



CHAPTER II

LITERATURE REVIEW

In this chapter, background information related to this work is described. First, introduction to hydrogen production processes is provided. Next, related works in hydrocarbons partial oxidation are reviewed.

2.1. Background

2.1.1 Thermodynamic of methane partial oxidation

The partial oxidation of methane is schematically shown in Figure 1.1 and also gives some thermodynamic information.

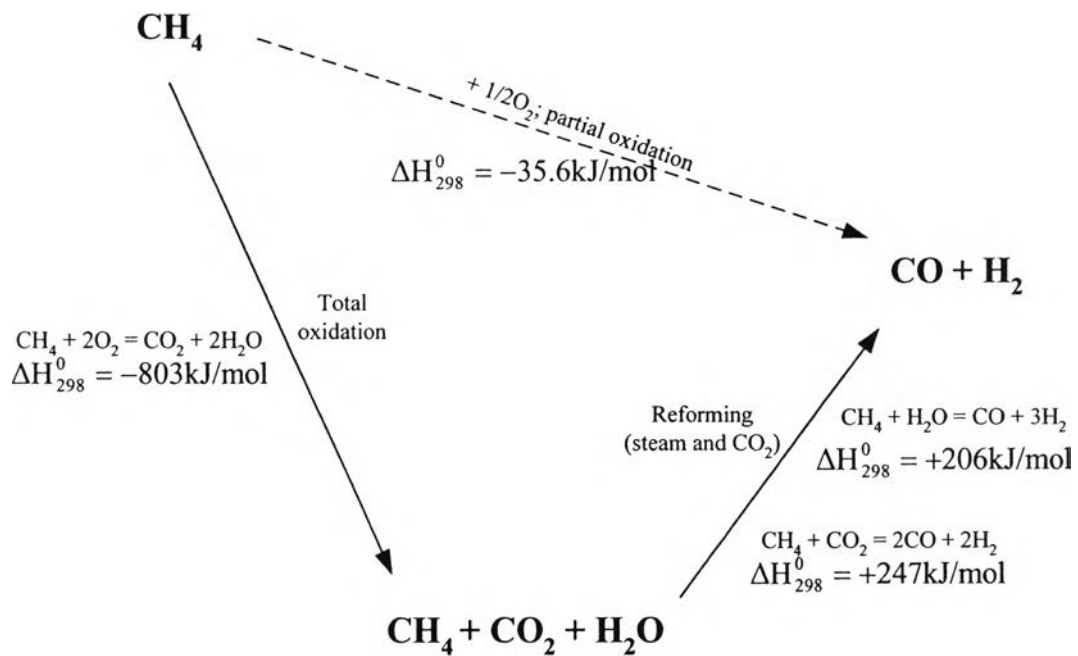


Figure 2.1 Thermodynamic representation of the partial oxidation of methane (York *et al.* 2003).

This process is likely to become more important in the future of methane conversion due to the thermodynamic advantages this process has over steam reforming are reported.

- 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 endothermic reactions, such as steam reforming with carbon dioxide to make these processes more energy efficient.

- The H₂/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 can be used downstream.

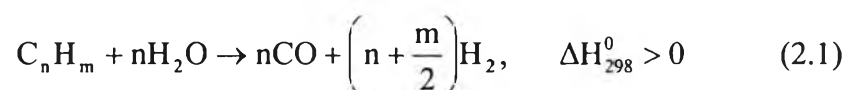
- Partial oxidation technology avoids the need for large amounts of expensive superheated steam. However, an oxygen separation plant, which is also costly, may be required in case where nitrogen (from air) is undesirable in high pressure down-stream process.

2.1.2 Processes for Hydrogen Production

In this time, the only economically available route for the conversion of methane into more valuable chemicals is via synthesis gas. Several synthesis gas production methods are available, depending on the propose of industrial application. Several processes are used to produce hydrogen such as steam reforming, partial oxidation, pyrolysis, gasification, and electrolysis. However, steam reforming and partial oxidation are important in the conversion of hydrocarbons to hydrogen.

