

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Synthesis gas production

Synthesis gas is a mixture of hydrogen and carbon monoxide. Its major uses are in fuel and chemical synthesis. Furthermore, for hydrogen production application, hydrogen can be separated to use in fuel cells via preferential oxidation (1), methanation (2) and membrane separation.



There are now several processes for synthesis gas production such as catalytic steam reforming of methane (CSRSM) and catalytic partial oxidation of methane (CPOM) depending on the purpose of industrial applications.

2.1.1.1 Catalytic steam reforming of methane (SRM)

Catalytic steam reforming of methane (CSRSM) is commercial process for production of synthesis gas using a mixture of methane and excess steam at temperature about 850°C and suitable catalyst. This process is considered as an economically and efficient process.

CSRSM is a two-stage-process. The first stage is highly endothermic reaction (3) which requires heat and catalyst. Catalyst used in this reaction typically is nickel or nickel complex on alumina oxide.



This reaction causes a higher yield of hydrocarbon by using iron (Fe) or chromium (Cr) oxide catalyst. The ratio of steam/methane in feed mixture is usually higher than unity in order to avoid carbon and excess carbon monoxide formation.

The next stage is water-gas-shift reaction (WGS reaction) (4) which usually taken place in another reactor at temperature about 130°C.



As a result of exothermic reaction of this reaction, it is possible to get high energy efficient heat by recovering and recycling heat to use in the first stage with heat exchanger but resulting in higher cost of production for heat exchanger.

Heat which needs to be supplied in the first reaction is provided by combustion of methane (5).



In practice, approximately 50% of the combustion energy contributes to the reaction process while the remaining heat is transferred to product stream and is recaptured and recycled.

Catalytic steam reforming of methane has efficiency about 80% and the need of heat recycling is mainly caused the high cost in this process.

Besides two main reactions process, there also are some side reactions occurring such as methanation (2), methane decomposition (6), and carbon monoxide disproportionation (Boudouard reaction) (7).



The last two reactions cause the carbon deposition on the catalyst which occurs in the form of filament and encapsulating carbon leading to the deactivation of catalytic activity and clogging the reforming reactor.

2.1.2 Catalytic partial oxidation of methane

Catalytic partial oxidation of methane (CPOM) is an alternative process to produce synthesis gas by passing methane and oxygen (air or pure oxygen) through a suitable catalyst at temperature range of 700-1000°C at atmospheric pressure. The reaction (8) occurs and yields synthesis gas product.



This reaction is mildly exothermic reaction, so it requires less energy to operate the reaction that causes this process more energy efficient. Furthermore, this process provides high methane conversion and also desired H₂/CO ratio for methanol and Fischer-Tropsch synthesis. Besides these benefits, catalytic partial oxidation of methane is considered more rapidly than the catalytic steam reforming of methane process.

Like a catalytic steam reforming of methane, the CPOM counter with some side reactions such as combustion (4), methanation (2), carbon monoxide disproportionation (7) and also water-gas-shift reaction (4).

The most challenge of CPOM is the deactivation of catalytic activity due to the carbon deposition from methane decomposition and carbon monoxide disproportionation reaction. Moreover, the sintering of metal catalyst at high temperature is also found. Thus, many studies have been focused on the catalytic partial oxidation of methane so as to modify the catalytic stability. Therefore, many literature surveys of this process are reviewed.

2.1.3 Carbon deposition on nickel catalyst

The two side reactions that cause the carbon to deposit on the nickel catalyst are the methane decomposition (6) and carbon monoxide disproportionation (7).

Bartholomew *et al.* (2001) proposed that carbon deposition can cause the deactivation of catalyst and breaking down the reactor by chemisorption on the catalyst surface resulting in blocking the reactant to metal active site, encapsulation the active site lead to the deactivation of the catalyst, plugging pore of the catalyst therefore reactant cannot react with many active site residing in the pore and in the worst case the carbon filament that occur in the pore cause the support fracture and disintegrate the catalyst pellet as well as plugging of reactor voids. The proposed mechanisms that accounted for the carbon deposition on metal catalyst from hydrocarbon such as methane and from carbon monoxide are illustrated in Figure 2.1 and 2.2, respectively.

