

CHAPTER I

INTRODUCTION

Important of production of hydrogen by steam reforming from methane, naphtha, heavy oil, and coal has achieved increasing in recent years. This because of a increased demand for hydrogen, both for petroleum refining processes such as hydrotreating and hydrocracking and for the petrochemical use in the production of methanol, methanol-to gasoline (MTG), ammonia and hydrocarbon synthesis via Fischer-Troph process.

Moreover, hydrogen has a good potential as an alternative fuel for the future. Hydrogen can be cost-effectively produced from renewable energy sources and made available for widespread use as energy carrier and a fuel.

Several processes are used to produce hydrogen: catalytic steam reforming, partial oxidation, pyrolysis and gasification. Most of the world's hydrogen is currently derived from hydrocarbon such as oil or natural gas, via the catalytic steam reforming. Hydrogen also can be produced from electrolysis of water, photoelectrolysis and photobiological. These methods are not widely used because they are more expensive than steam reforming of natural gas. Figure 1.1 shows the most obvious pathways for the production of hydrogen from different primarily energy sources.

1.1 Steam Reforming

Steam reforming is a reaction using steam to react catalytically with natural gas, Primarily methane, or with hydrocarbon feedstock, such as

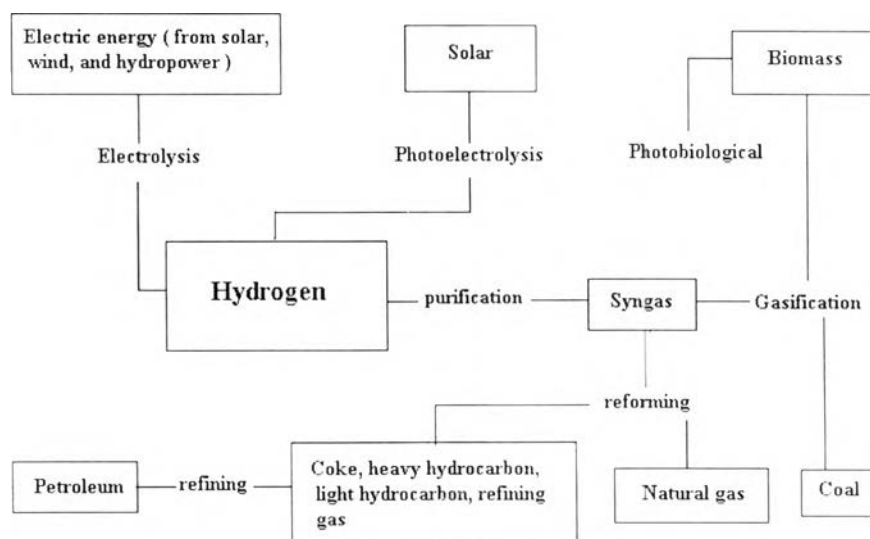
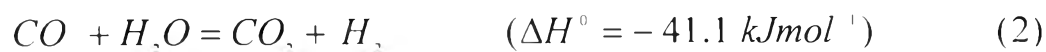


Figure 1.1 Sources of production of hydrogen

naphtha to form a mixture of hydrogen and carbon monoxide called synthesis gas (syngas) (Scatterfield, 1991).

Steam reforming is a mature technology, practiced industrially on large scale for hydrogen production and several reviews of the technology have been published (Rostrup-Nielsen, 1984. Twigg, 1989, Clarke *et al.*, 1997, and Trimm, 1997). The production of hydrogen and syngas by steam reforming is summarized in Figure 1.2.

This process has two main reactions; the reforming reaction (1), and the water gas shift reaction (2),



SYNGAS/CO PRODUCTION

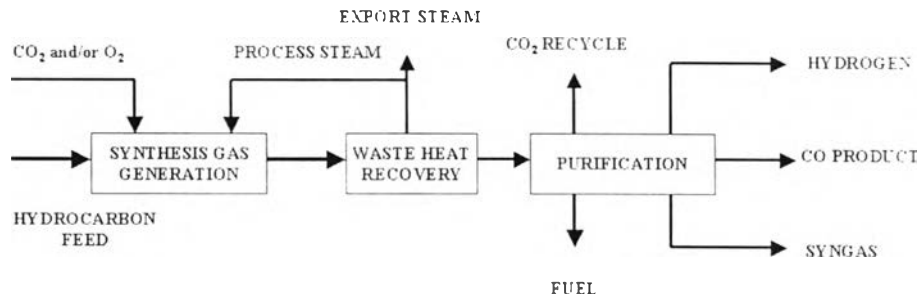
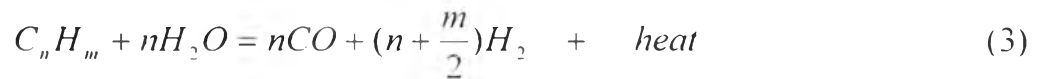


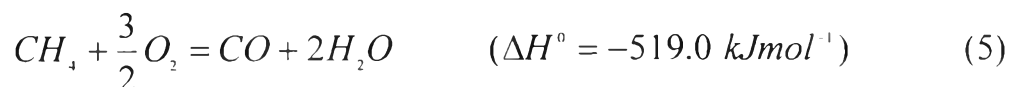
Figure 1.2 The diagram of hydrogen and syngas production

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



Reactions (1) and (2) are reversible and normally at equilibrium as the reaction rates are very fast. The composition of the product gas from a conventional reformer reactor is therefore governed by thermodynamics. Steam is normally added in excess of stoichiometric requirement of reaction (1) so that equilibrium of reaction (2) moves toward more CO_2 produced rather than CO consumed. This avoids carbon deposition via the Boudouard reaction (6) which is also catalyzed by nickel.