2.1.2.1 Steam Reforming

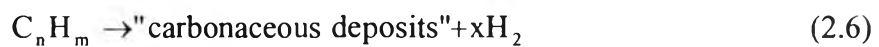
Steam reforming is established process for converting hydrocarbons into synthesis gas (a mixture of CO and H₂). Generally, the reforming of hydrocarbons can be expressed by:



and two simple reversible reactions, water-gas shift (2.2) and methanation reaction (2.3):



occur simultaneously. Moreover, reactions (2.1) to (2.3) may be accompanied by reactions forming carbon:

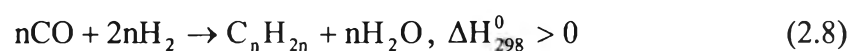


At high temperature (above 920K), the hydrocarbons may react in parallel to reaction (2.1) by thermal cracking (called "steam cracking") into olefins which may easily form coke by reaction (2.6). The risk of carbon formation must be eliminated in operations since carbon causes serious operational troubles 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 is hydrocarbons, particularly natural gas. Since the major component in the natural gas is methane, the steam reforming of methane can be expressed by:



This reaction is highly endothermic, typically has to be operated over supported nickel catalyst at pressure of 15 to 30 atm and high temperatures of 850 to 900°C. Therefore, a large amount of energy is consumed to supply this reaction. Furthermore, for Fischer-Tropsch or methanol synthesis:



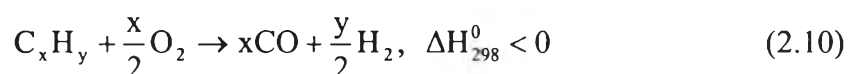
For these processes, the desired H₂/CO molar ratio is 2. Thus, the synthesis gas from steam reforming of methane must to be adjusted through the reverse water gas shift reaction (2.2).

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

As mentioned above, the disadvantages of the steam reforming process are high energy consumption, intensive capital cost, and coke deposition problem. Therefore, much research has been focused to investigate alternate process of producing synthesis gas.

2.1.2.2 Partial Oxidation

The other major route to hydrogen is non-catalytic partial oxidation of fossil fuels, often referred as gasification. 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 about 1300°C. The general reaction is described by:



This process needs to have huge quantities of O₂ available continuously, thus requiring the substantial investment in an adjoining O₂ plant. Additional unit operations are required gas purification and to remove soot from the waste water. Thus, the operations are quite complex and less energy efficient when compared with steam reforming. To avoid these problems, the catalytic partial oxidation of hydrocarbons is attractive nowadays, but the challenge to avoid the runaway oxidation of hydrocarbons to CO₂ and water.

Ideally, the partial oxidation of methane to synthesis gas is expressed as:



An exothermic reaction and yields a H_2/CO molar ratio of 2. This reaction may offer the greatest potential for fast and economical process due to the high conversion, high selectivity, suitable H_2/CO product molar ratio and very short residence time. For this reason, the partial oxidation of methane to synthesis gas has been extensively studied both in term of its mechanism and the characterization of the catalyst. The literature survey of this process will be reviewed in following section.

2.2. Literature Review

2.2.1 Methane Partial Oxidation

The natural gas has made methane an important raw material for the chemical industry. A summary of some of the routes that have been investigated for methane utilization and valorization is show in figure 2.1.

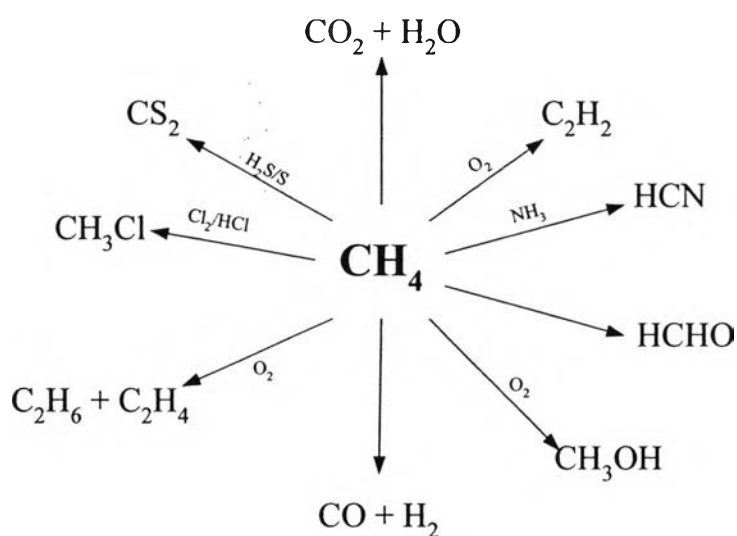


Figure 2.2 Summary of methane conversion routes (Pena *et al.*, 1996).

