

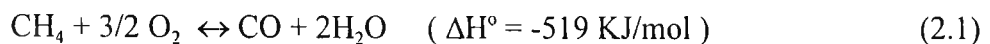
## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

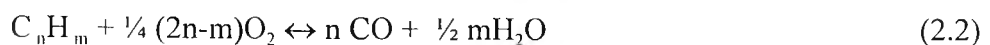
#### 2.1 Autothermal System

Autothermal system is the combination of non-catalytic partial oxidation and steam reforming reaction developed by Hardor Topsoe in the late 1950s with the aim of performing reforming in the single reactor (Pena *et al.*, 1996).

Chemical reactions in the autothermal system can be divided into two parts (Christensen and Primdahl, 1994). The first one is the combustion zone. The hydrocarbon and oxygen are gradually mixed and combusted. Combustion in the autothermal system is a substoichiometric process with overall oxygen to hydrocarbon ratio of 0.55-0.6. Methane combustion takes place through many radical reactions, but in a simplified model, it is considered as one molecule reaction such as;

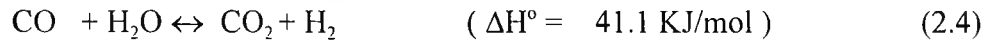


This reaction was selected because CO is the primary combustion production, which is converted to CO<sub>2</sub> by the slow secondary reaction. Excess methane is present at the combustion zone exit after all the oxygen has been converted. Combustion of higher hydrocarbons can be simplified by similar reactions.

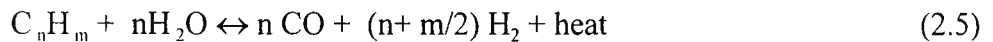


The thermal zone is a part of the combustion chamber, where further conversion occurs by homogenous gas phase reactions. The main reactions are thermal methane reforming and water-gas shift reaction.

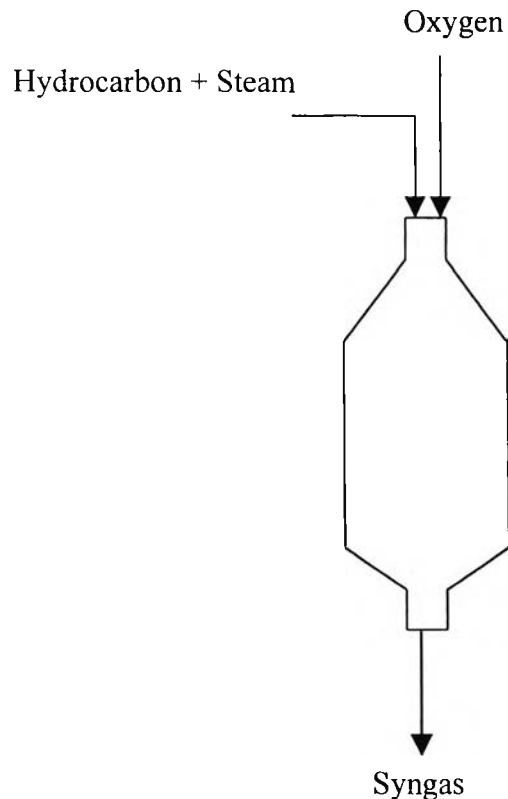
Methane reforming and water-gas shift reaction are:



Steam reforming reaction of higher hydrocarbon is



The second zone is catalytic zone. Final-hydrocarbons conversion takes place through heterogeneous catalytic reactions. At the exit of catalytic-zone, the syngas ( $\text{H}_2 + \text{CO}$ ) is in equilibrium with the methane reforming and water-gas shift reaction. The catalyst destroys any soot precursors formed in the combustion and thermal zone.



**Figure 2.1** Schematic of autothermal reformer (Pena *et al.*, 1996)

The autothermal system can solve the carbon formation problem by using of a proprietary burner and a fixed catalyst bed for equilibration of the gas. This results in lower oxygen consumption (oxygen to hydrocarbon ratio of 0.55-0.6), however, with a certain amount of steam added to the feed stock to eliminate carbon formation. The burner design is critical.

