



## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Background

##### 2.1.1 Processes of Synthesis Gas Production from Methane

Methane is the predominant component of Natural gas, which is forecast to become a major energy carrier because it is found plentifully in many locations around the world (B.P. Review of World Gas, 1987). Nowadays, the only economically available route for the conversion of methane to more valuable chemicals is via synthesis gas.

Several synthesis gas production processes are available for example steam reforming, partial oxidation, pyrolysis, gasification, thermolysis and electrolysis depending on the purpose of industrial application (York et al., 2003). Currently, the dominant industrial technologies for direct hydrogen production are steam reforming, partial oxidation and autothermal reforming process from methane or natural gas.

##### 2.1.1.1 *Steam Reforming (SR)*

To date, the only large-scale process for natural gas conversion is the endothermic reaction known as steam reforming to synthesis gas (J.R. Rostrup-Nielsen, 1984). Hydrogen is produced by the SR process in large centralized industrial plants for using in numerous applications, including chemical manufacturing and petroleum refining (York et al., 2003).

Steam reforming is the process to convert methane (and other hydrocarbons in natural gas) into hydrogen and carbon monoxide or synthesis gas by reaction with steam over catalyst.

The SR process consists of the following two important steps.

##### 2.1.1.1.1 *Reformation of Natural Gas*

The first step of the SMR process involves methane reacting with steam at 750-800°C (1380-1470°F) to produce a synthesis gas (syngas), a mixture primarily made up of hydrogen (H<sub>2</sub>) and carbon monoxide (CO).



This reaction is highly endothermic. Thus, a large amount of energy is necessary consumed to supply this reaction. Typically, this reaction has to be operated over supported nickel catalyst at pressures in the range of 15 to 30 atm and high temperature of 850 to 900°C.

#### 2.1.1.1.2 Shift Reaction

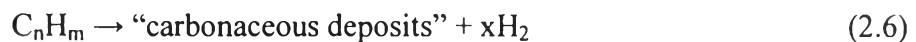
In the second step, known as a water gas shift (WGS) reaction, the carbon monoxide produced in the first reaction is reacted with steam over a catalyst to form hydrogen and carbon dioxide (CO<sub>2</sub>). This process occurs in two stages, consisting of a high temperature shift (HTS) at 350°C (662°F) and a low temperature shift (LTS) at 190-210°C (374-410°F).



The other reversible reaction which occurs in SMR is methanation reaction.



Both water-gas shift (2.2) and methanation (2.3) reactions occur simultaneously. Moreover, Reactions (2.1) to (2.3) may be accompanied by carbon forming reactions.



At high temperature (above 650°C), the hydrocarbons may react in parallel to Reaction (2.1) by thermal cracking (called “steam cracking”) into olefins which may easily form coke by Reaction (2.6). The risk of carbon formation must be eliminated in operation since carbon causes serious operational troubles such as deactivation of the catalyst and increasing pressure drop. Therefore, the addition of excess steam is normally used to avoid coke formation.

For the advantages, steam reforming of natural gas offers an efficient, economical, and widely used process for hydrogen production,

and provides near- and mid-term energy security and environmental benefits. The efficiency of the steam reforming process is about 65% to 75%, among the highest of current commercially available production methods. Natural gas is a convenient, easy to handle, hydrogen feedstock with a high hydrogen-to-carbon ratio.

Moreover, York et al.(2003) indicated the advantages of steam reforming are low carbon deposition , suitable for high-pressure processes and easy separation of the products. On the contrast, they also reported the disadvantages of the steam reforming process are high H<sub>2</sub>/CO ratio, need separation for follow-up F-T or methanol synthesis and energy intensive process. Besides, the other disadvantages are high energy consumption and intensive capital cost.

Therefore, a lot of research has been focused to investigate reforming catalyst conditions in order to solve these problems and improve reforming efficiencies.

#### *2.1.1.2 Partial Oxidation*

Recently, partial oxidation (POX) is considered an alternative route to synthesis gas production. The principal advantage of the partial oxidation process over steam reforming is that it can operate on any kind of hydrocarbon feed. Furthermore, no desulfurization is required prior to the partial oxidation step. The principal disadvantage is the necessity for providing a supply of 95 – 95% pure oxygen. This results in increasing plant investment and operating costs.

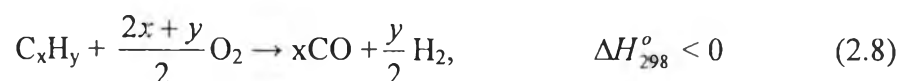
In POX, the processes carry out the partial oxidation by burning hydrocarbon with oxygen or oxygen-rich mixtures to produce gas that contains hydrogen and carbon monoxide small quantities of carbon dioxide, water vapor and methane. The thermal oxidation is run at 30–100 atm with pure O<sub>2</sub> using a special burner inside a refractory lined vessel at temperatures of 1200°C and above.

The partial oxidation can be separated into two processes including with and without catalysts. The first one is the partial oxidation with catalysts which is called “catalytic partial oxidation (CPOX)”. The general reaction can be described by:



In CPOX, the using several types of catalyst reduces the required temperature to around 800°C – 900°C. The CPOX has received intensive attention because of its mild exothermic reaction, short contact time, high methane conversion, high selectivity for CO and H<sub>2</sub>, and low cost (Dajiang *et al.*, 2007). The choice of reforming technique depends on the sulfur content of the fuel being used. CPOX can be employed if the sulfur content is below 50 ppm. The higher sulfur content would poison the catalyst, so the TPOX procedure is used for such fuels.

