

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

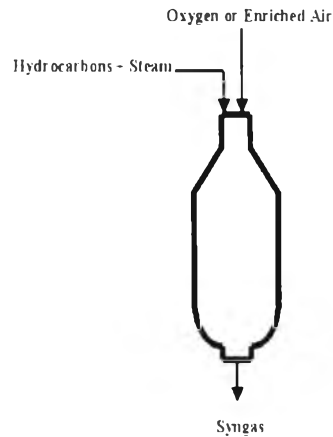
#### **Strategies for coke minimization:**

#### **2.1 Autothermal System**

An autothermal system is a combination of non-catalytic partial oxidation and steam reforming developed by Haldor Topsoe in the late 1950s with the aim of combination oxidation zone and reforming zone in a single reactor (Pena *et al.*, 1996).

Chemical reactions in the autothermal system can be divided into two main parts (Christensen and Primdahl, 1994). The first one is the combustion zone. This zone is the turbulent diffusion flame where hydrocarbon and oxygen are gradually mixed and combusted. Normally, the principle of "mixed-is-burnt" is assumed, because the exothermic combustion reactions are very fast. 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, i.e., the highly exothermic combustion of CH<sub>4</sub> to CO and H<sub>2</sub>O with an O<sub>2</sub>/CH<sub>4</sub> ratio of 1.5 (5). This reaction (5) was selected because CO is the primary combustion product, which is converted to CO<sub>2</sub> by a 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.



**Figure 2.1** Schematic of autothermal reformer

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 (1) and water-gas shift reaction (2), but various pyrolysis reactions involving higher hydrocarbon also occur.

In the catalytic zone, final-hydrocarbons conversion takes place through heterogeneous catalytic reactions. At exit of catalytic-zone, the syngas is in equilibrium with the methane reforming (1) and shift reaction (2). The catalyst destroys any soot precursors formed in the combustion and thermal zones.

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

feedstock to eliminate carbon formation. The burner design is critical. A typical reactor lay out is shown in Figure 2.1.

The catalyst bed in this system is exposed to high temperatures (1,100 °C to 1,400 °C) as the gas leaves the combustion chamber. High thermal stability catalyst 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.

## 2.2 Catalysts

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

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 Ni/Al<sub>2</sub>O<sub>3</sub> catalysts is at least threefold. The first one is that modifiers of metal supported interaction reduce the adhesion strength between nickel particles and alumina matrix. The second one is basic agent, as it neutralizes the alumina necessary for the generation of coke precursors, whereby deactivation of the smaller nickel crystallites does not occur. The last one is inhibitor of hydrogenolysis and coking, since when present at high K/Ni ratio potassium appears to block specific sites for these reactions. Furthermore, the alkali appears to promote the catalytic oxidation of filamentary carbon, without having much effect on the combustion of bidimensional carbon and coke. This would be in relation to the specific localization of the alkali between the nickel particle and the carbon tube of the filaments. Finally, potassium seems to favor hydrogen chemisorption on nickel, or the spillover of H atoms to the support, rather than to affect the metal particle size.

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 Bangala *et al.* (1998). This study has shown that the Ni-Cr catalyst supported with  $\gamma$ -alumina doped with MgO and La<sub>2</sub>O<sub>3</sub> has the best catalytic properties as far as the activity and robustness are concerned. The solid state reaction of MgO with Al<sub>2</sub>O<sub>3</sub> at high temperatures leads to the formation of MgAl<sub>2</sub>O<sub>4</sub> spinel, which is responsible for the robustness of the catalyst. The authors found that Cr significantly inhibits the formation of nickel carbide. They suggested that Cr form an alloy with Ni. Therefore, Cr geometrically rearranges the Ni crystal plane and alters the electronic properties of the Ni atoms in such a

way that the encapsulation of nickel by inactive carbon filaments is reduced. It has been also found that introduction of  $\text{La}_2\text{O}_3$  leads to a decrease of coke deposition. The role of  $\text{La}_2\text{O}_3$  is related to an increase of the nickel crystallites dispersion as well as the possible neutralization of strong acidic sites.  $\text{TiO}_2$  addition decreases the conversion and yield. The crystallinity of the catalyst containing  $\text{TiO}_2$  is rather poor, as is its robustness because  $\text{TiO}_2$  destroys the alumina matrix.

The developments of highly stable nickel catalyst for methane-steam reaction under low steam to carbon ratios was investigated (Yamazaki *et al.*, 1996). A Ni-Mg-O solid solution with low Ni content ( $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ ) 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 shows higher activity and much higher stability than a commercial reforming catalyst ( $\text{Ni}/\text{Al}_2\text{O}_3\text{-MgO}$ ). It was suggested that the suppressed coke formation of this catalyst be caused by very small nickel particles and a difference in the composition of surface carbonaceous species on the Ni metal particles.