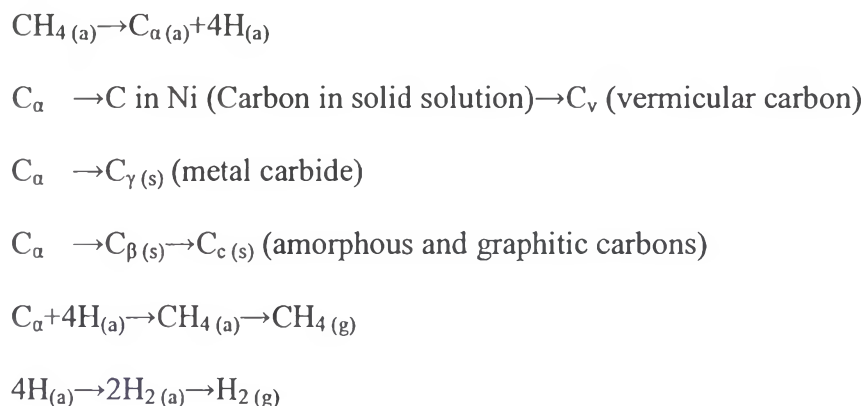


Figure 2.1 Carbon formation on metal surface from methane adapted from Bartholomew *et al.* (2001) (a, g, s refer to adsorbed, gaseous, and solid states, respectively).

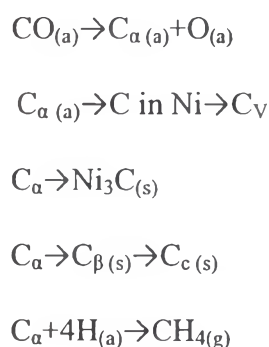


Figure 2.2 Carbon formation on metal surface from carbon monoxide. (a, g, s refer to adsorbed, gaseous, and solid states, respectively). (Bartholomew *et al.*, 2001).

C_{α} is the reactive atomic carbon species which may be polymerize to the less reactive carbon film C_{β} . Both C_{α} and C_{β} occur at low temperature (<300-375°C) and may be converted to the graphitic carbon at high temperature. The C_{β} film and graphitic carbon film encapsulate the metal surface causing the deactivation of the catalyst.

At temperature range of 375-650°C, the filamentous carbon may occur. The formation of this carbon causes by the precipitation of the dissolved carbon at the bottom of the metal active site and lifting up the metal away from the support.

The growth of filamentous carbon stops when the encapsulation on the metal surface occurs. Generally, the filamentous carbon does not cause the deactivation of the catalyst unless the large amount of this type of carbon forms and plugs the catalyst pore.

The factors that govern the rate and extent of carbon formation are reaction conditions namely; temperature, feed composition, catalyst structure i.e., metal type, crystal size, promoter, support and pore structure and the properties of catalyst such as the acidity and acid strength.

Temperature affecting on the rate of carbon formation can be considered in the kinetic aspect as shown in the following equation.

$$r_d = r_f - r_g \quad (9)$$

where r_d = rate of deactivation
 r_f = rate of carbon formation
 r_g = rate of gasification

The carbon formation can be avoided if the rate of gasification is higher than the rate of carbon formation. Nevertheless, these two reaction rates increase exponentially with the temperature, they are different in the pre-exponential factors and activation energy. Therefore, it is possible to operate at the safe region where the carbon formation can be avoided or reduced.

The reactivity of carbon formation depends on the type of the feed in the order: poly-nuclear-aromatics > aromatics > olefins > branch alkanes > normal alkanes. Furthermore, the higher CH_4/O_2 ratio leads to the more extent of carbon formation.

Catalyst structure such as metal active site can affect on the carbon formation in which the formation of carbon requires the larger ensemble site than methane dissociation due to the formation of C-C bonds.

The properties of the catalyst such as acidity and acid strength have an effect in which the higher acidity and acid strength lead to the more extent of carbon formation to occur.

2.2 Literature review

2.2.1. Methane partial oxidation

Methane is the most abundant organic compound on the earth. It is primary component in the natural gas. Methane mainly uses as fuel in industry, electricity, transportation and residence. Besides, it also use as a raw material to produce chemical by direct conversion such as oxygenation to methanol and formaldehyde, as well as oxidative coupling of methane to ethylene and ethane and indirect conversion that is synthesis gas which is then converted to methanol or higher chemicals.

Conversion of methane into synthesis gas is a technology that capable of contributing to a carbon-neutral energy chain in the future and for short term perspective, energy production or the production of fuels such as Fischer-Tropsch products and methanol from natural gas help reduce problems related to pollutants associated with coal (sulfur compound, heavy metals and fine air born particle) (Enger *et al.*, 2008).

A widely industrial-used process for converting methane into synthesis gas is catalytic steam reforming (CSR) (3).



This process is considered as economic and high efficient way for production of synthesis gas but there are some disadvantages. For instances, it requires a large amount of energy because of highly endothermic reaction (3), and it also needs excess steam to prevent carbon formation, last it gives high H₂/CO product ratio which is not suitable for application of Fischer-Tropsch synthesis.

Therefore, from the view of industry, it is quite attractive to develop a better steam reforming catalyst which can work under severe condition (lower temperature and lower steam/methane ratio) (Dong *et al.*, 2002)

An alternative route to produce synthesis gas is a catalytic partial oxidation of methane (8).



