity, 2001):

$$n \lambda = 2d \sin \theta \tag{3.1}$$

where n = integer called the order of reflection

λ = wavelength of the X-rays

d = distance between two lattice planes

θ = angle between incoming X-ray and the scattering plane

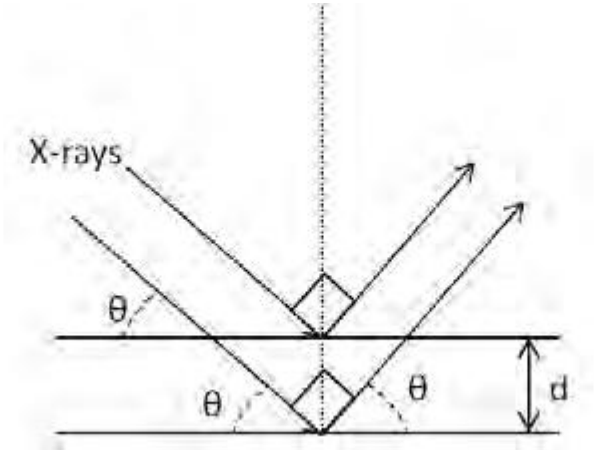


Figure 3-6: X-ray diffraction as given by Bragg's Law.

3.4.2 *Brunauer-Emmett-Teller (BET)*

Surface area, pore size and pore volume are among the most fundamentally important properties of a catalyst because they determine the measure of its internal surface available to accommodate active sites. Despite the fact that support surface are not uniform in nature, higher surface area is often a good indication of more active catalyst. Brumauer-Emmett-Teller (BET) method is a common technique used to measure solid surface area. In a pioneering work, Langmuir has developed a relationship between the amount of adsorbed gas and its equilibrium pressure at constant temperature (Langmuir, 1916).

The Langmuir's model for a monomolecular adsorption is generally expressed by:

$$\theta = \frac{\alpha\mu}{n(1+\frac{\alpha\mu}{n})} \tag{3.2}$$

Where

θ = fraction of surface of covered by adsorbed molecules,

α = ratio of number of gas of inelastic collisions resulting in absortion to total number of collisios of gas molecules on the surface,

n= number of adsorbed molecules desorbing in unit area of the surface,

μ = number of molecules clliding in unit time with a unit area of the surface.

Based on Langmuir's monomolecular model, Brunauner, Emmet and Teller derived an expression for multilayer adsorption, given as follow:

$$\frac{P}{V(Ps-P)} = \frac{1}{CVm} + \frac{(C-1)P}{CVmPs} \tag{3.3}$$

Where:

P =gas pressure,

P_s=saturation pressure of adsorbed gas,

V = volume of gas adsorbed,

V_m=volume of adsorbed gas corresponding to monolayer coverage,

C = a constant, characteristic of adsorbate.

A plot of $\frac{P}{V(Ps-P)}$ versus $\frac{P}{Ps}$ provides a straight line with the intercept and slope of $\frac{C-1}{Vm-C}$ and $\frac{1}{CVm}$ respectively from which the volume of adsorbed gas corresponding to monolayer coverage, V_m, and C will be calculated. The preferred range of $\frac{P}{Ps}$ for best results is 0.05 to 0.4 (Emmett, 1954). The surface area per weight unit can subsequently be computed by:

$$S_A\,(m^2\,g^{-1}) = (V_M, \frac{cm^3}{g})\,(\frac{6.023\ x\ 10^{23}\ molecules}{21400\ cm^3 STP})\,(\frac{cross\ sectional\ area, m^2}{molecule}) \tag{3.4}$$

Where:

S_A= surface area of solid,

V_M= volume of adsorbed gas corresponding to monolayer coverage.

And for N_2 the usual cross-sectional area is 16.2 $Á^2$ ($1\ Á^2 = 10^{-20}\ m^2$) (Gregg, 1991).

3.4.3 *Thermo Gravimetric Analyser (TGA)*

Thermo-gravimetric analysis (TGA) (TA Instrument Model Q 500 TGA with TA 5000 Controller) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. Measurements are made in a thermo-balance comprising of a microbalance, a furnace and a control and recording module which is usually a computer. Any reduction in the sample mass is usually due to the release of by-products from the reaction. Briefly, about 4 mg of catalyst was loaded in a tube. Catalysts were packed and held in the tube by a tiny pan.

A thermocouple was inserted as close as possible to the catalyst bed and ran axially through the reactor to measure and control bed temperature. Catalysts were initially heated with a heating rate of 10 K/min from ambient temperature to 373 K in N_2 flow of 100 ml/min. The catalysts were then kept constant at 373 K for 30 min in this inert gas for moisture removal.

After that, the catalysts were heated with the rate of 10 K/min to 1023 Kin a gas mixture (100 ml/min) with the composition of 80% N_2 and 20% O_2. The sample was kept constant at 1023 Kfor 30 min. Finally, the sample was cooled down to room temperature in the same gas mixture (80% N_2 and 20% O_2). Then, the processes were repeated again with the heating rate of 15 K/min and 20 K/min.