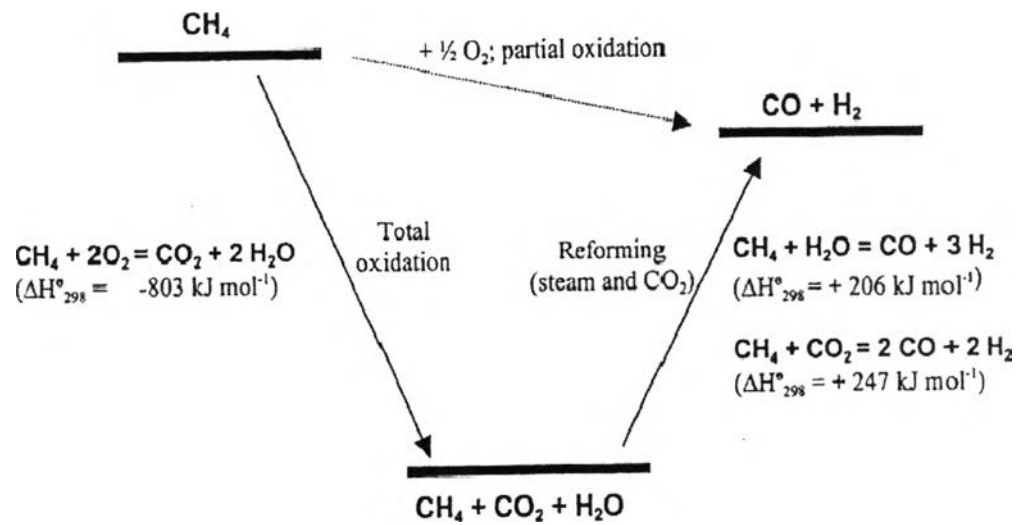
For the second one, the partial oxidation without catalysts can be called “thermal partial oxidation (TPOX) or non-catalytic partial oxidation”. This process is dependent on the air-fuel ratio. It is operated at temperatures of 1200°C and above. The general reaction can be described by:



Either CPOX or TPOX requires huge amounts of O<sub>2</sub> available continuously. Hence, these processes require the substantial investment in an adjoining O<sub>2</sub> plant. The additional unit operations are required for gas purification and to remove soot from the waste water. Thus, the operation is quite complex and less energy efficient when compared with steam reforming. Although, the CPOX of hydrocarbons is attractive nowadays, the challenge is to avoid the runaway oxidation of hydrocarbons to CO<sub>2</sub> and water.

Ideally, the partial oxidation of methane to synthesis gas is preferred as described below:





**Figure 2.1** Thermodynamic representation of the partial oxidation of methane (York *et al.*, 2003).

Figure 2.1 shows the partial oxidation of methane schematically. York *et al.* (2003) also indicated that this process provides many thermodynamic advantages over steam reforming :

- Partial oxidation is mildly exothermic, while steam reforming is highly endothermic. Thus, a partial oxidation reactor would be more economical to heat. In addition it can be combined with endothermic reactions, such as steam reforming or dry reforming with carbon dioxide to make these processes more energy efficient
- The  $\text{H}_2/\text{CO}$  ratio produced in stoichiometric partial oxidation is around 2, and this ratio is ideal for downstream processes, in particular methanol synthesis. This avoids the need to remove valuable hydrogen, which is produced in excess in steam reforming.
- The product gases from methane partial oxidation can be extremely low in carbon dioxide content, which must often be removed before synthesis gas. And these gases can be used in downstream.

- Partial oxidation technology avoids the need for large amounts of expensive superheated steam. However, an oxygen separation plant, which is also costly, may be required in cases where nitrogen (from air) is undesirable in high-pressure downstream processes.

The other advantages, which may provide the greatest potential for fast and economical process are high conversion, high selectivity and vary short residence time. For this reason, the partial oxidation of methane to synthesis gas has been extensively studied in terms of its mechanism and the characterization of the catalyst. Therefore, the many literature surveys of this process are reviewed.

## 2.2 Literature Review

### 2.2.1 Methane Partial Oxidation

Methane is the predominant component of natural gas as well as is an important raw material for the chemical industry. The methane conversion processes can be classified in two classes involved direct and indirect conversion.

The direct conversion of methane has focused on the oxidative of coupling to ethylene and ethane as well as on the oxygenation to methanol and formaldehyde (Chellappa and Viswanath, 1995). However, these processes exhibit either low conversion or low selectivity and have not been appreciable to commercial application.

The indiract process is convert methane to synthesis gas (CO and H<sub>2</sub>) as intermediate, which can be easily produced to methanol or higher hydrocarbons by methanol or Fischer–Tropsch synthesis.

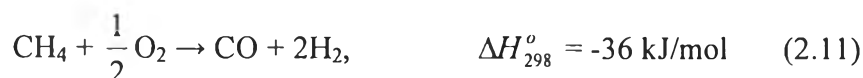
At this time, the only economically available route for the conversion of methane into more valuable chemicals is via synthesis gas. Using methane to prepare synthesis gas can be processed through three reactions i.e. steaming reforming, dry reforming and partial oxidation. To date, the only large-scale process for natural gas conversion is the endothermic reaction known as steam reforming to synthesis gas (J.R. Rostrup-Nielsen et. al., 1984):



In 1890, Mond and Langer improved the process by using a nickel catalyst. However, nickel also promotes carbon formation, which leads to catalyst deactivation and reactor plugging.

