



CHARTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Hydrogen

Hydrogen was first artificially produced in the early 16th century, via the mixing of metals with strong acids. It is the chemical element with atomic number of 1. It is composed of one hydrogen atom (H). At ambient temperature and atmospheric pressure, hydrogen is a colorless, odorless gas, and highly combustible diatomic gas with the molecular formula H₂ (<http://www.newworldencyclopedia.org/entry/Hydrogen>).

Conventional energy resources can significantly produce greenhouse gases, especially carbon dioxide, which is thought to be responsible for changes in global climate. Hydrogen is the cleanest fuel that has a minimum impact on the environment. The long-term environmental benefits of using hydrogen as a fuel are enormous. Hydrogen fuel produces few pollutants when burnt, and none at all when used in a fuel cell. Hydrogen is a carbon-free fuel, and when produced using renewable energy, the whole energy system can become carbon-neutral, or even carbon-free. So, hydrogen fuel can contribute to reducing greenhouse gas emissions and can reduce the production of many toxic pollutants.

Hydrogen gas is the simplest and lightest fuel. It contains low levels of carbon monoxide and carbon dioxide, depending on the production source. The energy density of hydrogen is very low under ambient conditions. This presents greater transportation and storage hurdles than for liquid fuels.

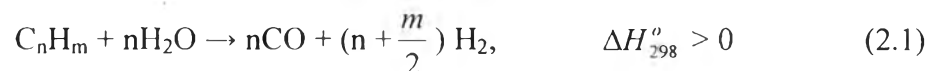
Currently, hydrogen is being surveyed for use in combustion engines and fuel cell electric vehicles. Moreover, it can be used in numerous applications, including petroleum refining process and petrochemical industry such as hydrotreating, hydrocracking, production of methanol, ammonia, and hydrocarbon synthesis via Fischer–Tropsch process.

2.1.2 Processes for Hydrogen Production

There have been processes utilizing methane to produce hydrogen e.g., steam reforming, partial oxidation, pyrolysis, gasification, electrolysis, and autothermal reforming. However, steam reforming, partial oxidation, and autothermal reforming process are widely used to produce methane into hydrogen and carbon monoxide or synthesis gas.

2.1.2.1 *Steam Reforming*

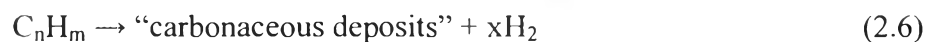
Steam reforming (SR), sometimes referred to as steam reforming of methane (SRM), is a well-established process and the largest process for converting natural gas into hydrogen or synthesis gas in industry. Normally, the steam reforming reaction of hydrocarbons can be described by:



and two sample reversible reactions, water-gas shift and methanation reaction can be respectively described by:



Moreover, Reactions (2.1) to (2.3) may be accompanied by reactions forming carbon.



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, addition of excess steam is normally used to avoid coke formation.

Currently, the most common source of synthesis gas produced by steam reforming are hydrocarbons and particularly natural gas. Since the major component in natural gas is methane, the steam reforming of methane can be described by:



SRM is highly endothermic reaction. Therefore, a large amount of energy is necessarily consumed to supply this reaction. Typically, this reaction has to be operated over supported nickel catalysts at pressures in the range of 15 to 30 atm and high temperature of 850 to 900 °C. Furthermore, Fischer–Tropsch or methanol synthesis can be described by:



For these processes, the desired H₂/CO molar ratio is 2. Thus, the synthesis gas from steam reforming of methane must be adjusted through the reverse water gas shift (Eq. 2.2).

Not only methane but also other hydrocarbons such as naphtha, butane, benzene and hexane are used as feedstocks for steam reforming. However, methane is still the most popular feedstock because of its low rate of coke formation when compared with other hydrocarbons.

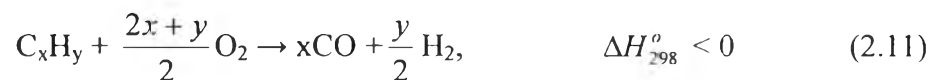
However, the disadvantages of the steam reforming process are high energy consumption, intensive capital cost, and coke deposition. Therefore, much research has been focused to investigate reforming catalyst conditions in order to solve these problems and improve reforming efficiencies.