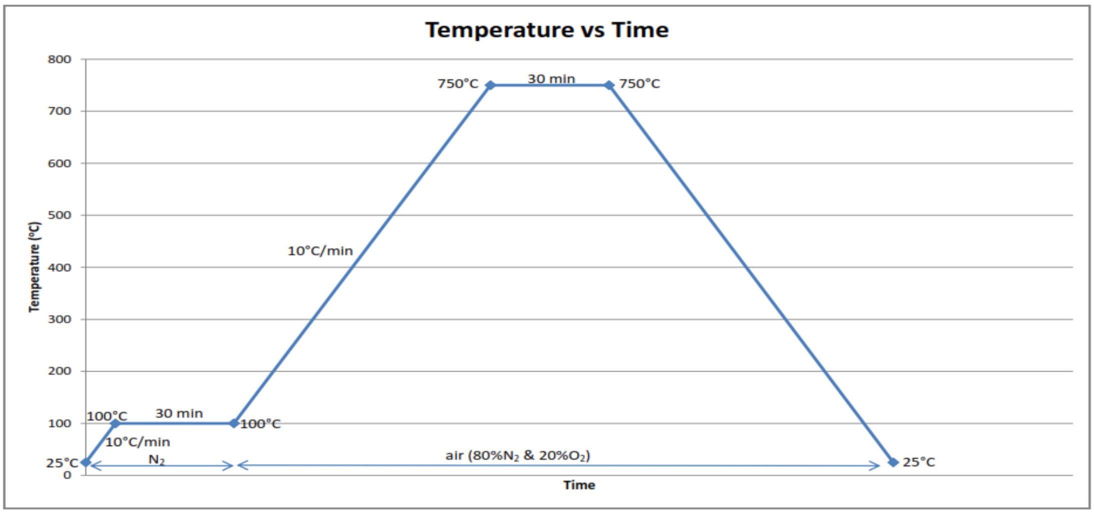


Figure 3-7: Illustrated graph for TGA process.

Temperature-programmed analysis was carried out on uncalcined catalyst under the continuous flow of high purity of air. While the sample was being heated, metal nitrate was decomposed into the various metal oxides, typically leading to a loss of sample mass.

Figure 3-8: Thermo-gravimetric Analysis

Temperature-programmed calcination was carried out on uncalcined catalyst under the continuous flow of high purity N_2 and O_2 with a ratio of 4 to 1. Metal nitrate was decaomposed into various type of metal oxides while the sample was being heated, leading to a loss of sample mass. Transient data from the thermogravimetric measurements may also be used to provide useful insights into the kinetic and mechanisms of gas-solid reactions.

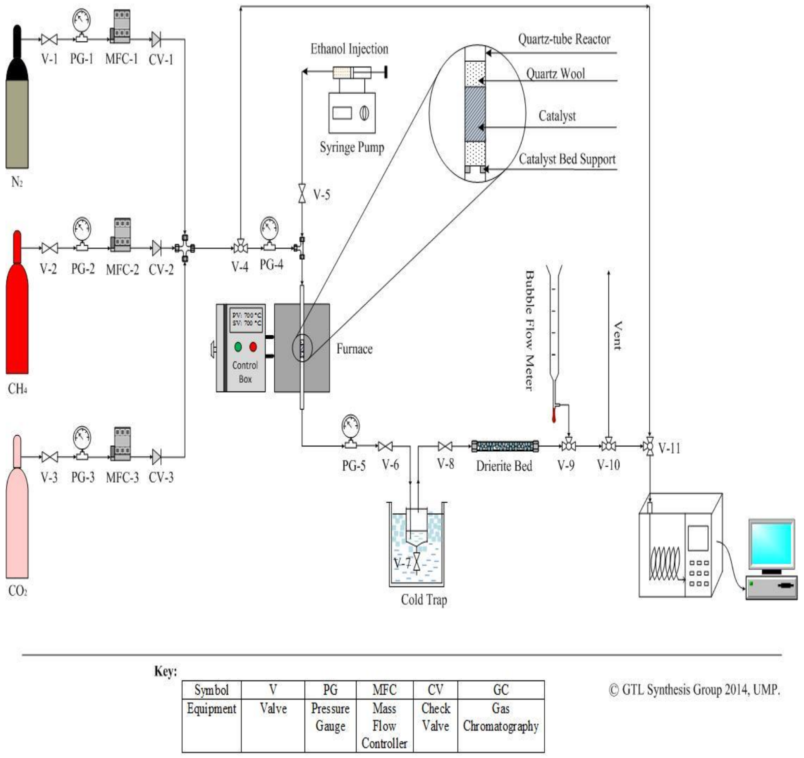
3.4.4 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties.

Figure 3-9: Scanning Electron Microscope (SEM) Analysis

3.5 *Reaction Runs*

Methane dry reforming reaction was carried out in a temperature-controlled tubular fixed-bed reactor (L=17 in and OD=3/8 in) with varying CO_2:CH_4 ratios of 1:1 to 2:1 at temperature range of 973 K and atmospheric pressure. About 0.15 g of catalyst with average catalyst particle size of 100 µm mounted in the middle of stainless steel reactor was used per run. CO_2 reforming of methane will be carried out at atmospheric pressure in a conventional vertical fixed-bed tubular reactor. A schematic diagram of the reactor setup is shown in figure 3.10



Symbol	V	PG	MFC	CV	GC
Equipment	Valve	Pressure Gauge	Mass Flow Controller	Check Valve	Gas Chromatography

Figure 3-10: Schematic diagram of the reaction

All feed and activation gas flow rates were digitally controlled by ALICAT Scientific mass flow controllers while the furnace temperatures were controlled by LT Furnance (Model: VTF50/150-1000) controllers. Action of leakage checking was taken before any reaction runs. Before commencement of the reaction, the flow was switched to bypass the reactor, and the gas switched to the reaction gas mixtures so that the feed composition can be measured and validated by the GC. The feed consisted of CH_4 and CO_2 gases. The gas flow was switched back to the reactor for the reaction to begin after the feed composition was verified to be correct. The total gas flow rate of the feed was set as 60 ml/min during each reaction run to minimize transport-disguised kinetics during data analysis, and each reaction was conducted at atmospheric pressure. A pair of pressure gauges were connected to the inlet and outlet of the reactor enabled monitoring of the pressure drop as well as at the front of both CH_4 and CO_2 storage tanks. Each reaction was conducted for 8 hours, during which pseudo-steady state was typically attained within an hour. On completion of reaction runs, the steel pipe reactor was allowed to cool to ambient conditions. The used catalysts were then replaced with fresh catalysts for further reaction run.