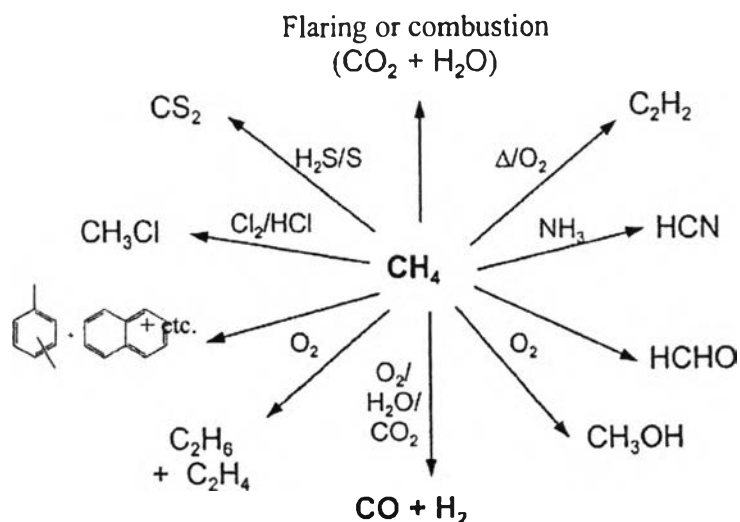
Rostrup-Nielsen et. al. (1984) reported that to overcome this problem, and render carbon formation thermodynamically unfavorable, industrial steam reformers add excess quantities of steam to the feedstock. While suppressing carbon formation, this practice creates a new problem, namely an increase in the  $\text{H}_2/\text{CO}$  and  $\text{CO}_2/\text{CO}$  ratios, where low ratios are desirable for optimal downstream processes.

An alternative process for synthesis gas formation is the exothermic methane partial oxidation reaction.



Normally, the partial oxidation of methane to synthesis gas occurs at very high temperature ( $>1200^\circ\text{C}$ ). The use of a catalyst can reduce the operating temperature to achieve thermodynamic equilibrium (Tsang *et al.*, 1995). Many metals have been investigated as the catalysts for methane partial oxidation.

A summary of some of the routes that have been investigated for methane utilization and valorization is shown in Figure 2.2.



**Figure 2.2** Summary of methane conversion routes (York *et al.*, 2003).

## 2.2.2 Catalysts for Partial Oxidation of Methane to Synthesis Gas

After nearly 100 years of development, two main types of catalysts have been investigated for the partial oxidation of methane to synthesis gas. They are supported nickel, cobalt or iron catalysts and supported noble metal catalysts

### 2.2.2.1 *Noble Metal Catalysts*

The group of noble metals such as Pt, Pd, Ru, and Rh is employed in the investigation of catalytic methane partial oxidation. Green and co-workers (1990-1995) showed that high yields of synthesis gas can be obtained over nearly all the noble metal catalysts used, as well as over the rare earth ruthenium pyrochlores. Further, all the catalysts were catalysing the partial oxidation reaction to thermodynamic equilibrium, ignoring elemental carbon formation. No carbon deposition was seen on these catalysts

Because of the high performance of the noble metal catalysts for the POM reaction to synthesis gas, these catalysts have attracted great attention and have been widely studied in the last many decades.

Hickman and Schmidt (1993) reported that Rh and Pt supported on monolith are excellent partial oxidation catalysts giving greater than 90% methane conversion and synthesis gas selectivity at temperature around 850°C with CH<sub>4</sub>/O<sub>2</sub> feed ratio of 2 and extremely fast space time (10<sup>-4</sup>–10<sup>-2</sup> sec). Other studies have also been carried out on Ru, Pd and Pt.

Elmasides et al. (2001) studied in Ru supported catalyst and reported that high selectivity to synthesis gas (>65%) is obtained over Ru/TiO<sub>2</sub> catalyst in the low methane conversion range. Whereas, small or zero selectivity to synthesis gas is observed over Ru catalysts supported on other materials.

Hochmuth(1992) has investigated partial oxidation of methane over Pt-Pt impregnated monolith catalyst. He also found that there was initial exothermic combustion on the front catalyst bed which generated H<sub>2</sub>O and CO<sub>2</sub>. Then this was followed by H<sub>2</sub>O and CO<sub>2</sub> reforming reactions together with the water-gas shift reaction. Moreover, he concluded that the precious metal based catalyst is



extremely active driving both H<sub>2</sub>O and CO<sub>2</sub> reforming reactions to equilibrium very quickly.

A study in Rh and Ru supported catalyst was investigated by Yan *et al.* (2004). They reported that the methane conversion and selectivity to H<sub>2</sub> and CO were higher over Rh/SiO<sub>2</sub> than over Ru/SiO<sub>2</sub> catalysts under the same condition.

Pantu and Gavalas (2002) reported that high methane conversion and high selectivity to CO and H<sub>2</sub> is obtained over Pt/CeO<sub>2</sub> at temperature over 650°C and CH<sub>4</sub> to O<sub>2</sub> feed ratio varied from 1.7 to 2.3.

Ji *et al.* (2001) studied the carbon deposition of many noble metal catalysts on the CPOX of methane to syngas in a fluidized bed. They reported that Rh-based catalyst could achieve the highest activity and lowest the carbon deposition when compared with Pt and Pd-based catalysts.

Among noble metals, Rh is found to be a suitable catalyst for methane partial oxidation by Mallens *et al.* (1997). They reported that the methane partial oxidation over Rh showed higher methane conversion and higher CO and H<sub>2</sub> selectivities than Pt at a comparable temperature.

#### 2.2.2.2 Transition Metal Catalysts

Although many noble metals based catalysts, especially Rh-based catalysts, are found to exhibit high activity and selectivity with good long-term stability. However, the high cost and limited availability over noble metals are the major problems to develop alternative catalysts. Thus, the transition metal group is also investigated for methane partial oxidation. Many different transition metals such as Cu, Co, Fe and Ni have been described in the literature.

