

## CHAPTER II

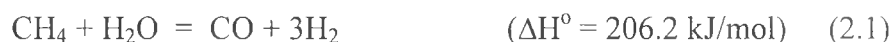
### LITERATURE SURVEY

#### 2.1 Processes For Hydrogen Production

Several processes are used to produce hydrogen: steam reforming, partial oxidation, pyrolysis and gasification. However, there are two main processes that are important in the conversion of hydrocarbon to syngas. They are steam reforming and partial oxidation processes.

##### 2.1.1 Steam Reforming

Steam reforming is the established process for converting natural gas and other hydrocarbons into synthesis gas (a mixture of CO and H<sub>2</sub>). The reforming of natural gas utilizes two simple reversible reactions: the reforming reaction (2.1) and the water-gas shift reaction (2.2).



The reforming reactions are normally carried out over a supported nickel catalyst at elevated temperatures, typically above 500°C. The heavy hydrocarbons also react with steam in similar fashion:



Reaction (1) and (2) are reversible and are normally at equilibrium as the reaction rates are very fast. The product gas from a traditional reformer reactor is therefore governed by thermodynamics. Steam is normally added well in excess of the stoichiometric requirement of reaction (1) so that the equilibrium of reaction (2) moves towards more CO<sub>2</sub> rather than CO. This is to avoid carbon deposition through the Boudouard reaction (9), which is also catalyzed by nickel.

Steam may be replaced completely (or in part) by CO<sub>2</sub>, which gives a more favorable H<sub>2</sub>/CO ratio for some applications:



Methane and other hydrocarbon can be converted to a hydrogen rich gas via partial oxidation, which may be catalyzed or non-catalyzed:



Several metals have been found to catalyze reactions (1)-(5), but nickel is generally preferred on cost grounds. In commercial steam reforming catalysts, the nickel is supported on a refractory oxide such as alumina, magnesia or mixed ceramics, which are able to tolerate high temperatures. The physical form has evolved over many years to maximize the activity and rate of heat transfer within the reformer reactor. The catalyst pellet size is a compromise between ensuring good packing, mechanical stability and low-pressure drop. The pressure drop is in turn governed by the vessel size and mass velocity for which the reactor is designed (Clake *et al.*, 1997).

Not only methane but also various hydrocarbons such as naphtha, butane, benzene and hexane are used as feedstock for steam reforming. However, methane is still the popular feedstock because a low rate

of coke formation is obtained. The relative rate of coke formation, from various hydrocarbon (Satterfield, 1980) are about as follows:

Ethylene >> benzene, toluene > n-heptane > n-hexane  
> cyclohexane > trimethylbutane~n-butane~  
carbon monoxide > methane

Coke formation from natural gas is generally not a significant problem, but it can be much more serious with other hydrocarbons. For example, aromatics such as benzene and toluene are more conducive to coke formation than paraffins and are reformed more slowly.

#### *2.1.1.1 Reforming Catalyst*

Industrial steam reforming catalysts are normally based on nickel. For many years nickel has been recognized as the most suitable metal for steam reforming of hydrocarbons. Other metals can be used, for example cobalt, palladium, platinum, iridium, ruthenium and rhodium. Although some precious metals are considerably more active per unit weight than nickel, nickel is generally preferred on cost ground. The support plays an importance role in steam reforming catalyst. It provides thermal stability and in assisting coke removal. It is well known that basic catalyst promotes the reaction between steam and carbon, and catalyst supports are chosen with this in mind.

In the early steam reforming processes operating at pressures up to about 0.3 MPa, the most common support was a calcium aluminate silicate, which was inexpensive and gradually became stronger with use. This catalyst support was unsatisfactory at higher pressures (up to about 3 MPa) because of migration of silica at the higher steam partial pressures.

In the early 1960s, this support was replaced with a low-silica calcium aluminate; it, however, had lower crush strength, gradually lost strength on use, and lost activity by gradual formation of nickel aluminate. This support, in turn, was replaced with a low-area  $\alpha$ -alumina that, although more expensive, was mechanically stronger and longer lasting. Potassium compounds or other alkaline substances are frequently added to accelerate carbon-removal reactions. However, they may be slowly lost from the catalyst by volatilization and be deposited downstream on heat-exchange surfaces or on other catalyst beds. Minimizing the sintering of nickel is also important, and this is related to support composition and method of catalyst preparation.