The benefits of this process over the catalytic steam reforming are shorter residence time, mildly exothermic reaction, therefore less energy usages and the desired H₂/CO product ratio of 2 that can be used directly for Fischer-Tropsch synthesis. (York et al., 2003) However, the main problem of this process is the deactivation of catalyst. This caused many efforts to study how to improve the stability of the catalysts.

2.2.2 Catalysts used in partial oxidation of methane

The catalysts that have been used in this reaction can be widely classified into two types which are the noble metal catalysts such as Rh, Ru, Pd and Pt and the non-noble metal catalysts such as Ni, Co and Fe.

2.2.2.1. Noble metal catalyst

The noble metal catalyst is well-known as a high activity and dominant stability in catalytic partial oxidation of methane. They have been many researches that studied about these noble metal catalysts such as Rh (Tanaka *et al.*, 2009; Salazar-Villalpando *et al.*, 2010; Mateos-Pedrero *et al.*, 2012), Ru (V. Choque *et al.*, 2009, 2010), Pt (Prieto *et al.*, 2010; Salazar-Villalpando *et al.*, 2011; Silva *et al.*, 2012) and Pd (Ryu *et al.*, 2008; Oemar *et al.*, 2011) supported catalyst.

Supported Rh catalyst is the one of the suitable component that is widely applied to various catalytic reaction especially partial oxidation of methane.

Tanaka *et al.* (2009) studied the effect of CeO₂ addition into 1wt% Rh/MgO on the catalytic partial oxidation of methane with and without N₂ dilution. They proposed that addition of CeO₂ had effect on the catalyst in two ways. One was prevention the oxidation Rh from the reaction with O₂. The other was the improvement of methane activation rate per the Rh surface site. Moreover, they found that the Rh-CeO₂/MgO (Ce/Rh = 4) exhibited comparable catalytic activity with Rh/MgO whereas exhibited the much lower in oxidation degree of the metal Rh.

Salazar-Villalpando *et al.* (2010) studied the role of the support in the conversion of methane to synthesis gas over Rh/Ce_{0.56}Zr_{0.44}O₂. They reported that the surface lattice oxygen was the chemical species participating in the

oxidation of methane to generate syngas. Furthermore, they also suggested that the feed oxygen was dissociatively adsorbed on the catalyst surface in atomic form by exchanging with oxygen of the solid catalyst that was limited by oxygen mobility. The Rh/Ce_{0.56}Zr_{0.44}O₂ exhibited the higher amount of oxygen exchange which was caused by the effect of oxygen spillover of metal particle, besides they also found the shift of maximum peak of oxygen exchange to lower temperature as compare to Ce_{0.56}Zr_{0.44}O₂.

Mateos-Pedrero *et al.* (2012) studied the effect of TiO₂ phase composition on the catalytic in performance and physic-chemical properties of supported Rh catalysts in the partial oxidation of methane. They found that the performance of supported Rh catalyst (conversion and selectivity) was improved when using anatase-rich TiO₂ support due to the improvement of dispersion and reducibility of rhodium particles. Moreover, the anatase-rich catalyst also exhibited the higher stability as compare with the rutile-rich catalyst due to the higher in reducibility of anatase-rich support.

Supported Ru catalysts provide the best performances among other noble metals in terms of H₂ and CO yields. The performance of supported Ru catalysts in the methane catalytic partial oxidation reaction strongly depends on the oxide used as support.

Choque *et al.* (2009) investigated Ru-based catalysts supported on Ta₂O₅-ZrO₂ and Nb₂O₅-ZrO₂. The effects of composition of support and ruthenium precursor were studied. They reported that Ru/Ta₂O₅-ZrO₂ and Ru/Nb₂O₅-ZrO₂ have higher catalytic activity than Ru/ZrO₂, Ru/Nb₂O₅, and Ru/Ta₂O₅ catalysts. Among these catalysts Ru/6TaZr and Ru/28NbZr exhibited the highest catalytic activity and syngas yield respectively. Moreover, no catalytic deactivation was observed on both two catalysts during 24 hours of time on stream. For the effect of Ru precursors, they reported that using RuCl₃ provided higher activity due to smaller particle sizes. Besides, they also reported that increased reaction temperature and adding CO₂-co feeding led to the higher in methane conversion and CO selectivity but lower the CO₂ selectivity.

Later, Choque *et al.* (2010) studied Ru/TiO₂-ZrO₂ catalyst for the partial oxidation of methane. The effect of support composition and the precursor

of ruthenium were also investigated. They reported that at the condition of catalytic test, the Ru/xTiZr catalysts exhibited the more active and selective to syngas than Ru/TiO₂ catalyst. For the effect of Ru precursor and increasing the temperature, they found the same results of their previous study.