The catalyst bed in this system is exposed to high temperatures (1100 °C to 1400 °C) as the gas leaves the combustion chamber. High thermal stability catalysts and carrier systems are required. The reactions, which occur in the reformer, are controlled by film diffusion at the outer catalyst pellet surface, meaning that the process can be carried out at high space velocities. Optimal flow distribution and pressure drop in the reactor determine the catalyst volume.

In addition, S. Freni *et al.* (2000) examined different process charts; fixed bed, fluidized bed, membrane etc., kinds of catalysts powder, foam etc. ,and catalytic active phases Ni, Pt, Rh, etc. They developed syngas production used for methane partial oxidation with and without steam, and found that the catalysts at high activity and low pressure drop (noble metals supported monoliths) gave good conversion also at low contact time ( $<10^{-2}$  sec) . Rh catalysts improve the selectivity by minimizing the water formation, but are still too expensive. New membrane technologies can represent a future improvement of partial oxidation methane and autothermal reaction.

CO<sub>2</sub> reforming of methane to synthesis gas over an Ni (1 wt%)-Al<sub>2</sub>O<sub>3</sub> catalyst was studied in lab-scale fluidized-bed reactors with I.D. of 3 and 5 cm. (T. Wurzel *et al.*, 2000). The catalytic performance strongly depended on the oxidation state of the catalyst. When applying a reduced catalyst, initial yields of carbon monoxide and hydrogen near the thermodynamic equilibrium were obtained. However, a slow decrease of methane conversion and syngas yields caused by carbon deposition was observed. The fresh unreduced catalyst exhibited significantly lower activity. The in- situ reduced catalyst was more active but yielded CH<sub>4</sub> and CO<sub>2</sub> conversions lower than those predicted at the thermodynamic equilibrium. The reaction was not influenced by interphase gas exchange. Based on these results,

reaction engineering modeling and simulation yielded a global kinetic model which described the experimental data with an error of less than 10%.

## 2.2 Catalysts

In 1983, Setzer *et al.* investigated the high activity steam reforming catalysts particularly adapted for using in the autothermal reforming processes. A rhodium catalyst on a calcium oxide impregnated alumina substrate allowed the autothermal reforming process to take place with substantially no carbon plugging at oxygen to carbon ratios below what had been considered critical for avoiding carbon plugging of the catalyst in the past.

Resistivities to coke formation and nickel sintering have been investigated over nickel alumina catalysts with promoters such as Li, Na, K, Mg, and Ca respectively (Chen and Chen, 1990). The resistivity to nickel sintering of promoted nickel alumina catalyst was improved significantly by the addition of alkali or alkaline-earth metal. The promoter K was found to help in decreasing the coking rate of the nickel catalyst. It was found that the coking rate of promoted nickel catalyst had a strong relationship with the electronegativity or the ionization potential of its promoters. The higher the electronegativity or the ionization potential of its promoters, the greater the coking rates of a promoted nickel catalyst. It was assumed that the addition of alkali metal or alkaline-earth metal caused electron transfer to crystalline nickel and changed the electron density of this crystalline nickel. The lower electronegativity of the promoter, the slower coking rate of the promoted nickel catalyst. The coking rate of the nickel with alkaline-earth metals was greater than that of the nickel catalysts promoted with alkali metals.

The influence of K on the hydrogenolysis of cyclopentane and on the simultaneous carbon formation over a series of alumina-supported catalysts was studied (Demicheli *et al.*, 1994). It was found that the role of K ion on the hydrogenolysis and coking of  $\text{Ni}_2\text{O}_3$  catalysts was better than that are modifiers of

metal supported interaction, basic agent (neutralized the alumina which is necessary for the generation of coke precursors) and inhibitor of hydrogenolysis and coking.

The developments of highly stable nickel catalyst for methane-steam reaction under low steam to carbon ratios were investigated (Yamazaki *et al.*, 1996). A Ni-Mg-O solid solution with low Ni content was found to be an active and stable catalyst for the steam reforming of methane at a steam to carbon ratio of 1.0. The authors observed that this catalyst showed higher activity and much higher stability than a commercial reforming catalyst (Ni/ Al<sub>2</sub>O<sub>3</sub>-MgO).