The most active alkali is  $K_2O$ , which is mobile on the catalyst surfaces but may be slowly lost by volatilization. ICI solved the problem by the use of complex potassium alumina-silicate and calcium magnesia silicate. In ICI catalyst 46-1, potassium is in the form of kalsilite  $K_2O \cdot Al_2O_3 \cdot SiO_2$ . This reacts slowly with  $CO_2$  to form  $K_2CO_3$ , which is then rapidly hydrolyzed to  $KOH$ . This formulation avoids an excessive rate of loss of volatile potassium compound.

Haldor Topsoe reported the role for magnesia in the support, with magnesium spinels offering good thermal stability. It is necessary to heat up the system with care, since hydrolysis equilibrium favors hydration at temperature below  $425^\circ C$ . The formation of hydroxide results in a decrease in the structural strength of the catalyst. As a result, steam is not introduced to the system on start-up until the temperature exceeds ca.  $425^\circ C$ .



The developments of highly stable nickel catalyst for steam-reforming reaction of methane 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.

With steam reforming of naphthalene, Ni-Cr/ $\text{Al}_2\text{O}_3$  catalysts doped with MgO,  $\text{TiO}_2$  and  $\text{La}_2\text{O}_3$  were investigated by Bangala *et al.* (1998). The Ni-Cr supported with  $\gamma$  - alumina doped with MgO and  $\text{La}_2\text{O}_3$  has the best catalytic properties as far as the activity and robustness are concerned. The solid state reaction of MgO with  $\text{Al}_2\text{O}_3$  at high temperatures leads to the formation of  $\text{MgAl}_2\text{O}_4$  spinel, which is responsible for the robustness of the catalyst. Cr significantly inhibits the formation of nickel carbide. The authors 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 contains the alumina matrix.

Although the presence of alkali may accelerate carbon-removal reactions, alkali may cause corrosion and/or fouling problems downstream. For natural gas feed the use of alkali is usually unnecessary, and a higher-activity catalyst may be used instead. With naphtha, control of carbon-forming reactions is more important, and alkali or alkaline earth substances are often added for this purpose.

Trimm (1999) reported that rare earth oxides appear slightly to enhance steam reforming and significantly to decrease coke formation by increasing coke gasification. For example, ceria, itself, is inactive for steam reforming but a combination of nickel, and ceria give a much-improved coking performance.

Praharso *et al.* (1999) had investigated the effect of the oxide of cerium, samarium and praseodymium as a promoter for nickel based catalysts for steam reforming of methane. The catalyst prepared by a two step impregnation method showed significant improvement of activity for methane reforming. The increase in loading of the rare-earth oxide increases the activity of the catalyst linearly. The positive effect of the rare earth on the steam activity decrease as  $\text{CeO}_2 > \text{PrO}_2 > \text{Sm}_2\text{O}_3$ . The cerium containing catalysts exhibits excellent anti-coking ability comparable to that of advanced commercial catalysts, this can be explained in the term of the larger adsorption of water on the surface of cerium oxide and the resulting relatively high rates of carbon gasification. The selectivity of the nickel-cerium oxide catalyst to hydrogen add carbon dioxide production during the methane steam reforming is also significantly improved due to the increase of importance of the water gas shift reaction.

The influences of ceria as a promoter for steam reforming of methane by supported Pd and Ni catalysts was examined by Cracuin *et al.* (1999). Intimate contact between either Ni or Pd and bulk or gamma- $\text{Al}_2\text{O}_3$  supported  $\text{CeO}_2$  results in a much higher catalytic activity than that found for any of the individual components, demonstrating that there is a clear catalytic synergism between the catalytic metals and ceria. The enhancement observed for  $\text{CeO}_2$  and alumina-supported  $\text{CeO}_2$  are similar, demonstrating that bulk  $\text{CeO}_2$  is not needed for the synergism. Furthermore, rates for  $\text{CeO}_2$ -supported Pd and Ni are very similar, suggesting that the rate-limiting step involves the transfer of oxygen from  $\text{CeO}_2$ .