Nickel based catalysts are attractive for this reaction due to their high activity and low cost. Hegarty *et al.* (1998) studied steam reforming and partial oxidation of methane over Cu, Co, Fe and Ni supported on ZrO<sub>2</sub> catalysts at the temperature from 400 to 800°C. The result showed that the activity of the catalysts were found to decrease in the order Ni>Cu>Co>Fe.

Au *et al.* (1996) studied the methane partial oxidation over Ni/SiO<sub>2</sub> catalyst compared with that over Cu/SiO<sub>2</sub> catalyst. They found that methane

conversion over Ni/SiO<sub>2</sub> was significantly higher than that over Cu/SiO<sub>2</sub>. The main products produced by methane partial oxidation over Cu/SiO<sub>2</sub> catalyst are CO<sub>2</sub> and H<sub>2</sub>O while those over Ni/SiO<sub>2</sub> catalyst are CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, surface carbon and small amount of CO.

However, Ni is easily deactivated by carbon deposition. The forms of carbon deposition presented on supported Ni catalysts during methane partial oxidation are both whisker and encapsulate forms (Takeguchi *et al.*, 2001). Tsipouriari *et al.* (1998) reported that Ni based catalyst are prone to carbon deposition and that activation rate is affected by the nature of used support. Therefore, the development of Ni based catalysts with stable operation can be achieved. Many types of support for Ni-supported catalyst were studied for methane partial oxidation such as Al<sub>2</sub>O<sub>3</sub> (Ji *et al.*, 2001), TiO<sub>2</sub> (Wu *et al.*, 2005), CaO (Tang *et al.*, 1998; Tsipourirari *et al.*, 2001), CeO<sub>2</sub> (Tang *et al.*, 1998; Zhu and Flytzani-Stephanopoulos, 2001), MgO (Tang *et al.*, 1998), and SiO<sub>2</sub> (Au *et al.*, 1996).

Dissanayake *et al.* (1991) studied the partial oxidation of methane over Ni/Al<sub>2</sub>O<sub>3</sub> in the temperature range of 450-900°C. They reported that carbon monoxide selectivities approaching 95% and virtually complete conversion of the methane feed can be achieved at temperature >700 °C.

Ji *et al.* (2001) studied the partial oxidation of methane over Ni/Al<sub>2</sub>O<sub>3</sub>. They showed that Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was a low rate of carbon formation in a fluidized-bed reactor. The CH<sub>4</sub> conversion as well as CO and H<sub>2</sub> selectivities remained constant at 92, 94 and 99.0%, respectively.

Wu *et al.* (2005) studied the partial oxidation of methane to H<sub>2</sub> and CO over a Ni/TiO<sub>2</sub> catalyst at temperature from 300 to 800°C. They found that Ni/TiO<sub>2</sub> catalyst showed higher CH<sub>4</sub> conversion as well as CO and H<sub>2</sub> selectivities at 800°C. POM conversion was decreased when reaction time increased due to the formation of NiO and NiTiO<sub>3</sub> in Ni/TiO<sub>2</sub>.

Tsipouriari *et al.* (1998) studied the catalytic partial oxidation of methane to synthesis gas over various Ni-based catalysts. They found that the rate of deactivation followed the order: Ni/γ-Al<sub>2</sub>O<sub>3</sub>>Ni/CaO-γ-Al<sub>2</sub>O<sub>3</sub>>Ni/CaO. They concluded that the higher deactivation rates observe over supports of higher acidity.

Tang *et al.* (1998) studied partial oxidation of methane to syngas over Ni/MgO, Ni/CaO and Ni/CeO<sub>2</sub> catalysts. They reported that all catalysts had similar high conversion of methane and high selectivity to syngas, which nearly approached the values predicted by thermodynamic equilibrium. However, only Ni/MgO showed high resistance to carbon deposition under thermodynamically severe conditions.

Au *et al.* (1996) studied the methane partial oxidation over Ni/SiO<sub>2</sub> catalyst compared with that over Cu/SiO<sub>2</sub> catalyst. They found that methane conversion over Ni/SiO<sub>2</sub> was significantly higher than over Cu/SiO<sub>2</sub>. The main products produced by methane partial oxidation over Cu/SiO<sub>2</sub> catalyst are CO<sub>2</sub> and H<sub>2</sub>O while those over Ni/SiO<sub>2</sub> are CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, surface carbon and small amount of CO.

Use of reducibility support could result in further activity and decrease coke deposition (Noronha *et al.*, 2001; Pantu and Gavalas, 2002). Currently, CeO<sub>2</sub> has been suggested for uses to store and release oxygen under lean and rich conditions. Therefore, a number of studies have been conducted to increase the stability of Ni catalysts by using CeO<sub>2</sub> as the support.

Otsuka *et al.* (1998) reported that CeO<sub>2</sub> could be able to convert methane to synthesis gas with H<sub>2</sub> to CO ratio of 2 and that adding Pt black could promote syngas formation rate. This finding similar for methane partial oxidation over Ni/CeO<sub>2</sub> catalyst was studied by Dong *et al.* (2002). They also proposed mechanism over Ni/CeO<sub>2</sub> that methane dissociates on Ni and the resultant carbon species quickly migrate to the interface of Ni-CeO<sub>2</sub> and then react with lattice oxygen of CeO<sub>2</sub> to form CO.