Reactor outlet gases were passed through an indicating water cold trap and followed by Drierite bed to remove all water content before being sent for GC analysis using gas collecting bags. The outlet gas sample was collected hourly and then subjected to Agilent Technologies 6890 Series GC System for further analysis. The Agilent Technologies 6890 Series GC System equipped with a TCD detector and fitted with an 6 ft long Alltech CTR-1 column which is suitable for separation of the components in this study since an inner column packed with porous polymer mixture to separate CH_4 and CO_2. Furthermore, an outer column packed with activated molecular sieve is employed to separate CH_4, H_2 and CO. The column was operated at pressure of 85 kPa with compressed air as the carrier gas while detector temperature was maintained at 393 K.

The conversion of carbon dioxide and methane are defined as the percentage of carbon dioxide carbon dioxide and methane that have reacted according to these following equations:

$$CO_2\text{conversion, \%} = 100 \text{ x } [(CO_2)_{in} - (CO_2)_{out}]/(CO_2)_{in}$$

$$CH_4\text{ conversion, \%} = 100 \text{ x } [(CH_4)_{in} - (CH_4)_{out}]/(CH_4)_{in}$$

$$r_{CH_4} = \frac{N_{CH_4}^{In} - N_{CH_4}^{Out}}{W_{catalyst}}$$

$$S_i = \frac{r_i}{\sum_{i=H_2,CO} r_i}$$

$$Y_{H_2} = \frac{F_{CH_4}^{Out}}{2F_{CH_4}^{In}}\ x\ 100$$

$$Y_{CO} = \frac{F_{CO}^{Out}}{F_{CH_4}^{In} + F_{CO}^{In}}\ x\ 100$$

The product's selectivity is represented as the molar ratio of H_2/CO. The comparisons of the activities of these catalysts were primarily characterized by the conversion and the product selectivity criteria.

4 RESULTS AND DISCUSSION

4.1 *Introduction*

This chapter represent the detailed outlined of the characterisation of catalyst and reaction run conducted for this research, so that appropriate physiochemical properties of the catalyst using the BET, SEM, TGA and XRD may be chosen and the detailed of these analyses as shown as below.

4.2 *Catalyst Characterisation*

4.2.1 *Physiochemical Properties*

Table 4-1 displays the properties of the catalysts determined from N_2 physisorption measurement. The BET area and pore volume catalysts were investigated. The bimetallic catalysts did not appear to have any significant effect on the BET surface area, pore volume and pore diameter of the catalysts. Theoretically, the catalyst activity has a proportional relation with the surface area (Cheng 1996, Roh 2004). The value of the BET surface area of 3%Ce-10%Ni/Al_2O_3 supposes has a better performance in the reforming reaction. Furthermore, the BET surface area value also revealed that the prepared catalyst has good thermal stability, where no sintering and phase transition were observed after the thermal treatment of the catalyst during the preparation.

Table 4-1: Summary of physisorption data.

Sample	BET area	Pore Diameter	Pore Volume
	(m^2g^{-1})	(nm)	(cm^3g^{-1})
10%Ni/Al_2O_3	107.3954	0.7763	0.0282
3%Ce-10%Ni/Al_2O_3	75.4016	0.7416	0.0397

4.2.2 X-ray Diffraction Analysis

X-ray diffraction measurements were carried out on a Match! system using Cuα target as radiation source with λ = 1.5418 Å operating at 30 kV for qualitative crystallographic identification of metal phases both monometallic and bimetallic Ni-based catalysts. Crystallographic database published by ASM International (Materials Park, Ohio, USA), edited by Pierre Villars and Karin Cenzual was used for analyzing XRD experimental data in all cases. The XRD patterns of 3%Ce-10%Ni/Al_2O_3 catalysts and aluminium oxide support calcined at 773 K for 5 h and 973 K for 5 h in air respectively are shown in Figure 4-1. As seen in the γ -Al_2O_3 (*see* Fig. 4.1 (a)). X-ray diffractogram, the support exhibited one broad peak at 2θ of 19.34^0, 32.50^0, 37.16^0, 45.84^0, 60.22^0 and 66.94^0.

XRD data were also collected for the bimetallic Ni-based catalysts in order to understand the effect of bimetallic addition on catalyst morphology. The X-ray diffractograms of 3%Ce-10%Ni/Al_2O_3 catalysts are shown in the same Figure 4-1 for comparison with monometallic catalyst.