Methane used as a fuel in combustion process. The conversion processes can be classified in two classes: direct and indirect conversion. The direct conversion of methane has focused on the oxidative of coupling to ethylene and ethane and on the oxygenation to methanol and formaldehyde. The other process is convert 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. The partial oxidation of methane to synthesis gas occurs at very high temperature (>1400 K). The use of a catalyst can reduce the operating temperature. Many metals have been investigated as the catalysts for methane partial oxidation containing transition metals (Ni, Cu, and Fe) (Au *et al.*, 1996; Lu *et al.*, 1998), noble metals (Ru, Rh, Pt, and Pd) (Hickman and Schmidt, 1993; Mallens *et al.*, 1997; Otsuka *et al.*, 1999) and metal oxides (Ruckenstein and Wang, 1999) were employed in investigation of methane partial oxidation. Among those, Ni-base catalysts show an excellent catalytic (Zhu *et al.*, 2001). However, there has been emphasis on the development of highly active and coke resistant catalysts for partial oxidation.

The pioneering work on partial oxidation of CH_4 to synthesis gas was carried out by Gavalas *et al.* (1984) studied the conversion of CH_4/O_2 mixtures at 820-1010 K on catalysts calcined and reduced at different temperatures. For CH_4/O_2 molar ratios 1.5-1.7, they observed a decrease in the initial activity for catalysts calcined at the highest temperatures and explained as due to changes in the Ni^{3+} surface concentration. For a given calcinations temperature, some activity decline with reaction time was also observed. CO_2 and H_2O were the only products observed under these conditions. However, after prereduction in H_2 at 920-1030 K led the initial activity to increase by one or three orders of magnitude, depending on the previous calcinations temperature. According to this, these authors assumed that Ni^0 obtained by prereduction is responsible for the reaction and converted to NiO under the reaction conditions, resulting in a decrease in activity with time on-stream. At a typical reaction temperature of 983 K and CH_4/O_2 molar ratios 1.5-1.7 they found CO_2 as the only C-containing product, but when changing the CH_4/O_2 ratio at values as high as ca. 10, selectivity to CO and CO_2 were comparable.

Hickman and Schmidt (1993) found 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_4/O_2 feed ratio of 2 and extremely fast space time (10^{-4} - 10^{-2} sec). Other studies have also been carried out on Ru, Pd, and Pt.

A study in Rh is found to be a suitable catalyst for methane partial oxidation by Mallens *et al.* (1997) 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.

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 over Cu/SiO₂. The main products produced by methane partial oxidation over Cu/SiO₂ catalyst are CO₂ and H₂O while those over Ni/SiO₂ are CO₂, H₂O, H₂, surface carbon and small amount of CO.

Otsuka *et al.* (1998) has reported that CeO₂ could be able to convert methane to synthesis gas with H₂/CO ratio of 2 and that adding Pt black could promote syngas formation rate. This finding similar for methane partial oxidation over Ni/CeO₂ catalyst was studied by Dong *et al.* (2002). They also proposed mechanism over Ni/CeO₂ that methane dissociates on Ni and the resultant carbon species quickly migrate to the interface of Ni-CeO₂ and then react with lattice oxygen of CeO₂ to form CO. However, ceria still has some disadvantages. Ceria has a poor thermal resistance and stability at high temperatures. Ceria-supported Ni with high loading (13 wt.%) was an active catalyst for methane partial oxidation but rapidly deactivated by carbon deposition was studied by Tang *et al.* (1998). Fornasiero *et al.* (1996); Gonzalez-Velasco *et al.* (1999); Roh *et al.* (2002) has been reported that addition of ZrO₂ to CeO₂ can improve its oxygen storage capacity, redox properties, thermal resistance and better catalytic activity at low temperature. It was demonstrated that CeO₂-ZrO₂ mixed oxides produced synthesis gas with a H₂/CO ratio of 2 and the formation rates of H₂ and CO were increased due to the incorporation of ZrO₂ into CeO₂.