However, ceria still has some disadvantages. Ceria has a poor thermal resistant and stability at high temperatures. Ni over ceria-supported was an active catalyst for methane partial oxidation but rapidly deactivated by carbon deposition was studied by Tang *et al.* (1998).

Gonzalez-Velasco *et al.* (1999); Vidal *et al.* (2000); Roh *et al.* (2002) has been reported that addition of ZrO<sub>2</sub> to CeO<sub>2</sub> can improve its oxygen storage capacity, redox properties, thermal resistance and better catalytic activity at low temperature. This was found to be due to the partial substitution of Ce<sup>4+</sup> with

Zr<sup>4+</sup> in the lattice of CeO<sub>2</sub>, which forms a solid solution formation (Otsuka *et al.*, 1999; Chen *et al.*, 2008). It was demonstrated that CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides produced synthesis gas with H<sub>2</sub> to CO ratio of 2 and the formation rates of H<sub>2</sub> and CO were increased due to the incorporation of ZrO<sub>2</sub> into CeO<sub>2</sub>.

Hori *et al.* (1998) reported that the beneficial effects of ZrO<sub>2</sub> were pronounced in solid solutions which had the oxygen storage capacity values 3–5 times higher than that of pure CeO<sub>2</sub>. When the optimum Zr dopant concentration was 25 mol%, solid solution material aged at 1000°C showed a higher oxygen storage capacity than that of pure CeO<sub>2</sub>. This result could be ascribed to an occurrence of Zr promotion via an alteration of bulk properties of the CeO<sub>2</sub>. Furthermore, the redox properties of the CeO<sub>2</sub> have been enhanced by the addition of Zr<sup>4+</sup> into the lattice of CeO<sub>2</sub> by formation of solid solution. Nevertheless, it was also reported that CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution showed a high catalytic activity, particularly for oxidation of CO, and CH<sub>4</sub> (Bozo *et al.*, 2000; Gonzalez-Velasco *et al.*, 1999; Otsuka *et al.*, 1999).

It has been reported that addition of ZrO<sub>2</sub> to CeO<sub>2</sub> can improve its oxygen storage capacity, redox properties, thermal resistance and better catalytic activity at low temperatures (Formasiero *et al.*, 1995; Gonzalez-Velasco *et al.*, 1999; Vidal *et al.*, 2000)

Villalpando *et al.* (2009) studied the catalytic performance of Ni dispersed on ceria-doped supports are Zr, Gd and La at different ratio. They found that the Ni/Ce<sub>0.56</sub>Zr<sub>0.44</sub>O<sub>2-x</sub> showed higher hydrogen production than the other catalysts, which may be due to its higher reducibility and higher surface lattice oxygen.

Pengpanich *et al.* (2002) reported that the CO oxidation activity of the mixed oxides was found to be dependent on the Ce to Zr ratio and Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> solid solution exhibited the highest reducibility. This might be due to the highly uniform solid solution particles of ceria-zirconia were obtained and the incorporation of Zr into the CeO<sub>2</sub> lattice was found to promote the good redox properties.

Pengpanich *et al.* (2004) studied methane partial oxidation over Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxide solid solution catalysts. They reported that catalysts prepared by impregnation method are more active than those prepared by gel impregnation method. The Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> mixed oxide catalysts were active at

temperatures above 550°C, and resist to coke formation more than the other catalysts due to their high degrees of metal dispersion and surface oxygen mobility.

### 2.2.3 Methane Partial Oxidation Mechanisms

Currently, many studies concerning the elucidation of the methane partial oxidation mechanism has been carried out. Nevertheless, the most convincing studies will be discussed. Two general mechanisms have been proposed for the oxidative conversion of methane to synthesis gas over metal catalysts. One is an indirect mechanism involving methane total combustion, followed by steam and dry reforming reactions. These reactions are often referred to as the combustion and reforming reactions mechanism (CRR).

The second mechanism is direct oxidation mechanism in which surface carbon and oxygen species can combine to form primary products. These known as the direct partial oxidation mechanism (DPO).

First mention of the DPO mechanism was made by Prettre et al. (1946). After that, their experiments were repeated by Vermeiren et al. in 1992 which their results indicated that the longitudinal temperature profile of the catalyst bed was not uniform. At the front of the catalyst bed, the temperature was significantly higher than that of the latter part of the catalyst bed and the furnace temperature.

In addition, York et al.(1993) used high reactant flow rates over a Ni/MgO catalyst in an attempt to achieve non-equilibrium product distributions. Their results clearly showed the presence of a hot-spot at the front of the catalyst bed. These studies point to an initial exothermic methane combustion to CO<sub>2</sub> and H<sub>2</sub>O, followed by endothermic reforming reaction of the rest of CH<sub>4</sub> with CO<sub>2</sub> and H<sub>2</sub>O to produce synthesis gas. The reaction mechanism as shown in figure 2.1 has been proposed to account for these observations.

Initially, part of the methane reacts with oxygen to form carbon dioxide and water, and then these products reform the remainder of the methane to give the product synthesis gas. Indeed, it should be noted that the noble metals and nickel have all been shown to catalyze methane steam and dry reforming to synthesis gas very efficiently. In this reaction mechanism synthesis gas is a secondary product.

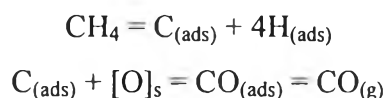
Green *et al.* (1990) studied the effect of reaction conditions on the product distribution for methane partial oxidation. Again the CRR mechanism was

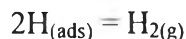
able to account for the fact that at higher space velocities or oxygen/methane ratios the selectivity to carbon dioxide and water increases at the expense of synthesis gas, again indicating that synthesis gas is a secondary product.