Chen *et al.*, (1998) studied effects of trivalent-metal oxides,  $\text{Cr}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  to a Ni-Mg-O (Ni/Mg:1/1 mol/mol) catalyst. Addition of small amount of  $\text{Cr}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  to Ni-Mg-O catalyst was found to remarkably improve the performance of the catalyst for coking-resistance. Doping of the small amount of  $\text{Cr}^{3+}$  and  $\text{La}^{3+}$  resulted in an increase in the degree of disorder in the solid solution, which is in favor of enhancing the mobility of the  $\text{O}^{2-}$  lattice, and thus speeding up the surface oxidation reactions. On the other hand, it also leads to the formation of rich-in-Ni surface layer, where the surface Ni-species were maintained with higher possibility in positive valence states so that deep dehydrogenation of methane to carbon was

inhibited to some extent. These factors are closely related to the performance of the catalyst for coking-resistance.

Ni/MgO shows high resistance to carbon formation under thermodynamic severe condition 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.

Another modifier that has been studied is 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 ethyne hydrogenation. They found that Ni-Zn-Al catalyst has a higher hydrogenation activity and a lower tendency to coke and methane formation compared to Ni-Al catalyst. These are because ZnO reduces the formation of NiAl<sub>2</sub>O<sub>4</sub> species. The presence of NiAl<sub>2</sub>O<sub>4</sub> gives rise to an irregular geometry of the metallic particles, with a very high concentration of active sites for the rupture of C-C bonds. This results in the coke formation. For Ni-Zn-Al catalyst, a lower strength of the metal ethyne bond gives a higher selectivity to hydrogenation product. The authors concluded that the interaction between the active metal and the support might influence the strength of ethyne adsorption via modification of the physical configuration of the metal particles and their electron density field.

Recently, there have been some studies trying to find alternative supports for metal catalyst which is used for steam reforming reaction. Hegarty *et al.* (1998) investigated ZrO<sub>2</sub>-supported metals for syngas production. The catalysts containing 1% of Co, Cu, Fe, Ni, Pd, and Pt 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 catalyst 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.

An alloy catalyst for steam reforming is another one of interesting catalyst studies. Rodriguez *et al.* (1997) studied the carbon deposition on iron-nickel alloy particles. They found that the amount and nature of the carbon deposit formed on iron-nickel particles during the decomposition of ethane at temperature in excess of 800°C is extremely sensitive to the composition of the alloy. An alloy powder rich in iron was found to exhibit a higher activity for the formation of carbon than the sample containing equal amount of the two components. Examination of the solid carbon deposit directly associated with the alloy powders revealed the existence of two types of material: (a) carbon nanofibers, and (b) graphitic shell-like growths. The latter structure appears to be more prevalent on the Fe-Ni (5:5) particles, whereas nanofibers are most abundant on the Fe-Ni (8:2) sample. The data obtained from the temperature programmed oxidation studies in CO<sub>2</sub> indicates that the deposit formed on the Fe-Ni (5:5) powder containing a large fraction of highly ordered carbon (graphite) than that formed on the iron-rich alloy. It was suggested that two alloys have different crystal structures, carbon solubility and diffusivity properties. These are all factors, which play an important role in determining the type, crystalline perfection and conformation of carbonaceous deposits. Another study of an alloy catalyst was taken by Besenbacher *et al.* (1998). They investigated a high-surface area gold-nickel catalyst for steam reforming. It was found that the Au-Ni surface alloy is a less reactive catalyst but more

robustness. For the Au-containing sample does not produce graphite while the typical Ni catalyst was deactivated by graphite formation in the severe conditions.

The future trend of research on the role of catalyst supports would appear to offer most chances of improved control of coking during steam reforming.

### **2.3 Addition of Sulfur**

It is well known that coke formation can be minimized during steam reforming if traces of sulfide are present in the feed. Not only does adsorbed sulfur on catalyst surface, will the deactivate nickel but also delineate ensembles of sites, where sulfur is not adsorbed. It was suggest that the size of these ensembles was critical in allowing steam reforming with minimal formation of coke. This is due to the ensemble free nickel are sufficient for the conversion of adsorbed methane with steam but they are too small to the normal dissolution precipitation-nucleation for the carbon whisker. Ensembles of 3-4 nickel atoms are involved in steam reforming, while carbon formation required 6-7 atoms.

The critical ensemble size was found to be generated at sulfur coverage more than 0.7-0.8 (corresponding to  $H_2S/H_2$  ratios of greater than about  $7.5 \times 10^{-7}$ ) (Trimm, 1997).

The effect of eliminating carbon formation by addition of sulfur is utilized in steam reforming for production of reducing gas and carbon monoxide rich gases.