Supported Pt catalyst is the widely studied noble metal catalyst due to its high stability and activity. There have been researched about modifying of supported Pt catalyst using oxygen conducting material.

Prieto *et al.* (2010) studied the new method to synthesis Pt-NPs/CeO₂-Al₂O₃ and Pt-NPs/Al₂O₃ catalyst. This method consisted of synthesizing of platinum nanoparticles (Pt-NPs) by colloidal method and then encapsulation of NPs in mesoporous Al₂O₃ and CeO₂-Al₂O₃ prepared by sol-gel method. Both Pt-NPs/CeO₂-Al₂O₃ and Pt-NPs/Al₂O₃ exhibited the well dispersed of metallic Pt on the support which no change occurred during calcinations and under partial oxidation of methane conditioning. They also suggested that doped CeO₂ improved the catalytic activity and stability due to the promotion of oxidation of carbon species that adsorbed on the active metal.

Salazar-Villapando *et al.* (2011) studied hydrogen production by catalytic partial oxidation of methane over Pt/(Ce_{0.91}Gd_{0.01})O_{2-x} and Pt/(Ce_{0.56}Zr_{0.44})O_{2-x}. They reported that both catalysts did not show the reduction of catalytic activity during 20 hours of time on stream. They suggested that the formation of a Pt-O-Ce bond caused high stability of Pt in Ce-containing supports under oxidizing conditions at high temperature because this bond act as an anchor which inhibiting the sintering of metallic Pt.

Silva *et al.* (2012) investigated the effect of ceria-zirconia content on the performance of Pt/x%CeZrO₂/Al₂O₃ (x=0-40%) during the partial oxidation of methane. They reported that Pt/10%CeZrO₂/Al₂O₃ and Pt/20%CeZrO₂/Al₂O₃ exhibited the highest stability during 24 hours of time on steam due to the high reducibility and consequently high oxygen mobility of the homogeneous solid solution form which promoted the mechanism of carbon removal from the metallic particle. At high CeZrO₂ content, the prepared catalysts exhibited the non-homogenous phase with ceria rich phase and zirconia rich phase for Pt/30%CeZrO₂/Al₂O₃ and an isolated zirconia phase was detected for

Pt/40%CeZrO₂/Al₂O₃. The non-homogeneous phase formation resulted in lower catalytic stability.

Even though, Palladium-based catalyst exhibits very good performance for methane combustion and alumina usually providing a good dispersion of the active metals, palladium catalyst supported on alumina is not stable at the high temperatures associated with methane oxidation reaction. There have been studies about adding some promoters to enhance the thermal stability of both the support and the active metal (Ryu *et al.*, 2008).

Ryu *et al.* (2008) investigated the effect of Ce, Ba and Sr addition on the activity of alumina-supported Pd catalysts used in the partial oxidation of methane. They reported that the addition of BaO resulted in a more stable support. Adding CeO₂ improved both thermal stability of the support and activity of Pd catalyst. Furthermore, the combined addition of BaO and CeO₂ exhibited the increasing of thermal stability and activity of catalyst. Moreover, addition small amount of SrO₂ to the CeO₂/BaO/Al₂O₃ support could increase the dispersion of the Pd particles leading to the higher partial oxidation activity and thermal stability. Therefore, the deactivation due to the sintering of the Pd particle was minimized. They proposed that the optimum composition for both high activity and the stability was Pd(2)/CeO₂(23)/BaO(11)/SrO(0.8)/Al₂O₃.

Oemar *et al.* (2011) studied the PdO-NiO/Y₂O₃ and PdO-NiO/Al₂O₃ on the catalytic performance for oxy-co₂ reforming of methane. They reported that PdO-NiO/Y₂O₃ showed the highest conversion in OCRM reaction due to the formation of metal-support compound (Pd_xO_yY_z compound) on the catalyst. The presence of β-oxygen species resulted in the promotion of the cracking of C-H bond in the CH₄. Besides, the PdO-NiO/Y₂O₃ also exhibited the high stability due to the ability of Y₂O₃ to form carbonate species which oxidizing the surface carbon on the metal.

Nematollahi *et al.* (2011) studied the noble metal such as Rh, Ru, Ir, Pd and Pt on Al₂O₃-MgO in combined dry reforming and partial oxidation of methane. They reported that increasing the reaction temperature led all catalyst to exhibit the higher conversion and both H₂ and CO selectivity. The following orders of activity were observed for different catalysts; Rh~Ru>Ir>Pt>Pd. All noble metal

catalyst also showed the high stability during reaction without any decreasing in methane conversion. However, they also found the carbon deposition of these catalysts. The combined dry reforming and partial oxidation of methane provided the higher in methane conversion and the lower in degree of carbon deposition and the H_2/CO ratio about 1 was obtained.