The mechanism of methane partial oxidation over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was investigated by Dissanayake *et al.* (1991). They reported that the mechanism was related to the oxidation state and phase composition of catalyst. Under operating condition, the previously calcined catalyst bed consists of three different regions. The first these, contacting the initial CH<sub>4</sub>/O<sub>2</sub>/He feed mixture, is NiAl<sub>2</sub>O<sub>4</sub>, which has only moderate activity for complete oxidation of methane to CO<sub>2</sub> occurs, resulting in an exotherm in this section in the bed. As a result of complete consumption of O<sub>2</sub> in the second region, the third portion of the catalyst bed consists of a reduced Ni/Al<sub>2</sub>O<sub>3</sub> phase. Formation of the CO and H<sub>2</sub> products occurs in this final region via reforming reactions of methane with the CO<sub>2</sub> and H<sub>2</sub>O produced during the complete oxidation reaction over the Ni/Al<sub>2</sub>O<sub>3</sub> phase.

The second partial oxidation mechanism or DPO mechanism has been proposed by Hickman and Schmidt in 1993. This mechanism was used to explain their results using rhodium- and platinum-coated monolith catalysts, under adiabatic conditions at very short residence times.

For the direct partial oxidation mechanism, CO and H<sub>2</sub> are produced directly by recombination of CH<sub>x</sub> and O species at the surface of the catalysts. Hickman and Schmidt claimed that CO and H<sub>2</sub> are the primary products of methane partial oxidation reaction over Rh coated monolith catalyst under adiabatic conditions at very short contact time. They proposed that the mechanism involved direct formation of H<sub>2</sub> initiated by CH<sub>4</sub> pyrolysis on the surface to give surface C and H species. The H atoms dimerize and desorb as H<sub>2</sub> while the surface C atoms react with adsorbed O atoms and desorbs as CO. In this proposed mechanism, 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 are shown in the equations below.





A similar finding was reported by Mallens *et al.* (1997). They studied the mechanism of methane partial oxidation over Rh catalyst by a Temporal Analysis of Products (TAP) set-up. It was found that synthesis gas is produced as primary product.  $\text{H}_2$  is formed via the associative adsorptions of two hydrogen adsorbed atoms from reduced Rh and the reaction between carbon adsorbed atoms and oxygen present as rhodium oxide results in the formation of carbon monoxide.

Recently there have been studies of partial oxidation mechanism over several specific catalysts and under specific condition. Weng *et al.* (2000) studied supported Rh and Ru catalysts using in situ time resolved FTIR spectroscopy. They found that CO is the primary product of partial oxidation of methane reaction over reduced and working state Rh/ $\text{Al}_2\text{O}_3$  catalyst. Direct oxidation of  $\text{CH}_4$  is the main pathway of synthesis gas formation over Rh/ $\text{SiO}_2$  catalysts.  $\text{CO}_2$  is the primary product of partial oxidation of methane over Ru/ $\text{Al}_2\text{O}_3$  and Ru/ $\text{SiO}_2$  catalysts. The dominant reaction pathway of synthesis gas formation over Ru/ $\text{Al}_2\text{O}_3$  catalysts is combustion and reforming reaction mechanism. On the Rh/ $\text{SiO}_2$  catalyst, the main reaction is apparently direct partial oxidation mechanism, and also the reaction mechanism appears to be related to the concentration of  $\text{O}_2$  in the feedstock.

Not only noble metals but also nickel catalysts are proposed for direct methane partial oxidation mechanism. Dong *et al.* (2002) proposed a mechanism over Ni/ $\text{CeO}_2$  where  $\text{CH}_4$  dissociates on Ni and the resultant carbon species quickly migrate to the interface of Ni- $\text{CeO}_2$  and then react with lattice oxygen of  $\text{CeO}_2$  to form CO.

Ruckenstein(1999) showed that over Ni/ $\text{SiO}_2$ , CH,  $\text{CH}_2$  and  $\text{CH}_3$  species are formed during the reaction.  $\text{CH}_4$  is activated via its dissociation before oxidation. The amount of methane involved in the isotopic exchange reaction was larger than that converted to CO and  $\text{CO}_2$ . Consequently, the dissociation of methane is not rate determining. Over an unreduced NiO/ $\text{SiO}_2$  catalyst, methane reacts directly with oxygen without its predissociation.

Jin *et al.* (2000) obtained similar results over Alumina-supported nickel catalysts. Their results indicated that the reaction temperature can significantly change the reaction mechanism. From Ruckenstein(1999), over NiO/MgO the

pyrolysis mechanism was dominant at 973 and 1023K , but at 123K the combustion reforming mechanism also played a role.

Li et al. (2000) conducted their research by keeping the catalyst surface in the reduced state is the precondition of high conversion of CH<sub>4</sub> and high selectivities to CO and H<sub>2</sub>. The surface state of the catalyst decides the reaction mechanism and plays a very important role in the conversions and selectivities of partial oxidation of CH<sub>4</sub>. Surface Ni–C and Ni–O bonds are proposed in the partial oxidation of methane to synthesis gas.

#### 2.2.4 Nickel-based Catalysts and Carbon Deposition

Many researchers found that synthesis gas with the product ratio of H<sub>2</sub>/CO = 2 could be produced at 1000–1200K and 1 atm over supported nickel catalysts. Most researchers had similar conclusions to these early researchers. The nickel is highly active for synthesis gas production, but that it also catalyses carbon formation.