2.1.2.2 Partial Oxidation

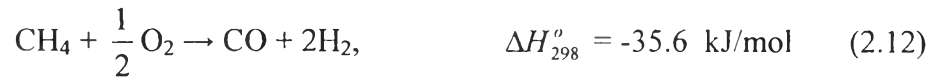
Currently, partial oxidation (POX) is considered an alternative route to synthesis gas production. The advantage of this process is that it accepts all kinds of hydrocarbon feeds. The thermal oxidation is run at 30–100 atm with pure O₂ using a special burner inside a refractory lined vessel at temperatures of 1200 °C and above. Partial oxidation can be separated into two processes including with and without catalysts. Firstly, the partial oxidation with catalysts can be called “catalytic partial oxidation (CPOX)”. The general reaction can be described by:



The CPOX has received intensive attention because of its mild exothermic reaction, short contact time, high methane conversion, high selectivity for CO and H₂, and low cost (Dajiang *et al.*, 2007). Several types of catalysts were used to reduce the required temperature processes to around 800 to 900 °C. Secondly, 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:



Both processes need to have huge quantities of O₂ available continuously, thus requiring the substantial investment in an adjoining O₂ plant. 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. To avoid these problems, the CPOX of hydrocarbons is attractive nowadays, but the challenge is to avoid the runaway oxidation of hydrocarbons to CO₂ and water. Ideally, the partial oxidation of methane to synthesis gas is preferred as described below:



The partial oxidation of methane is diagrammatic shown in Figure 2.2 and also gives some information below.

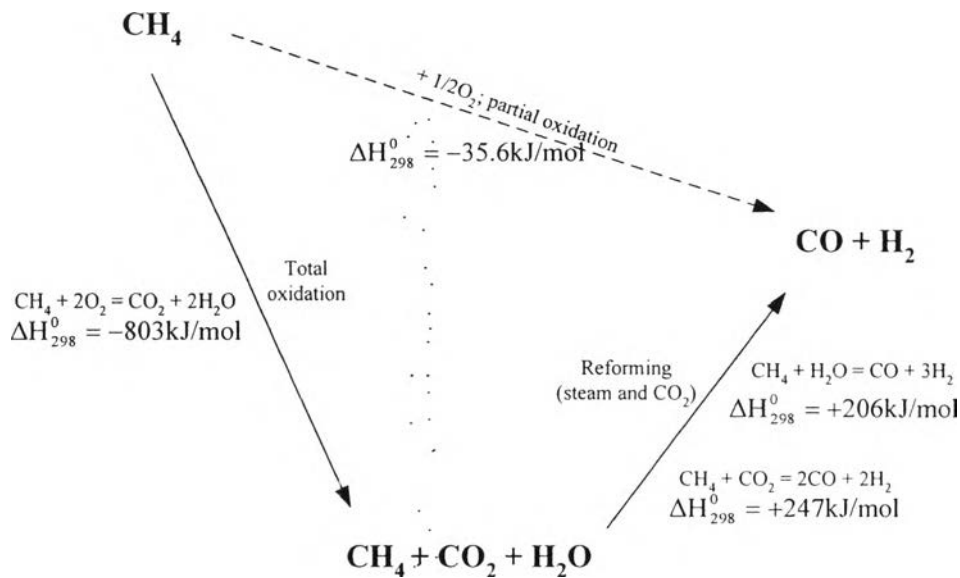


Figure 2.1 Thermodynamic representation of the partial oxidation of methane (York *et al.*, 2003).

The main thermodynamic advantages of partial oxidation over steam reforming are reported below by York *et al.* (2003).

Steam reforming is high endothermic reaction, but partial oxidation is mild exothermic reaction. Therefore, a partial oxidation reactor would be more saving to heat than steam reforming. The H₂ to CO ratio around 2 is produced by partial oxidation process, and this ratio is suitable for downstream processes, especially methanol synthesis. This avoids the need to remove valuable hydrogen, which is produced in excess in steam reforming. Synthesis gas production can be produced by methane partial oxidation with low carbon dioxide content, which must be removed before synthesis gas can be used to downstream processes.