2.2.2.2. Non-noble metal catalysts

Due to the rareness and high cost of noble metal catalysts, most studies move to the non-noble metal catalysts such as nickel, cobalt, iron and copper (Slagtern *et al.*, 1998; Rogatis *et al.*, 2009; Yu *et al.*, 2011) in order to use as the catalyst in the partial oxidation of methane.

Slagtern *et al.* (1998) studied the iron-, cobalt-, and nickel-based catalysts for partial oxidation of methane to synthesis gas. Their results indicated that nickel-based catalyst exhibited the highest reforming activity than the other catalysts whereas iron-based catalyst exhibited poor reforming activity. They suggested that the metallic form of metal was an active form for partial oxidation of methane reaction while the oxide form was favor for total combustion reaction. Moreover, they proposed the order of reducibility of these metals in the following order: $Ni > Co > Fe$.

Rogatis *et al.* (2009) reported that 10%Ni/Al₂O₃ catalyst showed good catalytic performance whereas 10%Cu/Al₂O₃ exhibited the very poor catalytic partial oxidation activity.

Yu *et al.* (2011) studied the modification of supported cobalt catalyst for catalytic partial oxidation by adding a series of alkaline-earth metal promoters (Mg, Ca, Ba and Sr) as well as nickel with different contents. They found that adding alkaline-earth metals and nickel improved the catalytic activity, selectivity and stability of supported cobalt catalyst. The optimum composition was 4%Ni6%Sr6%Co/ γ -Al₂O₃.

Among the non-noble metal catalysts, nickel-based catalyst is attractive due to its high activity, low cost and abundance. However, nickel-based catalyst is suffered from the deactivation caused by carbon deposition and metal sintering at reaction temperature. So, a number of researches have been focused on

modifying nickel-based catalyst stability. Most studies deal with the support and the introducing of some promoters in order to improve the stability, as well as catalytic performance.

Miao *et al.* (1997) investigated the effect of alkali metal oxide (Li, Na, K) and rare-earth metal oxide (La, Ce, Y, Sm) addition on the performance and stability of NiO/Al₂O₃ catalyst during the partial oxidation of methane to synthesis gas. They reported that addition of alkali metal oxide improved the dispersion of active component nickel and the activity for the partial oxidation of methane reaction over the nickel-based catalysts. Moreover, these alkali metal oxide and rare-earth metal oxide also enhanced thermal stability during high temperature reaction and resistivity to carbon deposition over the nickel-based catalysts during the partial oxidation of methane reaction.

Tsipourari *et al.* (1997) studied the partial oxidation of methane reaction over Ni/La₂O₃ catalyst compared with the conventional catalysts such as Ni/γ-Al₂O₃, Ni/CaO (10 mol%)/ γ-Al₂O₃ and Ni/CaO. They reported that the Ni/La₂O₃ catalyst exhibited good activity and excellent stability while the other catalysts showed rapidly deactivation following the order: Ni/γ-Al₂O₃ > Ni/CaO > Ni/CaO (10 mol%)/ γ-Al₂O₃. They suggested that the excellent stability of Ni/La₂O₃ catalyst resulted from the decoration of the Ni particles by LaO_x species, which favored the removal of excess carbon deposition on the nickel crystallites. Thus, a fraction of the nickel surface was continuously cleaned of carbon and continuously participated in the reaction. They proposed that the deactivation rate was affected by the nature of the support employed, higher deactivation rates observed over support of higher acidity. Moreover, they suggested that the partial oxidation of methane to synthesis gas over the Ni/La₂O₃ catalyst followed mainly the indirect reaction mechanism which CH₄ was first converting to CO₂ and H₂O by combustion of CH₄ and then the unconverted CH₄ was reformed with CO₂ and H₂O to produce synthesis gas. Besides, from the studies of catalytic activity, they reported that high methane conversion and high selectivity to syntheses gas could be obtained either by increasing contact time or by raising reaction temperature.

Tang *et al.* (1988) examined Ni/MgO, Ni/CaO and Ni/CeO₂ catalysts with nickel loading of 13wt% at atmospheric pressure and temperature of

750 °C on the activity, stability and carbon deposition for partial oxidation of methane (POM). They reported that all catalysts had similar high conversion of methane and high stability to syngas. Among these catalysts, Ni/MgO exhibited the high resistance to carbon deposition even in severe condition ($\text{CH}_4/\text{O}_2=2.5$) due to its ability to inhibit carbon deposition especially from the carbon monoxide disproportionation. They suggested that the excellent performance of NiO/MgO resulted from the formation of solid solution between NiO and MgO that caused the nickel to have low reducibility, uniform dispersion and decreasing the donor ability of nickel.