In the XRD pattern of the 3%Ce-10%Ni/Al_2O_3 catalyst (*see* Fig. 4-1(b)). detected intensity peaks located at 2θ of 33.48^0 and 46.5^0 indicates the presence of $CeAlO_3$ phase, via;

$$CeO + Al_2O_3 \rightarrow CeAlO_3 \qquad (4.1)$$

Similarly, as seen in 5%Ce-10%Ni/Al_2O_3 catalyst in Figure 4-1(a), the identified $NiAl_2O_4$ phase might be given eq. (2) and eq. (3);

$$Ni(NO_3)_2 \rightarrow NiO + 2NO_2 + 0.5O_2 \qquad (4.2)$$

and

$$NiO + Al_2O_3 \rightarrow NiAl_2O_4 \qquad (4.3)$$

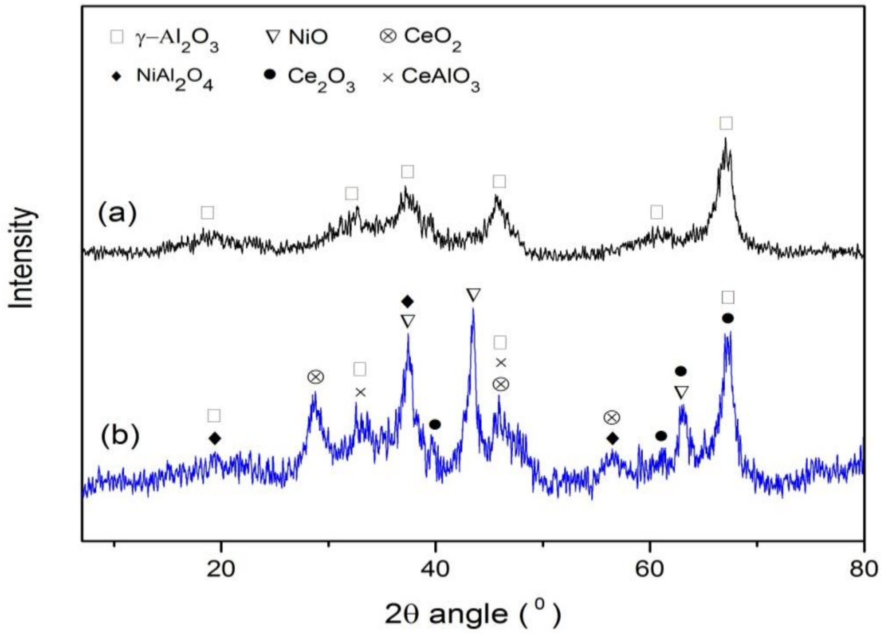


Figure 4-1: X-ray diffractograms of : (a) γ -Al_2O_3, (b) 3%Ce-10%Ni/Al_2O_3

4.2.3 *Thermogravimetric Analyzer (TGA) Study*

The temperature-programmed calcinations were performed by using TGA (RESEARH INSTRUMENTS, model: TGA Q500). Prior to the actual measurement, the sample of catalysts were subjected to heating at 373 K with heating rate of 10 K/min from ambient temperature with N_2 as flow of 100 ml/min. When the temperature reached 373 K, the sample was heated isothermally for 30 min for moisture removal. Then, the sample was heated with the heating rate of 10 K/min to 1023 K with a gas mixture of 4 N_2 : 1 O_2 with 100 ml/min of flow rate. At this stage, the sample was heated isothermally for another 30 min. Finally, the sample was allowed to cool down to room temperature in the same gas mixture. A comparison of the derivative weight profiles of the catalysts during temperature programmed calcination is shown in Figure 4-2.

From the figure, each thermal profile has 1 characteristic peaks (P1) located at same temperatures. Throughout the process, first step in the formation of metal oxide phases during calcination is the decomposition of precursors to metal oxides, represented by P1 at between 490 K and 510 K. It has also been suggested that the occurrence of intermetallic oxide phase of $CeAlO_3$ at this stage for the case of 3%Ce-10%Ni/Al_2O_3 catalyst:

$Ni(NO_3)_2 \rightarrow NiO + 2NO_2 + 0.5O_2$ (4.4)

$2Ce(NO_3)_3 \rightarrow Ce_2O_3 + 3NO_2 + 1.5O_2$ (4.5)

Subsequently, Ce_2O_3 oxidation takes place at about 490 K, 495 K, and 520 K respectively:

$NiO + 0.5O_2 \rightarrow NiO$ (4.6)

$Ce_2O_3 + NiO + 3O_2 \rightarrow 2CeNiO_3$ (4.7)

Finally, metal aluminates will be formed following prolonged calcination at high temperatures:

$CeO + Al_2O_3 \rightarrow CeAlO_3$ (4.8)

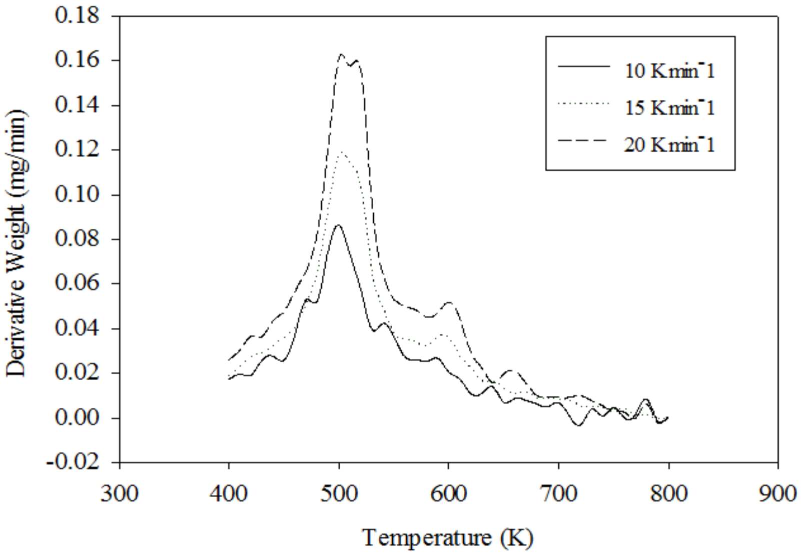


Figure 4-2 : Derivative weight profiles of 3%Ce-10%Ni/Al_2O_3 catalyst during temperatureprogrammed calcination at different heating rate.