For this reason, the partial oxidation of methane to synthesis gas has been investigated in terms of its mechanism and the characterization of the catalyst. Therefore, the number of the literature of this process is reviewed.

2.1.2.3 Autothermal Reforming

Autothermal methane reforming (ATR) is combined by two processes that are steam reforming (2.1) and partial oxidation of methane (2.10) (Escritori *et al.*, 2009). The ATR is more attractive than steam reforming, because it needs less energy to produce the same amount of hydrogen. The operating temperature from this process is in the range of 950 to 1100 °C and a gas pressure about 100 atm.

Oxygen and carbon dioxide/steam are used for ATR process in a reaction with methane to form syngas. The reaction is exothermic due to the oxidation. The general reactions can be described by using CO₂ and steam, respectively.



The SMR process and ATR process possess a main difference in which SMR uses no oxygen. The advantage of ATR is that it can produce hydrogen more economically than can SMR process.

2.2 Literature Review

2.2.1 Methane Partial Oxidation

The natural gas has made methane an important raw material for the chemical industry. Methane is directly used as a fuel in combustion process. The conversion processes can be classified in two classes; direct and indirect conversions. The direct conversion of methane has focused on the oxidative of coupling to ethylene and ethane, and 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 applications. The other process converts methane to synthesis gas (CO and H_2) as intermediate, which can be easily produced to methanol or higher hydrocarbons by methanol or Fischer–Tropsch synthesis. Normally, the partial oxidation of methane to synthesis gas occurs at very high temperatures (>1200 °C). The use of a catalyst can reduce the operating temperature to achieve a 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.

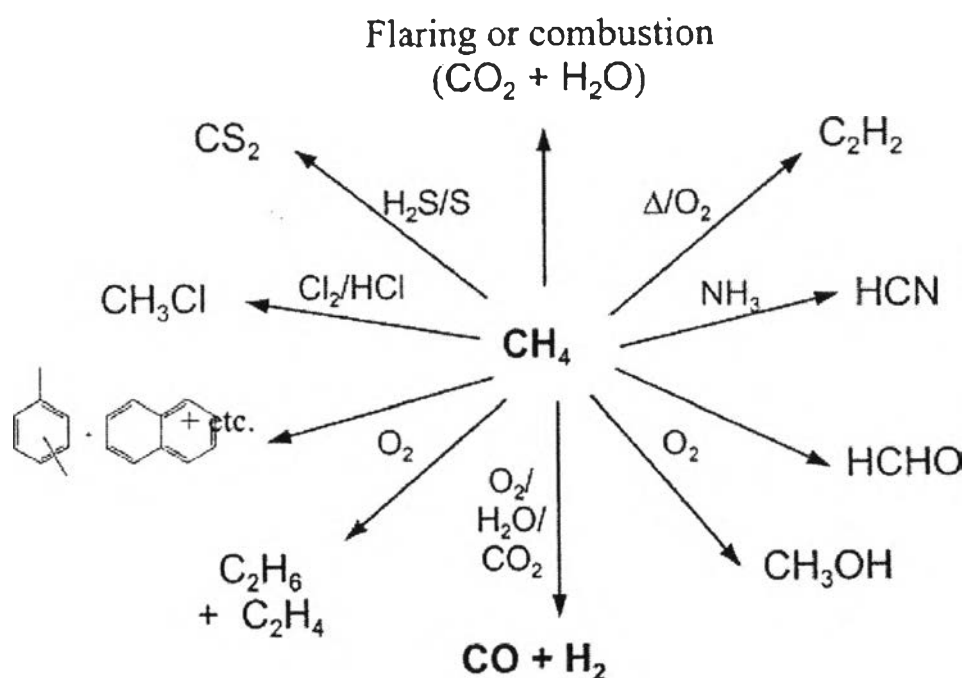


Figure 2.2 Summary of methane conversion routes (York *et al.*, 2003).

2.2.1.1 Noble Metal Catalysts

The group of noble metals such as Pt, Pd, Ru, and Rh is used to the investigation of catalytic methane partial oxidation.