Lunsford and co-workers (1990) studied a nickel supported on alumina partial oxidation system in the temperature range 720–1173K. They reported that CO selectivity approaching 95% and virtually complete conversion of methane could be achieved at temperatures higher than 973 K. However, that stable operation is not sustainable unless an amount of oxygen larger than the stoichiometric requirement (i.e. O<sub>2</sub>/CH<sub>4</sub> > 0.5) is supplied. They also found that three regions existed in the catalyst bed: (i) NiAl<sub>2</sub>O<sub>4</sub> , (ii) NiO/Al<sub>2</sub>O<sub>3</sub> which is active for complete combustion of methane to CO<sub>2</sub> and H<sub>2</sub>O, and (iii) supported nickel metal particles which are active for reforming of methane with CO<sub>2</sub> and H<sub>2</sub>O to synthesis gas.

Generally, Ni metal which is the active component for synthesis production via methane partial oxidation. However, under conditions where synthesis gas is produced, carbon deposition also occurs. Nickel is deactivated easily by carbon deposition and/or its sintering. Carbon deposition on supported nickel catalyst mainly comes from methane decomposition reaction (Eq.2.5) and/or to the slightly exothermic Boudouard reaction (or CO disproportion) (Eq. 2.4).

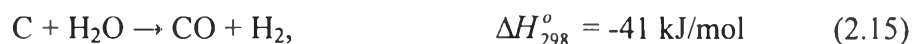
While methane decomposition is a dominating carbon source at temperatures above 700°C, the reverse Boudouard reaction is the dominating carbon



source at lower temperatures. Carbon deposition may lead to catalyst deactivation, plugging of the reactor, and breakdown of the catalyst.

Koerts *et al.* (1991) have identified three types of surface carbonaceous species generated by methane decomposition:  $C^{\alpha}$  (or carbidic carbon can be hydrogenated at temperatures below 50°C),  $C^{\gamma}$  (or amorphous carbon, hydrogenable between 100 and 300°C), and  $C^{\beta}$  (or graphitic carbon, hydrogenable at temperatures > 400°C).

In general, the deposition of carbon would occur over the metallic sites as well as on the acid site of the support. However, carbon deposition can be removed by steam gasification:



or burnt off by oxygen. Typically, the burning temperatures of carbon increase with the degree of crystallization of carbon species. Amorphous carbon is active, unstable and easily burnt off by oxygen at temperatures as low as 300°C, while crystalline carbon can only be burnt off at the temperature as high as 700°C.

Carbon deposition on catalysts during the partial oxidation of methane has been investigated by Claridge *et al.* (1993), and it was found that the relative rate of carbon deposition follows the order Ni > Pd > Rh > Ir. Methane decomposition was found to be the principal route for carbon formation over a supported nickel catalyst, and electron micrographs showed that both whisker and encapsulate forms of carbon are present on the catalyst. Negligible carbon deposition occurred on iridium catalysts, even after 200 hours.

To decrease the carbon deposition and increase the stability of the support and thus to extend the catalyst lifetime, much work has been done on the modification of the support.

Choudhary and co-workers (1993) have studied nickel catalysts supported over ytterbium oxide, CaO, TiO<sub>2</sub>, ZrO<sub>2</sub>, ThO<sub>2</sub>, UO<sub>2</sub> and rare earth oxide-modified alumina supports. They found that the NiO containing MgO, CaO, rare earth oxides or alumina catalysts showed high catalytic activity in the process at a very low contact time. The order of the performance for nickel containing ZrO<sub>2</sub>, ThO<sub>2</sub> and UO<sub>2</sub> is NiO/ThO<sub>2</sub> > Ni/UO<sub>2</sub> > NiO/ZrO<sub>2</sub>.SiO<sub>2</sub> and TiO<sub>2</sub> are not good

supports for the reaction. Because sintering of Ni gives inactive binary metal oxide phases under the high-temperature reaction conditions. Although modification of the supports can improve the catalyst stability to some extent, catalyst deactivation is still unavoidable due to both carbon deposition and to loss of the nickel metal surface area.

Many additives were found to reduce carbon deposition for Ni supported catalysts. Miao *et al.* (1997) studied the NiO/Al<sub>2</sub>O<sub>3</sub> catalyst to improve the thermal stability and the carbon deposition resistance during the partial oxidation of methane to synthesis gas. It was modified by alkali metal oxide (Li, Na, K) and rare earth metal oxide (La, Ce, Y, Sn). They reported that modification with metal oxides and rare earth metal oxides not only improves the activity for partial oxidation of methane to synthesis gas reaction and the thermal stability of nickel-base catalysts during high temperature reaction, but also enhance the ability to suppress the carbon deposition over nickel-base catalysts during the partial oxidation of methane.

Trimm (1999) reported that use of tetra- and penta-valence p metals such as Ge, Sn and Pb could also reduce coke formation. It would seem possible that tetra- or penta- valence p metals could also interact with Ni 3d electrons, thereby reducing the change of nickel carbide formation.

In 2001, Dong and co-worker investigated the Ni catalysts supported on various supports in order to develop highly active and stable catalyst for H<sub>2</sub> production.

The results of CH<sub>4</sub> conversion, H<sub>2</sub> yield and CO yield indicated that Ni/CeZrO<sub>2</sub> exhibited the highest activity and excellent stability among the tested catalyst. Based on their results, they concluded the remarkable catalytic performance of Ni/Ce-ZrO<sub>2</sub> is attributed to the combination of several advantages:

The first one was high oxygen storage capacity of Ceria in Ce-ZrO<sub>2</sub> solid solution. Thus, the CeZrO<sub>2</sub> support had the ability to store, release and transfer active oxygen species. These oxygen species could react with carbon that normally accumulates on the metal or the interface of metal-support to form CO. The oxidation of carbon benefited to decrease carbon deposition and promote the stability of catalyst.