Table 4-2 shows that the weight of reduction percentage estimation from the temperature programmed calcinations.

Table 4-2: Weight reduction percentage estimation.

Catalyst	**Ramping rate (K min^{-1})**	**Initial Weight (mg)**	**Final Weight (mg)**	**W_R (%)**
3%Ce-10%Ni/Al_2O_3	10	5.7340	4.265	25.61
	15	5.4680	4.003	26.79
	20	5.7520	4.189	27.17

4.2.4 Scanning Electron Microscope (SEM)

The morphology of the used catalysts was observed by FE-SEM with an emphasis on the formed carbon residuals. The SEM images of the calcined and fresh Ni-based samples (3%Ce-10%Ni/Al_2O_3), used in methane during reforming reaction, are shown in Figures 4-3. The images before zooming to the calcined 3%Ce-10%Ni/Al_2O_3 catalyst and Figures 4-4 the images after zooming to the calcined 3%Ce-10%Ni/Al_2O_3 catalyst**.**

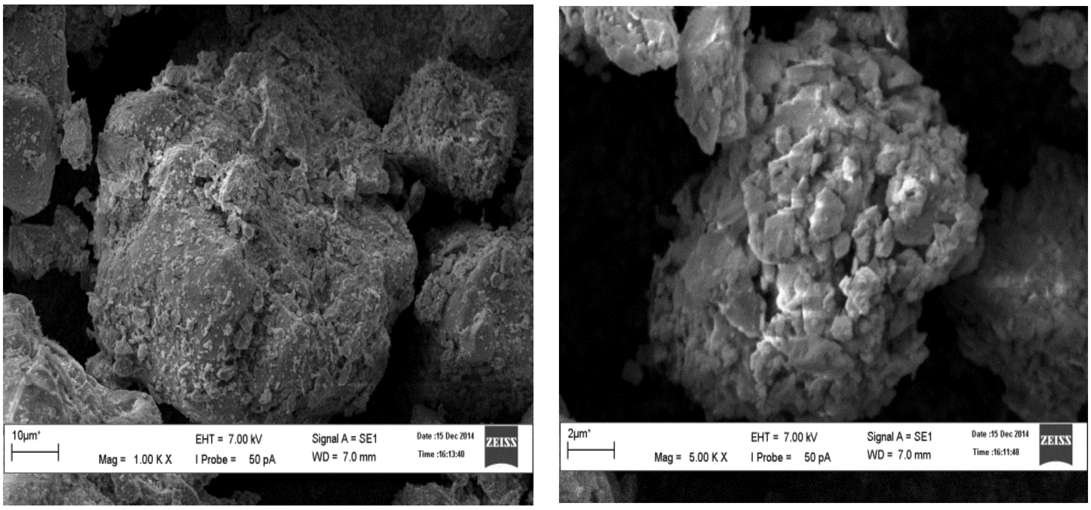


Figure 4-3 : SEM images of calcined 3%Ce-10%Ni/Al_2O_3

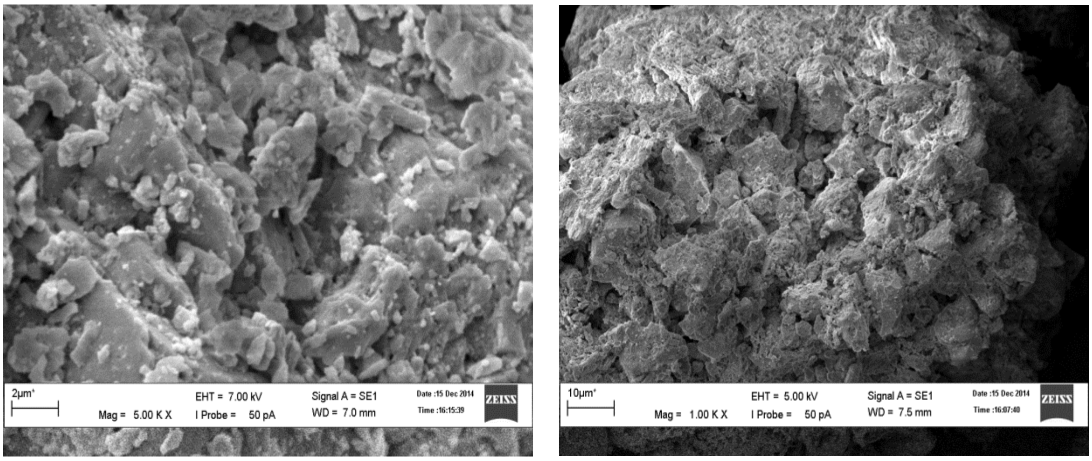


Figure 4-4 : SEM images of calcined 3%Ce-10%Ni/Al_2O_3

In the figure, the morphology of the sample 3%Ce-10%Ni/Al_2O_3 catalyst altered considerably size of the support and promoted, since the catalyst had two difference metal promoted it was not clearly showed the images of the promoted instead of the support with one promoted.