The alternative catalyst supports had been studied. Hegarty *et al.* (1998) examined ZrO<sub>2</sub>-support metal for syngas production. The catalysts containing 1 %wt. of Co, Cu, Fe, Ni, Pd, and Pt supported on ZrO<sub>2</sub> was tested the activity for steam reforming of CH<sub>4</sub>. The Pt, Pd and Ni material were found to be the most active in the presence of steam. The catalyst containing Pt and Ni remain stable in the presence of the excess steam. However, Ni catalyst deactivates due to carbon deposition at equimolar amounts of H<sub>2</sub>O and CH<sub>4</sub>, while the Pt catalyst maintains its activity.

Subsequently, Otsuka *et al.* (1999) prepared a series of CeO<sub>2</sub>-ZrO<sub>2</sub> composite oxides (Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>) for the gas-solid reaction with CH<sub>4</sub> in the absence of gaseous oxidant. From the characterization result, a solid solution with fluorite structure is formed for the sample with Zr content below 50% (x ≤ 0.5). For Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>, both desorption of O<sub>2</sub> and reduction by H<sub>2</sub> took place at lower temperatures as compared with that for CeO<sub>2</sub> alone. Like CeO<sub>2</sub>, the reaction of Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> with CH<sub>4</sub> selectively produced synthesis gas with a H<sub>2</sub>/CO ratio of 2, but the formation rates of H<sub>2</sub> and CO is increased and the activation energy was remarkably decrease due to the incorporation of ZrO<sub>2</sub> into CeO<sub>2</sub>. The reaction was further accelerated by the presence of Pt catalyst. The conversion of CH<sub>4</sub> to H<sub>2</sub> and CO could be achieved at temperature as low as 500°C by using Ce<sub>0.8</sub>Zr<sub>0.2</sub>O<sub>2</sub> in the presence of Pt.

The preparation method also plays the important role on the properties of steam reforming catalyst. For the precipitation method, the nickel and alumina are coprecipitated and hydroxy-carbonates by addition of alkali to an aqueous solution of their salts. The precipitate is subsequently separated by filtration, washed, dried and then calcined to decompose the precursor to nickel oxide and alumina. Unfortunately, this method of preparation leads to the formation of  $\gamma$ -alumina which is thermodynamically less stable than the  $\alpha$ -alumina form. Under high pressure of steam at elevated

temperatures, such as are present under steam reforming conditions, the  $\gamma$ -alumina converts to the  $\alpha$ -alumina over period of time. This process is called hydrothermal sintering. It results in a substantial change in the microstructure of the catalyst and leads to degradation of the catalyst activity. For impregnation method, the nickel can be incorporated by impregnating a performed catalyst support with a solution of a nickel salt that is subsequently decomposed by heating to the oxide. Impregnated catalysts are widely used because they are generally stronger than precipitated catalysts. Many method of producing stable supports have been devised over the past 30 years and commercial catalysts frequently contain mixtures of alumina, magnesia, zirconia, and other ceramic oxide.

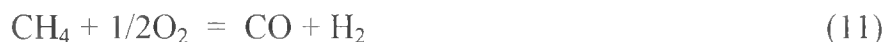
Wang *et al.* (1998) prepared Ni/Al<sub>2</sub>O<sub>3</sub> catalysts by using different nickel precursor compounds. The catalytic activities of all samples were studied for the reaction of methane reforming with CO<sub>2</sub>. The authors found that the nickel precursor employed in the catalyst preparation plays an important role. The catalyst based on nickel nitrate exhibited higher catalytic activity and stability over a 24-h test period than the other two catalysts derived from nickel chloride and nickel acetylacetonate. A comprehensive characterization of the catalyst show that the weak interaction between Ni particles and gamma-alumina. Coking studied show that carbon deposition on Ni catalysts derived from inorganic precursors (nitrate and chloride) is more severe than on the organic precursor-derived catalyst. However, the Ni nitrate-derived catalyst was found to have the highest stability (or lowest deactivation rate) mainly due to the active carbon species (-C-C-) of the resulting graphitic structure and their close contact with the metal particles. In contrast, the carbon formed on Ni-AA catalyst (from Ni acetylacetonate) is dominated by inactive -CO-C- species, thus leading to a rapid accumulation of carbon in this catalyst and more severe deactivation.