Zhu *et al.* (2001) studied the partial oxidation of methane to syngas over Ni-CeO₂ catalysts with various nickel loading (5, 10 and 20at%). They reported that all catalyst exhibited high active and selective for partial oxidation of methane to syngas at temperature higher than 550°C but only 5 at% loading of nickel catalyst showed excellent resistance to carbon deposition and thus, had a high stability under reaction condition. They believed that the high stability of this catalyst was caused by the transfer of oxygen from ceria to the nickel interface, effectively oxidizing carbon species produced from methane dissociation on nickel.

Takeguchi *et al.* (2001) studied the performance of Ni/CeO₂-ZrO₂ catalysts for the partial oxidation of methane to synthesis gas. They reported that the catalytic activities of the Ni/CeO₂-ZrO₂ catalysts for the partial oxidation reaction of methane increased with increasing of oxygen storage capacity of the CeO₂-ZrO₂ solid solution indicating that this reaction proceeded by means of the redox mechanism. Furthermore, they also reported that Ni particles that having weak interaction with the support showed large amount of coke whereas the nickel particles having a strong interaction showed small amount of coke.

Wu *et al.* (2005) studied the partial oxidation reaction of methane to synthesis gas over the Ni/TiO₂ catalyst using a fixed-bed reactor. They reported that the Ni/TiO₂ exhibited high initial activity but lost activity during reaction. They suggested that this was because the SMSI between nickel oxides and titania, besides this, the occurring of NiO and NiTiO₃ in Ni/TiO₂ also caused the deactivation. Moreover, they reported that no appearance of carbon deposition on the

catalyst, therefore the decreasing of activity was not on account of carbon deposition on the Ni/TiO₂ catalyst.

Among various support of nickel-based catalyst, cerium oxide (CeO₂) is seem to be a promising one due to its unique redox properties and high oxygen storage capacity but is has some disadvantage about its poor thermal stability at high temperature. Therefore many studies have been focused on improving its properties by adding some additives such as zirconia (Otsuka *et al.*, 1999; Dong *et al.*, 2002; Roh *et al.*, 2002; Pengpanish *et al.*, 2002, 2004) as well as other promoters. Moreover, the prevention of coke formation has also been studied.

Otsuka *et al.* (1999) investigated a series of CeO₂-ZrO₂ composite oxide (Ce_{1-x}Zr_xO₂) for the gas-solid reaction with CH₄ in the absence of gaseous oxidant. They reported that at Zr content below 50 at%, the CeO₂-ZrO₂ solid solution still showed the fluorite structure and no change in degree of reducibility. Ce_{1-x}Zr_xO₂ provided synthesis gas with a H₂/CO ratio of 2 and higher in producing rate and lower activation energy than CeO₂ due to the incorporation of ZrO₂ into CeO₂ this caused the mobility of lattice oxygen to increase. Moreover, they reported the presence of Pt helped enhance the reaction rate.

Roh *et al.* (2002) studied the synthesis gas production by steam reforming of methane and reported that 15%Ni/Ce-ZrO₂ exhibited the best activity and stability. This high performance resulting from the combination of high oxygen storage capacity of ceria in Ce-ZrO₂, strong interaction between Ni and Ce-ZrO₂, basic properties of the catalyst and high capability of H₂ uptake.

The studies of Ni/Ce-ZrO₂ in oxy-reforming of methane were further investigated by Dong *et al.* (2002). They studied the effect of nickel content of Ni/CeZrO₂ catalysts on the performance of catalyst in oxy-reforming of methane (ORM) to synthesis gas. They reported that Ni/Ce-ZrO₂ catalyst with 15%Ni loading exhibited highest catalytic activity, selectivity, as well as stability. They suggested that Ni incorporation into Ce-ZrO₂ caused ceria more reducible which helped to produce mobile oxygen during the reforming reaction. Thus, decoking activity would likely be enhanced through the participation of the lattice oxygen. Moreover, they believed that the high performance of 15%Ni/CeZrO₂ was resulted from the well

balance between two kind of active sites which one for the activation of methane and the other one for the steam or oxygen.

Pengpanich *et al.* (2002) reported that the $\text{CeO}_{0.75}\text{Zr}_{0.25}\text{O}_2$ mixed oxide solid solution exhibited the good performance for methane oxidation due to the incorporation of Zr into CeO_2 lattice that promoted the redox properties. Later work (Pengpanich *et al.*, 2004) they studied methane partial oxidation (MPO) to synthesis gas over Ni/CeZrO_2 by varying the Ce/Zr ratio, nickel loading, and also studied the effect of preparation method. They reported that the catalyst prepared by impregnation method were more active than those prepared by gel impregnation method due to the higher degree of metal dispersion and reducibility. The 15wt%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst exhibited the best performance and stability to carbon deposition due to its high degree of metal dispersion and surface oxygen mobility. They also suggested that the carbon deposition on this catalyst was mainly from the methane decomposition. Furthermore, this catalyst also showed the regenerability under oxidizing atmosphere.