4.2.5 *Reaction Run*

Methane dry reforming reaction was carried out in a temperature-controlled tubular fixed-bed reactor (L=17 in and OD=3/8 in) with varying CO_2:CH_4 ratios of 1:1 to 2:1 at temperature range of 973 K and atmospheric pressure. About 0.15 g of catalyst with average catalyst particle size of 100 µm mounted in the middle of stainless steel reactor was used per run. The total gas flow rate of the feed was set as 60 ml/min during each reaction run to minimize transport-disguised kinetics during data analysis. Each reaction was conducted for 8 hours, during which pseudo-steady state was typically attained within an hour. Gaseous products were measured by Agilent 6890 Series gas chromatograph equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors.

4.2.6 *Transient Profiles*

As an promoted bimetallic Ce-Ni catalyst, in this study, it is able to give a good performance in the reforming reaction at different CO_2 pressure. The transient conversion profiles for CH_4 and CO_2 at 973 K with varying feed composition with CO_2= 20, 30 and 40 kPa (CO_2 / CH_4 = 1; CO_2 / CH_4 = 1.5; CO_2 / CH_4 = 2) are shown in Figures 4-5 and 4-6.

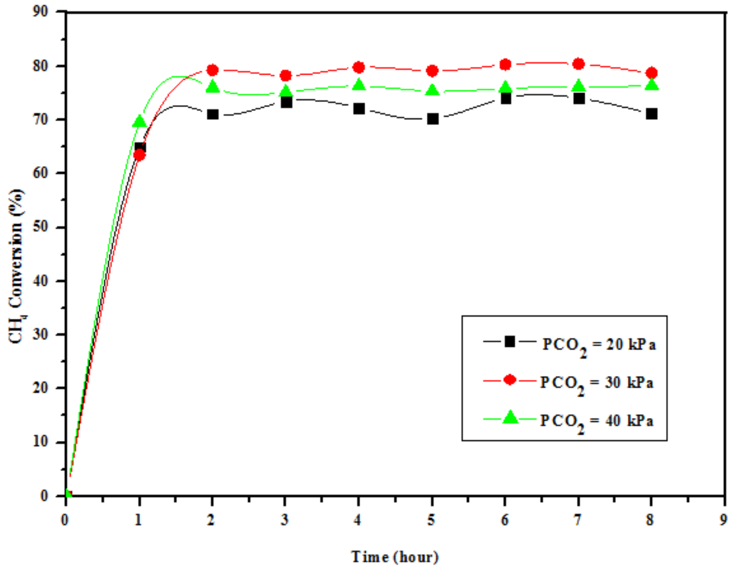


Figure 4-5 : CH_4 conversion profile at T = 973 K with varying feed composition of CO_2 / CH_4

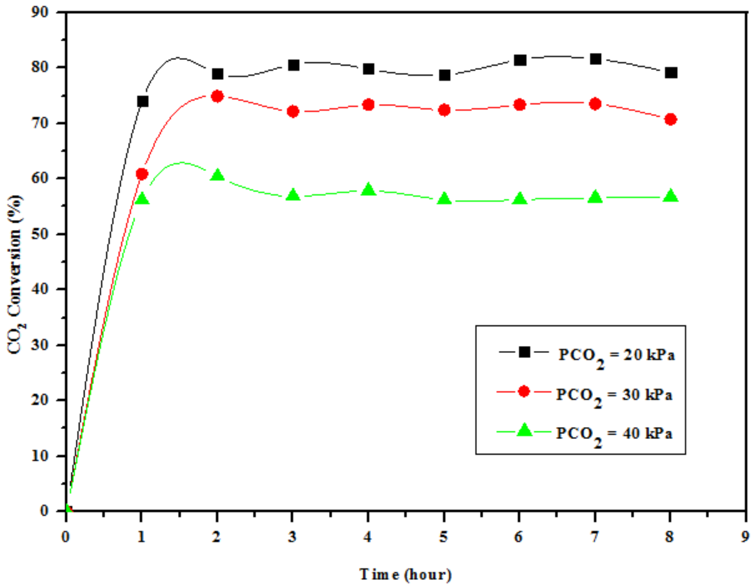


Figure 4-6 : CO_2 conversion profile at T = 973 ^{o}C with varying feed composition of CO_2 / CH_4

Figure 4-5 and 4-6 above shows that a study of effect of feed ratio towards the bimetallic catalyst was also been carried out. Figure 4-5 shows the percentage of CH_4 conversion higher at the feed ratio 30 kPa of CO_2 and lowest at 20 kPa CO_2. Meanwhile, for figure 4-6 the CO2 conversion higher at 20 kPa. From these 2 parameters showed that the undeniably, increase the feed ratio of CO_2/CH_4 will minimize the occurrence of carbon deposition on catalyst during the reforming reaction but at the same time, the H_2 and CO formation will be decreased as well as shown figure 4-7 and 4-8.

4.2.7 Steady-state Reaction Analysis

A comparison of the steady-state reaction rates for CH_4, CO_2, H_2 and CO at temperature 973 K with flowing an inert gas N_2 at varying P_{CO2} (20 kPa, 30 kPa and 40 kPa). From the observation in Figure 4-7 and 4-8, CH_4, $CO_{2,}$ H_2 and CO reaction rates experienced an inversely proportional to CH_4 and CO_2 reaction rates enhanced with growing CO_2 partial pressure (P_{CO2}) and exhibited a maximum at P_{CO2}= 30 kPa. Furthermore, this is also the reason to illustrate that the H_2/CO ratio is always impossible to be greater than 1 in this reaction. In their review paper, (Foo, 2012) and (Bodrov, 1964) suggested H_2 production first took place via CH_4 dehydrogenation into carbonaceous species, C_xH_{1-x} as follow:

$$xCH_4 \rightarrow C_xH_{1-x} + \left(\frac{5x-1}{2}\right)H_2 \tag{4.9}$$

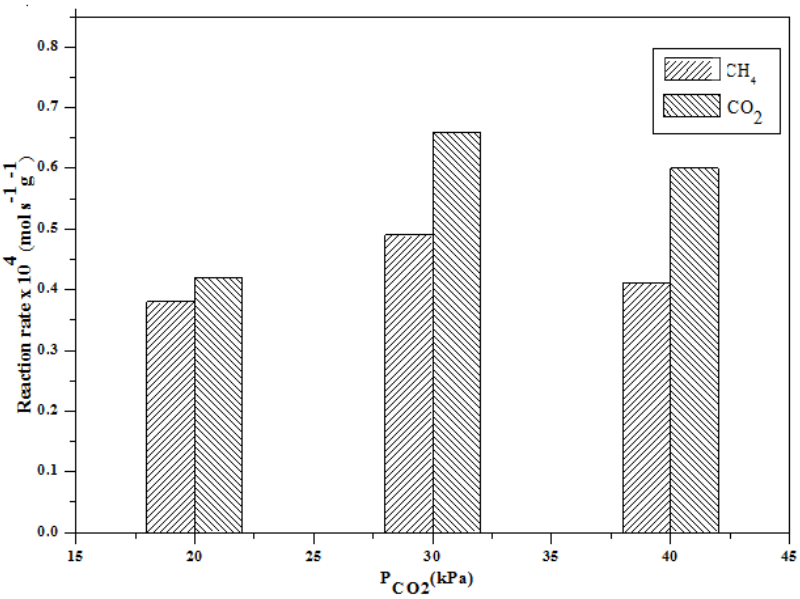


Figure 4-7 : Consumption rate of CH_4 and CO_2 during methane dry reforming 3%Ce-10%Ni/Al_2O_3 catalyst.

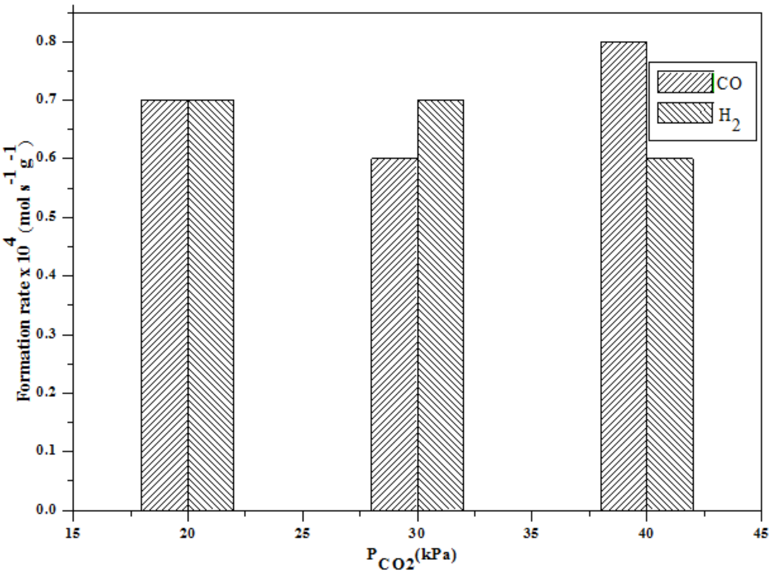


Figure 4-8 : Production rate of H_2 and CO during methane dry reforming 3%Ce-10%Ni/Al_2O_3 catalyst.

Subsequently, CO_2 reacts with the carbonaceous deposit to produce CO along with H_2 formation via:

$$C_xH_{1-x} + xCO_2 \rightarrow 2xCO + \left(\frac{1-x}{2}\right)H_2 \tag{4.10}$$

Therefore, the combination of eq. (4.10) and (4.11) gives the overall reaction:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (4.11)$$

As the CO_2 partial pressure increased, the presence of excess CO_2 react with the deposited carbon on surface of catalyst to yield high CO partial pressure and hence, the reduced H_2:CO ratio observed. Figure 4-9 shows the H_2:CO ratio value by using bimetallic 3%Ce-10%Ni/Al_2O_3 catalyst at temperature 973 K with varying P_{CO2}. Product H_2:CO ratios experienced a nonlinear drop with increased P_{CO2} for bimetallic 3%Ce-10%Ni/Al_2O_3 catalyst, as shown in figure 4-9.

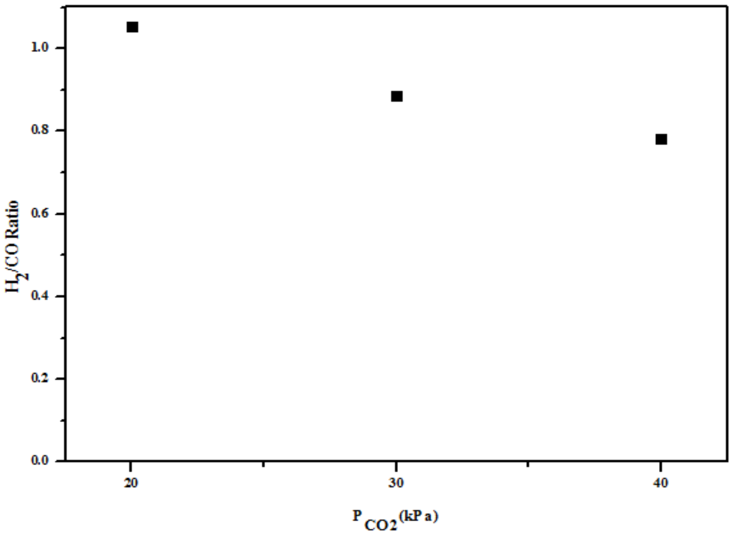


Figure 4-9 : Product H_2:CO ratios for dry reforming at 973 K.