Another was strong interaction between Ni and Ce-ZrO<sub>2</sub> solid solution resulting in small and finely dispersed Ni metal particles. Consequently, the ensemble size on metal surface becomes smaller resulting in good coke resistance.

Pengpanich *et al.* (2007) investigated the effect of Nb loading in 5 wt% Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst on the catalytic performance of methane partial oxidation. The solid solution of catalysts was prepared by urea hydrolysis. They reported that the surface areas were insignificantly decreased with increasing Nb loading, this result indicated that adding Nb species in to the Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst did not decorate the surface of catalysts. For Nb species present in the catalyst might depress the amount of NiO and its surface reducibilities. However, it was found that the catalytic activities for methane partial oxidation were decreased and amount of carbon deposition was increased with increasing amount of Nb loading.

Pengpanich *et al.* (2008) studied the iso-octane partial oxidation over Ni-Sn/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst. They reported that the addition of small amount of Sn (<0.5 wt.%) into Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalysts retards the amount of carbon deposition and when added in high amount, a total coverage of Ni particles by Sn leads to loss of catalytic activity. Furthermore addition of Sn could also reduce the amount of whisker carbon growth by retarding the solubility of carbon in Ni particle.

#### 2.2.5 Magnesium (Mg)

Magnesium oxide is a white solid mineral. It is created naturally as periclase and a source of magnesium. It is formed by an ionic bond between one magnesium and one oxygen atom as a formula MgO. Magnesium oxide is an alkaline earth metal oxide, and is the basicity properties. Magnesium oxide can be used in many applications such as medication, steel and nuclear industry, feeding animals, and raw materials for making cement.

The Ni/MgO catalyst system has been studied by Ruckenstein (1999). It is believed that the observed high catalyst stability results from the formation the solid solution e.g. Ni occupies sites in the MgO lattice and is distributed evenly in the catalyst. The Ni is present as very small particles and the weak basicity of the MgO somewhat suppresses carbon deposition. However, the formation of the solid

solution in the catalyst only extends the catalyst life and deactivation eventually occurs due to carbon deposition.

Hu and Ruckenstein, (2002) studied the binary MgO-based solid solution catalysts for methane conversion to syngas. They reported that the the strong NiO–MgO interaction and basicity in binary NiO–MgO solid solution catalysts in methane partial oxidation, which inhibit carbon deposition and/or catalyst sintering after the reaction, result in an excellent catalytic performance for the methane conversion to synthesis gas. They also purposed that the excellent resistance of Ni/MgO to carbon deposition most likely results from the formation of solid solution between NiO and MgO. Because of similar crystalline structure (NaCl type) and approximate cation radii ( $\text{Ni}^{2+}$  0.69 $\text{\AA}$ ,  $\text{Mg}^{2+}$  0.65 $\text{\AA}$ ), NiO and MgO are completely miscible and can form a solid solution through a mechanism of lattice substitution.

Yejun *et al.* (2007) studied effects of MgO promoter on properties of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for partial oxidation of methane to syngas. They reported that MgO improve the POM reactivity of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. This might be due to a NiO–MgO is formed to a solid solution, and MgO loading 4 w% had a higher specific surface area, which probably result from the improvement of Ni dispersion owing to MgO promoter and inhibited the growth of Ni crystallites after reduction than other condition. But the excessive MgO promoter caused the NiO crystallinities to aggregate, which was reduce the catalytic performance.

Their results revealed that MgO has many beneficial effects as a promoter. First, MgO improved the interaction between Ni and support. Thus, NiO particles were small and finely disperse inhibiting the sintering of active sites. Second, MgO had basic property to prevent coke formation which is favorable on acid sites. As a consequence, the Ni/Al<sub>2</sub>O<sub>3</sub> with MgO promoter had lower carbon deposition and better thermal stability.

Pue-on *et al.* (2011) studied about NiO–MgO/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> (CZO) mixed oxide catalysts by investigating the effect of MgO promoter on the catalytic performance and carbon deposition of Ni–MgO/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> mixed oxide catalysts. The Ni loading was fixed at 15 wt% whereas MgO loading was varied from 5 to 15 wt%. Moreover, they also investigated the effect of catalyst preparation method on

that of catalyst by comparing between the co-impregnation and multi-step incipient wetness impregnation methods.

Their results revealed that the addition of MgO caused the light-off temperatures shifted to higher temperatures. They proposed that the Ni surface was partially covered with MgO, and the strong interaction between NiO and NiMgO<sub>2</sub> over CZO support can lead to the difficulty in reducing NiO resulting in less catalytic activity. However, the addition of MgO could diminish the Boudouard reaction and prevent the agglomeration of Ni particles on MPO at high temperatures resulting in the higher stability of the catalyst. Among all tested catalysts, the 15Ni5Mg/CZO catalyst exhibited the best catalytic stability for MPO. An appropriate H<sub>2</sub>/CO ratio of 2 also was obtained for 15Ni5Mg/CZO catalyst which prepared by multi-step incipient wetness impregnation method.

For the effect of catalyst preparation method, the catalysts prepared by incipient wetness impregnation possessed slightly higher catalytic activity for MPO than those prepared by co-impregnation. Moreover, the carbon deposition on the 15Ni5Mg/CZO which prepared via incipient wetness impregnation was significantly less than that of the 15Ni5Mg/CZO from co-impregnation. This result indicated the significant influence of mixed oxide catalyst preparation method.