Pengpanich *et al.* (2007) studied the effect of Nb addition into 15wt%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ on the catalytic activity and resistivity to carbon deposition. They found that adding Nb caused catalytic activity and resistivity to carbon deposition of the 15wt%Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ to decrease. They suggested that this lower properties caused by the strong interaction between NiO and Nb-modified support, as well as the reduction of surface oxygen reducibility.

2.2.3 Methane Partial Oxidation Mechanisms

The mechanism of methane partial oxidation to synthesis gas has been intensively studied and proposed for a long time. It can be concluded that the mechanism of methane partial oxidation can be classified into two general types. The first one is the indirect partial oxidation of methane and the second one is the direct partial oxidation of methane

2.2.3.1 The indirect mechanism

The indirect mechanism involve with the methane total combustion and follows by the steam and/or carbon dioxide reforming reaction. Therefore this mechanism was called the combustion and reforming reactions mechanism (CRR).

York *et al.* (2003) concluded the studies of Vermeiren *et al.* in 1992 and their repeat work of Choudary. They suggested that the mechanism of the methane partial oxidation reaction proceeded by two steps. The first step was exothermic reaction followed by the second endothermic reaction. The following reaction mechanism was proposed to explain for these observations.



It could be explain that initially some of methane reacted with oxygen to form carbon dioxide and water which then reformed with the remaining portion of methane to generate the synthesis gas as the secondary product.

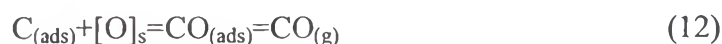
The studies that had done by Green and co-workers (1990) about the effect of reaction condition on the product distribution for methane partial oxidation. Applying the CRR mechanism was able to explain their experiments that at high space velocities or oxygen/methane ratios, the selectivity to carbon dioxide and water increased with the decrease of synthesis gas yield which implied that the synthesis gas was the secondary product.

2.2.3.2 Direct Partial Oxidation mechanism (DPO)

DPO mechanism or pyrolysis mechanism, produces CO directly without the pre-formation of CO₂. This mechanism involves two steps, namely the pyrolysis (CH₄→C+4H), followed by the oxidation of C to CO. (Dong *et al.*, 2002)

Hickman and Schmidt had proposed this mechanism in order to describe their results using rhodium- and platinum- coated monolith catalysts

under adiabatic conditions at very short contact times. For this mechanism synthesis gas was produced as a primary product.



They constructed a model incorporating the elementary adsorption, desorption and surface reaction steps involved in a mechanism of which some of the most important steps were shown in the above equations. This mechanism model could be explained their experiment results.

Dong *et al.* (2002) studied methane reforming over 15%Ni/CeZrO₂ catalysts. They suggested that the mechanism of this reaction over 15%Ni/CeZrO₂ catalysts followed the pyrolysis mechanism as shown below. (this mechanism they simplified from the work of Hu and Ruckenstein).



They explained that both methane and oxygen dissociated rapidly on the metallic Ni site and the presence of CeO₂ increased the dispersion of Ni on the surface of the catalyst and enhanced the methane dissociation.

2.2.4 Magnesium oxide (MgO)

Since the deactivation is the major problems of the Ni-based catalyst. The carbon deposition on the nickel-based catalyst and the sintering of metallic nickel at high temperature are responded for this problem. Therefore, there have had many investigations to improve the stability of the catalysts by modifying the properties of support or adding some additives to improve the stability of the catalyst. MgO is the one of additive that exhibits the ability to reduce the coke formation and also the sintering of metal at reaction temperature (Li *et al.*, 2009).

Ruckenstein *et al.* (1999) studied the partial oxidation of methane over NiO/MgO solid solution catalyst. They reported that NiO/MgO catalysts prepared by impregnation provided high conversions and selectivities, as well as high stabilities. They suggested that the NiO-MgO solid solution was account for the high performance and stability. The formation of NiO-MgO consisted of two steps. The first step was the diffusion of NiO over the surface of MgO, following with the diffusion of NiO from the surface to the MgO lattice. The NiO-MgO solid solution caused the Ni atoms to segregate over the surface of the catalyst, resulting in a high dispersion of Ni metal inhibiting the coke formation which requires large cluster of nickel. Moreover, the segregated Ni atoms interacted strongly with those remaining in the substrate resulting in the inhibition of their sintering at high temperature.