From the Figure 4-9, the H_2:CO ratio on the bimetallic 3%Ce-10%Ni/Al_2O_3 catalyst was decreased with increasing P_{CO2} to below 1, indicating that the formation of carbon layer on the latter would have a lower H:C ratio and therefore more likely to undergo polycondensation to more resistant naphthalenic type species with time on-stream. Subsequently, the bimetallic Ni based hydrocarbon reforming catalysts would exhibit greater coking resilience than the undoped system (Hardiman, 2004). Although the H_2:CO ratio in CO_2-deficient environment (feed CO_2:CH_4 = 1) is highest in the bimetallic Ce-Ni catalyst, this trend was reversed when the P_{CO2} increased. Interestingly, H_2/CO ratio also reduced with an increase in CO_2 partial pressure and the ratio of H_2/CO was always inferior to unity for all runs reasonably due to the reverse water-gas shift reaction has a greater contribution and subsequently results a lower H_2 selectivity.

5 CONCLUSIONS

5.1 Conclusions

This project was carried out to investigate CH_4 dry reforming to produce synthesis gas and to explore the performance of alumina supported bimetallic Ni-based catalysts under different reaction conditions. Dry reforming has attracted attention due to the utilization of CO_2, which is a greenhouse gas, to produce syngas (H_2 and CO). Generally, water is used as one of the reactants in reforming, namely methane steam reforming while increasingly attention has been paid to CO_2 due to environmental issues. However, it require a higher energy in operating compared to methane steam reforming. It is also allows the procurement of carbon deposition kinetics to better understand the pathways leading to catalyst deactivation. Since it was believed that CH_4 decomposition is the root cause of carbon deposition. In order to have a better understanding in bimetallic system, the investigation and characterization of the catalysts studied were carried out. Accordingly, the effect of varying reaction conditions on the catalyst behavior under methane dry reforming was also probed.

Physical and chemical characteristics of the catalysts were also determined from N_2 physisorption, SEM, XRD and thermogravimetric studies. While the surface area of the calcined catalysts were lower than that of the calcined γ-Al_2O_3 support due to blockage of the pores by the metal oxides, the doping of the catalyst with second metal did not alter the surface area significantly. XRD analysis of the calcined catalysts showed the presence of γ-Al_2O_3 and metal oxide phases, in agreement with the observations from thermogravimetric calcination.

At first stage, fixed-bed reaction runs were performed at constant temperature 973 K and feed ratio of $CO_2/CH_4 = 1$ over the 3%Ce-10%Ni/Al_2O_3 catalyst and the steady-state reaction data was analysed. A higher H_2 and CO production rates were obtained due to the redox reaction between surface C_xH_{1-x} and nickel oxides. Among the catalysts employed, the bimetallic 3%Ce-10%Ni/Al_2O_3 catalyst has been further investigated and studied due to its superior performance in coking resistance. At second stage, the fixed-bed reaction runs were performed at constant temperature 973 K and various feed ratios ($CO_2/CH_4 = 1$; $CO_2/CH_4 = 1.5$; $CO_2/CH_4 = 2$) over only the bimetallic 3%Ce-

10%Ni/Al_2O_3 catalyst and subsequently the steady-state reaction data was analysed. Along the increase of the feed ratios, it is apparent that a decrease change of the H_2 formation rate but suggesting more effective utilisation of the surface carbonaceous species due to Boudourad reaction from excess CO_2.

5.2 Recommendations

For future work, the following remarks can be considered to further develop and improve the performance of methane dry reforming. Since it is important that catalystic properties such as surface area and active site dispersion may be influenced by the synthesis method, various catalyst preparation techniques, such solution precipitation methods, should be investigated. This thesis has demonstrated the benefits of doping dry reforming catalysts with second metals, Ce and Ni. A wider range of noble metals should be studied to further validate the advantages of incorporating this class of metal oxides into catalysts. Reaction runs could be performed on regenerated catalysts to study the amount of activity recoverable from the catalyst regeneration schemes. The temperature of reaction should be varied in a wide range from until 1273 K, So that, it would be best result kinetic studies of Considering the suitability of the product ratios to Fischer-Tropsch synthesis, an integrated reactor, incorporating dry reforming of CH_4 in the first stage and Fischer Tropsch synthesis of the resulting syngas in the second stage, may be investigated.

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APPENDICES

Preparation of 3%Ce-10%Ni/Al_2O_3 Catalyst

Similarly, the mass of components is calculated based on desired weight percentage for preparation of 3% Ce-10% Ni /Al_2O_3 catalyst.

Mass of Al_2O_3 = 0.87 x 20g = 7.4g

Mass of Ni required = 0.1 x 20g = 2.0g

Mass of Ce required = 0.03 x 15g = 0.6g

Given that 1 mol of metal is present in every 1 mol of salt used in the study, the amount of Ce and Ce needed has been determined by using calculation below.

Amount of Ce needed = (MW of $Ce(NO_3)2.6H_2O$ x 0.6g) / MW of Ce in $Ce(NO_3)2.6H_2O$

= (434.22g x 0.6g) / 140.11g

= 1.859 g

Amount of Ni needed = ($Ni(NO_3)_2.6H_2O$ x 2g) / MW of Ni in $Ni(NO_3)_2.6H_2O$

= (290.795 g x 2g) / 58.69g

= 9.90895 g