Another modifier that has been studied was ZnO. Rodriquez *et al.* (1997) investigated the effect of the addition of structure modifying agents such as ZnO on the process of coke formation and sulphur poisoning of ethylene hydrogenation. They found that Ni-Zn-Al catalyst had a higher hydrogenation activity and a lower tendency to coke and methane formation when compared to Ni-Al catalyst.

Ni-Cr/Al<sub>2</sub>O<sub>3</sub> and Ni-Ce/Al<sub>2</sub>O<sub>3</sub> were investigated for autothermal system by Pongpuak(1997). Ni-Cr and Ni-Ce catalyst were found to perform well during steam reforming of iso-octane with autothermal system. For the Ni-Ce catalyst, the H<sub>2</sub>/CO ratios (product ratio) were slightly effected by increasing oxygen concentrations. This indicated that ceria acts as the oxygen storage. Moreover, the H<sub>2</sub>/CO ratio was substantially dependent on the steam/carbon in Ni-Ce catalyst reaction. For the reaction carried on the Ni-Cr catalyst, both of steam/carbon and oxygen/carbon ratios had strong effects on the H<sub>2</sub>/CO ratio. It was observed that the optimum H<sub>2</sub>O/C ratios and the optimum O<sub>2</sub>/C ratios are 0.5 and 0.2, respectively. Cerium and chromium were excellent promoters of steam reforming catalyst with autothermal system because not only they promote the autothermal reaction but also prevent and reduce the coke formation.

Steam reforming of naphthalene on Ni-Cr/Al<sub>2</sub>O<sub>3</sub> catalysts doped with MgO, TiO<sub>2</sub>, and La<sub>2</sub>O<sub>3</sub> was investigated by Banggala *et al.*(1998). This study showed that the Ni-Cr catalyst supported with  $\gamma$ -alumina doped with MgO, TiO<sub>2</sub>, and La<sub>2</sub>O<sub>3</sub> had the best catalytic properties as far as the activity and robustness were concerned. It has been also found that introduction of La<sub>2</sub>O<sub>3</sub> led to a decrease of coke deposition.

TiO<sub>2</sub> addition decreased the conversion and yield because it destroyed the alumina matrix.

At the same time, Chen *et al.* (1998) studied effects of trivalent-metal oxides, Cr<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> to a Ni-Mg-O catalyst. Addition of small amount of Cr<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> to a Ni-Mg-O catalyst was found to remarkably improve the performance of the catalyst for coking-resistance.

Ni/MgO showed high resistance to carbon formation under thermodynamically severe conditions in the partial oxidation of methane to syngas (Tang *et al.*, 1998). The performance of Ni/MgO, Ni/CaO and Ni/CeO<sub>2</sub> was compared. It was revealed that the excellent performance of Ni/MgO resulted from an ideal solution between NiO and MgO.

There have been some studied trying to find alternative supports for metal catalysts used for steam reforming reactions. Hegarty *et al.* (1998) investigated ZrO<sub>2</sub>-supported metals for syngas production. The catalysts containing 1% of Co, Cu, Fe, Pt, Pd, and Ni supported on Zirconia were tested for the steam reforming of methane. The Pt, Pd, and Ni materials were found the most active. The Cu, Co and Fe catalysts exhibited significant deactivation, despite the presence of excess steam. The catalysts containing Pt and Ni remained stable in the presence of excess steam, however, with equimolar amounts of H<sub>2</sub>O and CH<sub>4</sub>, the Ni catalyst deactivated due to carbon deposition while the Pt catalyst maintained its activity. The stability of Pt/ZrO<sub>2</sub> catalyst was improved by the addition of O<sub>2</sub>. There was no significant deactivation after 15 hours for all feed composition. In the other words, the Pt/ZrO<sub>2</sub> catalyst was found to be stable under all catalytic partial oxidation combined with steam reforming feed composition.