Yejun *et al.* (2007) studied the effect of adding MgO on the physico-chemical properties and catalytic performance of Ni/Al₂O₃ catalyst for partial oxidation of methane to synthesis gas. They reported that the strong interaction occurred between NiO and MgO indicating the formation of NiO-MgO solid solution. They proposed that the formed solid solution enhanced the NiO dispersiveness and inhibited the sintering of NiO crystallites. Both resulted effects improved the catalytic activity and stability, respectively. Conversely, the excessive MgO content caused the NiO crystallites to agglomerate led to the reduction of the catalytic performance. Moreover, adding the MgO also promoted the basicity of the catalyst resulting in increasing the CO selectivity.

Pue-on *et al.* (2011) studied the effect of preparation methods of NiO-MgO/Ce_{0.75}Zr_{0.25}O₂ and MgO contents on the catalytic performances (activity and selectivity) and resistivity to carbon deposition for POM. NiO-MgO/Ce_{0.75}Zr_{0.25}O₂ mixed oxide catalysts were prepared by the co-precipitation and multistep incipient wetness impregnation of MgO prior to NiO method. The amount of Ni content was fixed at 15wt% whereas the amount of MgO was varied of 0, 5, 10, and 15wt% on the supported catalysts. They reported that the multistep-impregnation method catalyst exhibited the higher activity and selectivity due to its higher metallic nickel dispersion at high temperature and lower in NiO-MgO interaction than co-impregnation catalyst. MgO caused the reduction in catalytic activity because the strong interaction between NiO and MgO which led to the

difficulty in reducing of NiO. Moreover, they proposed that the 15wt%Ni5wt%Mg/CZO catalyst exhibited the highest activity and possessed the highest stability. This catalyst could suppress the carbon deposition from the carbon monoxide disproportionation reaction.

Qiu *et al.* (2012) studied the effect of NiO-MgO on the reforming of biomass fuel gas. They proposed that the formation of NiO-MgO solid solution was the main reason for good catalytic performance which restrained the active nickel from agglomeration and provided high Ni dispersion and small Ni particles that stabilized the reduced nickel surface from carbon deposition.

Arusingkarat *et al.* (2012) studied the effect of low Mg loading and metal incorporated sequences on 15wt%Ni/Ce_{0.75}Zr_{0.25}O₂ for catalytic partial oxidation of methane. They reported that the addition of Mg resulted in lower the catalytic activity of the catalyst but caused the higher in catalytic stability. At the same loading of Mg, Ni-Mg/CZO exhibited the higher in catalytic activity whereas Mg-Ni/CZO provided the better in resistivity to carbon deposition. These results indicated that the sequence of metal loading had influence on the properties of prepared catalysts and the optimum content of Mg providing high activity and resistivity to carbon deposition was observed at 3%Mg.

2.2.5 The ternary oxides

Recently, there have been investigated the ceria-zirconia containing ternary oxide to use as a support for catalytic reaction. The various preparation methods, catalytic performance and carbon formation resistivity have been studied (Rathod *et al.*, 2010; Khan *et al.*, 2012; Sengupta *et al.*, 2012).

Rathod *et al.* (2010) studied the Ce₁Mg_xZr_{1-x}O₂ mixed metal oxides prepared by co-precipitation as the polymer synthesizing catalyst. They suggested that the incorporation of magnesia in the ceria-zirconia solid solution provided the increasing in the catalytic activity caused by the well dispersed in the ceria-zirconia solid solution

Khan *et al.* (2012) prepared the 5wt%Ni/Ce_{0.5}Zr_{0.33}M_{0.17}O_{2-δ} catalysts where M = Al, Ba, Ca, Hf, Pr, Sm, Sr, Tb, and Y for methane reforming reaction via the surfactant-assisted route under the basic condition. They found that the ternary

oxide supported catalyst provided superior surface area, pore volume, nickel dispersion, oxygen storage capacity (OSC) as well as the reducibility than the binary oxide supported catalyst. Among these catalysts the 5wt% Ni/Ce_{0.5}Zr_{0.33}M_{0.17}O_{2-δ} catalyst which M=Ca, La and Y exhibited the highest activity.

Sengupta *et al.* (2012) investigated 5wt%Ni/Ce_{0.5}Zr_{0.33}M_{0.17}O_{2-δ} catalyst where M = Mg, Ca, Y, La, CaMg and Gd for reforming reaction in application of hydrogen production. These catalysts prepared by surfactant-assisted methods under the basic condition. They proposed that the catalytic activity depended on metal dispersion and reducibility as well as the pore volume/surface area (PV/SA) ratio. They suggested that the addition of the promoter has strongly effect on metal dispersion, surface area and reducibility. Among the prepared catalysts, 5wt%Ni/Ce_{0.5}Zr_{0.33}Mg_{0.17}O_{2-δ} showed the best catalytic performance corresponding to the highest nickel dispersion.