Steam may be replaced completely or in part by CO_2 :



Methane may also be converted to a hydrogen rich gas by means of oxygen through partial oxidation:

Several metals have been found to catalyze reactions (1)-(5), but nickel is generally preferred on the cost grounds. In commercial steam reforming catalysts, nickel is supported on a ceramic oxide. The choice of support is governed by the surface area required, as well as the need for stability in the operation environment. Various modifications of alumina are frequently used. Corundum or α -alumina is an ideal support for high temperature steam reforming application where a high specific activity is not required because it is the most stable form of alumina.

The steam reforming catalysts can be prepared from precipitation method and impregnation method. For the precipitation method, the nickel and alumina are coprecipitated as 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 γ -alumina which is thermodynamically less stable than the α -form. Under high pressure of steam at elevated temperatures, such as are present under steam reforming conditions, the γ -alumina converts to α -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 preformed catalyst support with a solution of a nickel salt which is subsequently decomposed by heating to the oxide. Impregnated catalysts are widely used because they are generally stronger than precipitated catalysts. Many methods 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.

The physical form of steam reforming catalysts has also evolved over the years to maximise 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.

1.2 Carbon deposition

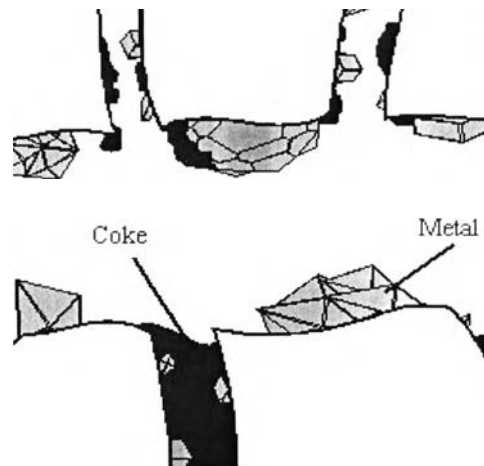
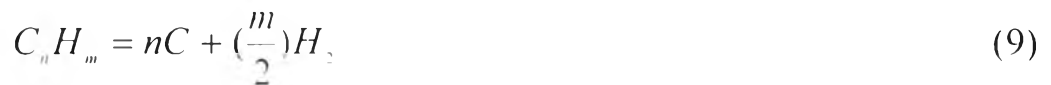


Figure 1.3 The deactivation by coke formation in a supported metal catalyst (Adapted from Larsson *et al.* (1998))

Formation of carbon or coke is a major problem in the operation of an industrial steam reformer, not only because of catalyst deactivation, but also because of the severe consequences of maldistribution of heat and the damage of tube metal failure due to overheating caused by formation of "hot spots", "hot band" or "hot tubes".

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



For a given steam to carbon ratio, it is possible to predict thermodynamics of carbon deposition via reaction (6) from equilibrium gas mixtures containing carbon oxides, hydrogen, steam and methane. However, it has been well established that the minimum steam to carbon ratio for carbon formation 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 a layer is allowed to build up, a filament or whisker of carbon, because of the low steam partial pressure, can start to grow and attach to a nickel crystallite. Carbon filaments can generate massive force within catalyst pellets and once started can lead to rapid catalyst break down, and the blocking of reactor tubes.

Carbon may also be formed by thermal cracking of hydrocarbons in the absence of air. Reactions (8) and (9) tend to lead to a surface, pyrolytic carbon, which in a catalyst can encapsulate the nickel particles, again causing deactivation. Reaction (8) and (9) have the greatest risk of occurring at the inlet to a reformer, where there is almost no hydrogen present. At this point the likelihood of carbon deposition is governed not so much by equilibrium

considerations as by the relative kinetics of carbon formation reaction and the carbon removal 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 polymer which can dehydrogenate to produce coke.

There are two explanations for the carbon-induced reaction of the activity of nickel catalysts: (1) encapsulations of nickel crystallites by the layers of inactive carbonaceous material, and (2) the formation of inactive, bulk nickel carbide phases. Figure 1.3 shows the deactivation by coke formation in a supported metal catalyst. The active metal is blocked and the pores in a support are plugged.

There are several ways to solve the coke formation, which is the one of main problems in steam reforming catalysts. Autothermal system is the one of solution. Not only it can remove and reduce coke formation on catalysts but it also can provide energy (heat) to steam reforming reaction, which is strongly endothermic reaction.

This study would like to improve the catalyst used in autothermal system. The effects of Ce and Cr loading were studied. The effects of O₂/C ratio, H₂O/C ratio, and temperature on Ni-Ce and Ni-Cr catalyst were studied as well. Chromium was studied as the promoter that can be reduce coke formation (Sabak, 1999, Bangala *et al.*, 1998). Cerium was interested as the good promoter for oxidation (Barbier and Duprez, 1992, Tiernan and Finlayson, 1996, Cheng, 1996, and Maillet, 1997)