Pengpanich *et al.* (2004) studied the methane partial oxidation of Ni/Ce_{0.75}Zr_{0.25}O₂ to synthesis gas over the temperature range of 400-800°C at atmospheric pressure. They reported that the catalysts prepared by impregnation method showed higher catalytic activity than those prepared by gel impregnation method. The methane conversion slightly increased while CO and H₂ selectivity remained unchanged with increasing Ni loading for Ni/Ce_{0.75}Zr_{0.25}O₂.

Among of methane partial oxidation, Silva *et al.* (2007) studied the effect of use of cerium-doped alumina in the physical and chemical properties of

Pt/CeO₂/Al₂O₃ and Pt/CeZrO₂/Al₂O₃ catalysts. They reported doped alumina supported CeZrO₂ catalyst exhibited the best performance on partial oxidation of methane, it higher metal dispersion, higher oxygen storage capacity and larger degree of coverage of alumina by CeZrO₂ oxides, which promoted the removal from metal particles.

Pengpanich *et al.* (2006) investigated the activity, selectivity and stability of both the 5 wt% Ni/Ce_{0.75}Zr_{0.25}O₂ and 5 wt% Ni/ β' -Al₂O₃ catalysts for iso-octane partial oxidation in the temperature range of 400-800°C at atmospheric pressure. They found that Ni/Ce_{0.75}Zr_{0.25}O₂ is more active than Ni/ β' -Al₂O₃. For both catalysts, the carbon dioxide and carbon monoxide selectivities were decreased while the hydrogen selectivities were increased with increasing C/O ratio. For Ni/ β' -Al₂O₃ catalysts, the iso-octane conversion started to increase rapidly as temperature was increased from 600 to 700°C also the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst gave almost 100% conversion at low temperature (ca. 550°C), indicate that Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst has higher catalytic activity than Ni/ β' -Al₂O₃ catalyst. This may be due to that the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst has much higher BET surface area and a higher degree of Ni metal dispersion than Ni/ β' -Al₂O₃ catalyst. Hence, the catalyst has higher catalyst activity indicating that has higher BET surface area and degree of metal dispersion. So under the partial oxidation reaction condition, synthesis gas was produced at temperature above 550°C on the Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst.

2.2.2 Mechanisms of Methane Partial Oxidation

The catalytic partial oxidation of methane to synthesis gas was proposed two mechanisms. One is designated as the combustion and reforming reaction mechanism and the other one is direct partial oxidation 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 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 H₂ initiated by CH₄ pyrolysis on the surface to give surface C and H species. The H atoms dimerize and desorb as H₂ while the surface C atoms react

with adsorbed O atoms and desorbs as CO. 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. H₂ 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.

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 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 CH₄/O₂/He feed mixture, is NiAl₂O₄, which has only moderate activity for complete oxidation of methane to CO₂ occurs, 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 consists of a reduced Ni/Al₂O₃ phase. Formation of the CO and H₂ products occurs 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 condition. Weng *et al.* (2000) studied supported Rh and Ru catalysts using in situ time resolved FTIR spectroscopy and found that CO is the primary product of partial oxidation of methane reaction over reduced and working state Rh/Al₂O₃ catalyst. Direct oxidation of CH₄ is the main pathway of synthesis gas formation over Rh/SiO₂ catalysts. CO₂ is the primary product of partial oxidation of methane over Ru/Al₂O₃ and Ru/SiO₂ catalysts. The dominant reaction pathway of synthesis gas formation over Ru/Al₂O₃ catalysts is combustion and reforming reaction mechanism. On the Rh/SiO₂ catalyst, the main reaction is apparently direct partial oxidation mechanism, and also the reaction mechanism appears to be related to the concentration of O₂ 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/CeO₂ where CH₄ dissociates on Ni and the resultant carbon species quickly migrate to the interface of Ni-CeO₂ and then react with lattice oxygen of CeO₂ to form CO.

2.2.3 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:



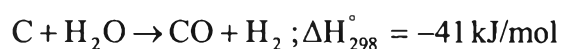
and/or to the slightly exothermic Boudouard reaction (or CO disproportionation):



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^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 > 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 hr.

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 oxide (Li, Na, K) and rare earth metal oxide (La, Ce, Y, Sm). 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 reaction.