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.

### 2.1.2 Partial Oxidation

The other major route to H<sub>2</sub> is non-catalytic partial oxidation of fossil fuels, or gasification. One key advantage of this approach is that it accepts all kind of hydrocarbon feeds. 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 ~ 1300°C (Dicks et. al., 1996). The general reaction is described by (11).



In the absence of catalyst, the reactor temperature must be high enough to reach complete CH<sub>4</sub> conversion. Combustion product like CO<sub>2</sub> and H<sub>2</sub>O are also formed to a certain extent. Subsequently, endothermic reactions like steam reforming are also involved, which determine the outlet temperature in the order of 1000-1100°C. At this stage, the gas composition is near thermodynamic equilibrium. According to the stoichiometry of reaction (11) the combustion of O<sub>2</sub> should be, in the absence of combustion product, approximately 0.5 O<sub>2</sub>/CH<sub>4</sub>. However, actual use requires O<sub>2</sub>/CH<sub>4</sub> ratio of about 0.7 (Pena *et al.*, 1996).

## 2.2 Coke Formation

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.

The high temperature associated with steam reforming to produce hydrogen favor the formation of carbon. Four reactions may be involved (Trimm, 1999)



For a given steam /methane ratio, it is possible to predict the thermodynamic likelihood of carbon deposition via reaction (6) from equilibrium gas mixture containing carbon monoxide, hydrogen, steam and methane. However, it has been well established that the thermodynamic minimum steam/methane ration for carbon deposition over nickel catalysts via reaction (6) is lower than predicted 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 are 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.

Reaction (8) and (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 dehydrogenate to produce coke.

### 2.3 Autothermal System

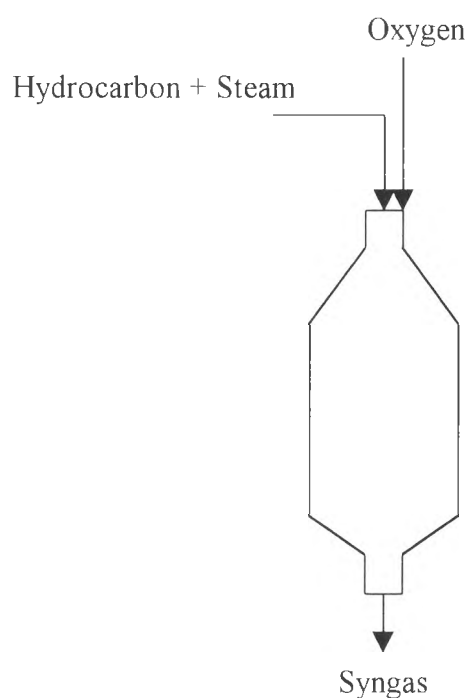
Autothermal systems is a combination of non-catalytic partial oxidation and steam reforming developed by Haldor Topsoe in the late 1950s with the aim of combination of oxidation zone and reforming zone in a single reactor (Pena *et al.*, 1996).

There are two main reactions in the autothermal system; combustion zone and reforming zone (Christensen *et al.*, 1994). The feed stream of hydrocarbon, such as methane, and steam are mixed with oxygen in a burner where the partial oxidation reaction (5) take place. This zone is called “combustion zone”. Heat from the exothermic reaction or the partial oxidation reaction will be provided for the endothermic reaction or steam reforming reaction in the reforming zone. Operating temperature in this zone is about 2200 K. This results in a lower oxygen consumption with overall oxygen to CH<sub>4</sub> ratio of 0.55-0.60. While the simplified model of methane combustion has O<sub>2</sub>/CH<sub>4</sub> of 1.5 (5).

Excess methane from the combustion zone is fed to the reforming zone that packed with Ni-based catalyst. Methane will reacted with water in this zone. The main reactions are steam reforming reaction (1) and water-gas shift reaction (2). No external heat is required for the steam reforming

reaction. In this zone, the catalyst will destroy any soot precursors formed in the combustion zone. The operating temperature is 1200-1400 K.

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 0.55-0.60), however, with a certain amount of steam added to the feedstock to eliminate carbon formation. A typical reactor of autothermal system lay out is shown in Figure 2.1.



**Figure 2.1** Schematic of autothermal reformer