A study in Ru supported catalysts was demonstrated by Elmasides *et al.* (2001). They reported that high selectivity to synthesis gas ($>65\%$) was obtained over Ru/TiO₂ catalysts in the low methane conversion range, whereas

small or zero selectivity to synthesis gas was observed over Ru catalysts supported on other materials.

A study in Rh and Ru supported catalyst was investigated by Yan *et al.* (2004). They reported that the methane conversion and selectivity to H₂ and CO were higher over Rh/SiO₂ than over Ru/SiO₂ catalysts under the same condition.

Pantu and Gavalas (2002) reported that high methane conversion and high selectivity to CO and H₂ were obtained over Pt/CeO₂ at temperatures over 650 °C, and CH₄ to O₂ feed ratio varied from 1.7 to 2.3.

Hickman and Schmidt (1993) reported that Rh and Pt supported on monolith were excellent partial oxidation catalysts giving greater than 90% methane conversion and synthesis gas selectivity at temperature around 850 °C with CH₄/O₂ feed ratio of 2 and extremely fast space time (10⁻⁴–10⁻² sec).

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

A study in Rh was 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 a higher methane conversion and also higher CO and H₂ selectivities than Pt at a comparable temperature.

2.2.1.2 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 has also been 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 ZrO₂ catalysts at

the temperature from 400 to 800 °C. The results showed that the activity of the catalysts was found to decrease in the order Ni>Cu>Co>Fe.

However, Ni is easily deactivated by carbon deposition. The forms of carbon deposition present 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 catalysts are prone to carbon deposition and that activation rate was affected by the nature of supports used. Therefore, the development of Ni based catalysts with stable operation can be achieved. Many types of support for Ni-supported catalysts were studied for methane partial oxidation such as Al₂O₃ (Ji *et al.*, 2001), TiO₂ (Wu *et al.*, 2005), CaO (Tang *et al.*, 1998; Tsipourirari *et al.*, 2001), CeO₂ (Tang *et al.*, 1998; Zhu and Flytzani-Stephanopoulos, 2001), MgO (Tang *et al.*, 1998), and SiO₂ (Au *et al.*, 1996).

Ji *et al.* (2001) studied the partial oxidation of methane over Ni/Al₂O₃. They showed that Ni/Al₂O₃ catalyst gave a low rate of carbon formation in a fluidized-bed reactor. The CH₄ conversion as well as CO and H₂ selectivities remained constant at 92, 94 and 99.0%, respectively.

Wu *et al.* (2005) studied the partial oxidation of methane to H₂ and CO over a Ni/TiO₂ catalyst at temperatures from 300 to 800 °C. They found that Ni/TiO₂ catalyst showed a higher CH₄ conversion as well as CO and H₂ selectivities at 800 °C. POM conversion was decreased when reaction time increased due to the formation of NiO and NiTiO₃ in Ni/TiO₂.

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-Al₂O₃>Ni/CaO-γ-Al₂O₃>Ni/CaO. They concluded that the higher deactivation rates were observed over supports of higher acidity.

Tang *et al.* (1998) studied the partial oxidation of methane to syngas over Ni/MgO, Ni/CaO and Ni/CeO₂ catalysts. They reported that all the 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 a high resistance to carbon deposition under thermodynamically severe conditions.

Au *et al.* (1996) studied the methane partial oxidation over Ni/SiO₂ catalyst compared with that over Cu/SiO₂ catalyst. They found that methane conversion over Ni/SiO₂ was significantly higher than that over Cu/SiO₂. The main products produced by methane partial oxidation over Cu/SiO₂ catalyst were CO₂ and H₂O while those over Ni/SiO₂ were CO₂, H₂O, H₂, 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). Recently, CeO₂ has been suggested for use 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 CeO₂ as the support.

Nevertheless, Otsuka *et al.* (1998) reported that CeO₂ could be able to convert methane to synthesis gas with H₂ to CO ratio of 2 and that adding Pt black could promote a syngas formation rate. This finding subjected to methane partial oxidation over Ni/CeO₂ catalyst was studied by Dong *et al.* (2002). They also proposed a mechanism over Ni/CeO₂ that methane dissociated on Ni and the resultant carbon species quickly migrated to the interface of Ni-CeO₂ and then reacted with oxygen in the lattice of CeO₂ to form CO.