Kaspar (1999) found that minimization of coke is also a function of the support, the role of rare earth oxides was also investigated. The oxides appeared slightly to enhance steam reforming and significantly to decrease coke formation by increasing coke gasification. Ceria is the rare earth oxide widely used in the three-way catalyst as a promoter. It can promote the noble metal dispersion, the water-gas

shift reaction and steam reforming reaction. Moreover, it can act as oxygen storage system by storing and releasing O<sub>2</sub> due the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox couple.

The catalytic activity of cerium/zirconium mixed oxides has been investigated by Gonzalez-Velasco *et al.* (2000) with the aim of optimizing the Ce/Zr composition. Their catalytic activity was surprisingly high, considering no noble metal was present in the composition, particularly for oxidation reactions (CO and C<sub>3</sub>H<sub>6</sub>), while their reduction activity was very small (NO). The specific activity in practice was found for the mixed oxide with a Ce/Zr ratio of 80/20, giving high specific activity and the highest specific surface area.

In the hydrogen production for fuel cell by steam reforming, methane and methanol are the main materials in the process. Studies have been done on methane reforming, carbon dioxide reforming and methanol synthesis. For methanol production, there are many processes that are complex than methane or hydrocarbons reforming, since methanol has to be converted from methane.

The catalytic cracking of methane over supported nickel catalyst was a potential route to the production of CO-free hydrogen and filamentous carbon. In this study, Rita Aiallo *et al.* (2000) showed that a 15wt.%Ni/SiO<sub>2</sub> catalyst was able to be fully regenerated at 923 K with steam for up to 10 successive cracking/generation cycles without any significant loss of catalytic activity.

In this year, Katsutoshi Nagaoka *et al.* (2001) studied the carbon deposition during carbon dioxide reforming of methane. They studied the relation between coke formation and the deactivation of supported Pt catalyst during reforming at above 1070 K and comparison between Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/ZrO<sub>2</sub>. Gradually, the coke on the support (Pt/Al<sub>2</sub>O<sub>3</sub>) increased to an extent that it blocked the reaction also at the location. In contrast with Pt/Al<sub>2</sub>O<sub>3</sub>, coke was not observed on Pt/ZrO<sub>2</sub> even after the exposure to reforming gas for 12 hr.

### 2.3 Coke Formation

The high temperature associated with steam reforming to produce hydrogen favor the formation of carbon. Four reactions may be involved (Trimm, 1997)



Minimization of coking is one of the major factors controlling the industrial application of steam reforming process. Carbon will deposit on the catalyst and cause the blockage of catalyst pores and catalyst deterioration, leading to reactor shutdown.

For a given steam/methane ratio, it is possible to predict the thermodynamic likelihood of carbon deposition via reaction (2.6) from equilibrium gas mixture containing carbon monoxide, hydrogen, steam and methane. However, it has been well established that the minimum thermodynamic steam/methane ration for carbon deposition over nickel catalysts via reaction (2.6) is lower than the predicted ratio calculated from the thermodynamic data for graphite formation. It has been fairly well established that the key reactions occur over a surface layer of nickel atoms. If such a layer is allowed to build up (e.g., because of low steam partial pressure) a filament or whisker of carbon can start to grow attached to nickel crystallite. Such carbon filaments can generate massive forces within catalyst pellets, and, once started, can lead to rapid catalyst breakdown, and the blocking of reactor tubes.

Reactions (2.8) and (2.9) tend to lead to a surface pyrolytic carbon which can encapsulate the nickel particles. Such reactions have the greatest risk of occurring at the inlet of a reformer where there is no hydrogen present. At this point likelihood of carbon formation is governed not so much by equilibrium



considerations, but by the relative kinetic of carbon reforming and carbon removal (gasification) reaction.

Higher hydrocarbons have a greater propensity for carbon deposition than methane. Thermal or steam cracking of hydrocarbons can occur above 600-650°C even in the absence of nickel catalysts. The cracking leads to olefins and then to a carbonaceous, which can be dehydrogenated to produce coke.