Chen *et al.* (2005) studied the role of boron in the coking resistance and the mechanisms of carbon deposition were carefully investigated by temperature programmed oxidation (TPO) and TEM. Three kinds of catalysts, i.e., supported Ni, NiB and Rh catalysts were prepared by incipient wetness impregnation method. They found that the smaller the crystal, the more difficult is the initiation of carbon formation. That mean graphite does not grow on small Ni particles (<5 nm in diameter) under typical methane conversion reaction conditions. Therefore, reducing Ni particle size and preventing Ni sintering seems extremely important in the design of carbon-free partial oxidation of methane catalysts. The Ni particle size on the NiB catalysts is smaller than that on the Ni catalysts without boron. Thus, the very small size of metallic Ni species must be a key factor to inhibit the coke formation during POM. Also, boron addition can further improve the dispersion and thermal stability of Ni particles by serving as the structural promoter.

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. 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_{0.75}Zr_{0.25}O₂ catalyst. They reported that the addition of small amount of Sn (<0.5 wt.%) into Ni/Ce_{0.75}Zr_{0.25}O₂ 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.

2.2.4 Perovskite-type oxides

Metal oxides with a perovskite structure were recognized since the early 1970s when perovskites were proposed as promising automobile exhaust catalysts by Libby (1971) with a lower cost in comparison with their noble metal.

Perovskites can be represented by the general formula ABO₃ structure, in which the cation A of large size is responsible for the thermal resistance of the catalyst, while the cation B of smaller size is associated with the catalytic activity and stability of the whole crystal configuration. These compounds also offer the possibility to partially substitute A and B cation by other kinds of cations, thus allowing to tailor both thermal stability and catalytic performance.

The Ni catalysts have been used widely due to their high activity and relatively low cost. However, it is difficult to prevent sintering of nickel and deposition of carbon at high temperature, Ni catalysts with various additives have been reported. One promising method for inhibition of carbon deposition over Ni catalysts is using perovskite-type oxides. Choudhary *et al.* (1996) reported that complex oxide with a perovskite structure, like LaNiO₃, La_{0.8}Ca_{0.2}NiO₃, and LaNi_{1-x}Co_xO₃ were resistant to carbon deposition. Lago *et al.* (1997) observed that a series

of LnCO_3 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{or Gd}$) perovskites gave high activity and selectivity for the methane partial oxidation to synthesis gas.

Utaka *et al.* (2003) studies on partial oxidation of methane were investigated over perovskite-type Ni catalysts. The result from X-ray photoelectron spectroscopy (XPS) analysis revealed that catalysts calcined and reduced at higher temperature had Ni-rich surfaces and highly dispersed Ni species, resulting in high activity for partial oxidation of methane. Moreover, Qi *et al.* (2005) found that the good performances of $\text{La}_{0.8}\text{Ce}_{0.2}\text{NiO}_3$, better thermal stability and immunity to carbon deposition than LaNiO_3 could be ascribed to the increased oxygen mobility with the presence properties of cerium.

de Araujo *et al.* (2008) work on perovskite-type oxides $\text{LaNi}_{1-x}\text{Ru}_x\text{O}_3$ ($x = 0.0, 0.1, 0.2$ and 1.0) were studies with the aim of developing alternative catalysts, which can be resistant deactivation by carbon deposition. Samples were prepared by thermal decomposition of amorphous citrate precursors followed by heating at 800 to 1000°C for 12 hr in air. They found that the oxide precursors showed low specific surface areas and different reducing behavior. Nickel is more active and selective to hydrogen than ruthenium but the later improved the stability of the catalysts decreasing coke formation. The most promising catalyst was the $\text{LaNi}_{0.8}\text{Ru}_{0.2}\text{O}_3$ sample, which was the most resistant carbon deposition.

Xiaoping *et al.* (2008) investigated the effect of calcination temperature, reaction temperature, and different amounts of replenished lattice oxygen on the partial oxidation of methane (POM) to synthesis gas using perovskite-type LaFeO_3 oxide as oxygen donor instead of gaseous oxygen, which was prepared by the sol-gel method. The results indicated that the particle size increased with the calcination temperature increasing, while BET and CH_4 conversion declined with the calcination temperature increasing using LaFeO_3 oxide as oxygen donor in the absence of gaseous oxygen. CO selectivity remained at a high level such as above 92% , and increased slightly as the calcination temperature increased.