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

Gonzalez-Velasco *et al.* (1999); Vidal *et al.* (2000); Roh *et al.* (2002) reported that addition of ZrO₂ to CeO₂ can improve its oxygen storage capacity, redox properties, thermal resistance and better catalytic activity at low temperatures. This was found to be due to the partial substitution of Ce⁴⁺ with Zr⁴⁺ in the lattice of CeO₂, which formed a solid solution formation (Otsuka *et al.*, 1999; Chen *et al.*, 2008). It was demonstrated that CeO₂-ZrO₂ mixed oxides produced synthesis gas with H₂ to CO ratio of 2 and the formation rates of H₂ and CO were increased due to the incorporation of ZrO₂ into CeO₂.

Hori *et al.* (1998) reported that the beneficial effects of ZrO₂ were pronounced in solid solutions which had the oxygen storage capacity

values 3–5 times higher than that of pure CeO₂. When the optimum Zr dopant concentration was 25 mol%, solid solution material aged at 1000 °C showed higher oxygen storage capacity than that of pure CeO₂. This result could be ascribed to an occurrence of Zr promotion via an alteration of bulk properties of the CeO₂. Furthermore, the redox properties of the CeO₂ have been enhanced by the addition of Zr⁴⁺ into the lattice of CeO₂ by formation of solid solution. Moreover, it was also reported that CeO₂-ZrO₂ solid solution showed a high catalytic activity, particularly for oxidation of CO, and CH₄ (Bozo *et al.*, 2000; Gonzalez-Velasco *et al.*, 1999; Otsuka *et al.*, 1999).

Villalpando *et al.* (2009) studied the catalytic performance of Ni dispersed on ceria-doped supports of Zr, Gd and La at different ratios. They found that the Ni/Ce_{0.56}Zr_{0.44}O_{2-x} 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_{0.75}Zr_{0.25}O₂ solid solution exhibited the highest reducibility. This might be due to that the highly uniform solid solution particles of ceria-zirconia were obtained and the incorporation of Zr into the CeO₂ lattice was found to promote the good redox properties.

Moreover, Pengpanich *et al.* (2004) studied methane partial oxidation over Ni/CeO₂-ZrO₂ mixed oxide solid solution catalysts. They reported that the catalysts prepared by impregnation method were more active than those prepared by gel impregnation method. The Ni/Ce_{0.75}Zr_{0.25}O₂ 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.

2.2.1.3 Mechanisms of Methane Partial Oxidation

The catalytic partial oxidation of methane to synthesis gas was proposed as for two mechanisms. One is designated as the direct partial oxidation mechanism and the other is the combustion and reforming reaction mechanism.

For the direct partial oxidation mechanism, CO and H₂ are produced directly by recombination of CH_x and O species at the surface of the catalysts. Hickman and Schmidt (1993) claimed that CO and H₂ were the primary products of methane partial oxidation reaction over Rh coated monolith catalysts under adiabatic conditions at very short contact time. They proposed that the mechanism involved a direct formation of H₂ initiated by CH₄ pyrolysis on the surface to give surface C and H species. The H atoms dimerized and desorbed as H₂ while the surface C atoms reacted with adsorbed O atoms and desorbed as CO. A similar finding was reported by Mallens *et al.* (1997). They studied the mechanism of methane partial oxidation over a Rh catalyst by a Temporal Analysis of Products (TAP) set-up. It was found that synthesis gas was produced as primary product. H₂ was 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 resulted in the formation of carbon monoxide.

For the combustion and reforming reaction mechanism involves initially exothermic methane combustion to CO₂ and H₂O followed by the strongly endothermic reforming reaction of the rest of CH₄ with CO₂ and H₂O to produce synthesis gas. The mechanism of methane partial oxidation over Ni/Al₂O₃ 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 consisted of three different regions. The first of these, contacting the initial CH₄/O₂/He feed mixture, is NiAl₂O₄, which had only moderate activity for complete oxidation of methane to CO₂, resulting in an exotherm in this section in the bed. As a result of complete consumption of O₂ in the second region, the third portion of the catalyst bed consisted of a reduced Ni/Al₂O₃ phase. Formation of the CO and H₂ products occurred in this final region via reforming reactions of methane with the CO₂ and H₂O produced during the complete oxidation reaction over the Ni/Al₂O₃ phase.

