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

MUHAMAD HISYAM BIN ZAKARIA

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UNIVERSITI MALAYSIA PAHANG

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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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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 $T > 600\ ^{o}C$.	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

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

(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)

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

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