Recently, there have been studies of partial oxidation mechanism over several specific catalysts and under specific conditions. Weng *et al.* (2000) studied supported Rh and Ru catalysts by in situ time resolved FTIR spectroscopy. They found that CO was the primary product of partial oxidation of

methane reaction over the reduced and working state Rh/Al₂O₃ catalyst. Direct oxidation of CH₄ was the main pathway of synthesis gas formation over Rh/SiO₂ catalysts. CO₂ was the primary product of partial oxidation of methane over the Ru/Al₂O₃ and Ru/SiO₂ catalysts. The dominant reaction pathways of synthesis gas formation over Ru/Al₂O₃ catalysts were combustion and reforming reaction mechanisms. On the Rh/SiO₂ catalyst, the main reaction was apparently direct partial oxidation mechanism, and also the reaction mechanism appeared to be related to the concentration of O₂ in the feedstock.

Not only noble metals but also nickel catalysts were proposed for direct methane partial oxidation mechanism (Dong *et al.*, 2002).

2.2.1.4 Nickel-Based Catalysts and Carbon Deposition

Nickel-based catalysts are attractive for partial oxidation reaction due to their low cost, but 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 leads to catalyst deactivation, plugging of the reactor, and breakdown of the catalyst.

Koerts *et al.* (1991) identified three types of surface carbonaceous species generated by methane decomposition: C^α (or carbidic carbon can be hydrogenated at temperatures below 50 °C), C^γ (or amorphous carbon, hydrogenable between 100 and 300 °C), and C^β (or graphitic carbon, hydrogenable at temperatures over 400 °C).

In general, the deposition of carbon would occur over the metallic sites as well as on the acid sites 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 was 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 encapsulated forms of carbon were present on the catalyst.

Many additives were found to reduce carbon deposition for Ni supported catalysts. Miao *et al.* (1997) studied the NiO/Al₂O₃ 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 (Li, Na, K) oxides and rare earth metal (La, Ce, Y, Sn) oxides. They reported that modification with alkali metal oxides and rare earth metal oxides not only improved 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 enhanced 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.

Pengpanich *et al.* (2007) investigated the effect of Nb loading in 5 wt% Ni/Ce_{0.75}Zr_{0.25}O₂ 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_{0.75}Zr_{0.25}O₂ catalyst did not decorate the surface of catalysts. As for Nb species present in the catalyst, it might depress the amount of NiO and its surface reducibilities. However, it was found that the catalytic activity for methane partial oxidation was decreased and the amount of carbon deposition was increased with increasing Nb loading.

Pengpanich *et al.* (2008) studied the iso-octane partial oxidation over Ni-Sn/Ce_{0.75}Zr_{0.25}O₂ catalysts. They reported that the addition of small amount of Sn (<0.5 wt%) into Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts retarded the amount of carbon deposition and when added in high amount, a total coverage of Ni particles by Sn led 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 particles.

2.2.1.5 Magnesium Oxide (MgO)

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 in properties. Magnesium oxide can be used in many applications such as medication, steel and nuclear industry, feeding animals, and raw materials for making cement.

Hu and Ruckenstein, (2002) studied the binary MgO-based solid solution catalysts for methane conversion to syngas. They reported that the strong NiO–MgO interaction and basicity in binary NiO–MgO solid solution catalysts in methane partial oxidation, which inhibited carbon deposition and/or catalyst sintering after the reaction, resulted in an excellent catalytic performance for the methane conversion to synthesis gas.

Recently, Yejun *et al.* (2007) studied the effect of MgO promoter on properties of Ni/Al₂O₃ catalysts for partial oxidation of methane to syngas. They reported that MgO improved the POM reactivity of Ni/Al₂O₃ catalysts. This might be because a NiO-MgO is formed to a solid solution, and MgO loading of 4 w% had a higher specific surface area, which probably resulted from the improvement of Ni dispersion owing to MgO promoter and inhibited the growth of Ni crystallites after reduction than other conditions. However, the excessive MgO promoter caused the NiO crystallites to aggregate, reducing the catalytic performance.