CHAPTER I

INTRODUCTION

Production of hydrogen has achieved increased importance in the recent years because the demand of hydrogen rises beyond its industrial uses (Hairston, 1996). Hydrogen is currently used in both petroleum refining processes, such as hydrotreating and hydrocracking, and the petrochemical industries such as the production of producing methanol, methanol-to-gasoline (MTG), ammonia and hydrocarbon synthesis via Fischer-Trophs process.

Other applications include hydrogenation of edible fats and oils, metallurgy and the manufacture of electronic components. In the future, hydrogen will be used to power fuel cells in motor vehicles, residential and industrial stationary power plants and battery powered consumer products. In other words, hydrogen will power anything requiring energy. Molecular hydrogen stored as liquid or gas, is distributed via pipelines (Armor, 1999), and is a clean burning because only water is formed as a by-product. Therefore, It is forecasted to become a major source of energy in the future.
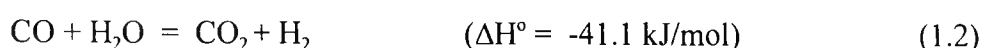
Hydrogen can be cost-effectively produced from renewable energy sources and made available for widespread uses as energy carrier and a fuel. It has been also described as a long-term replacement for natural gas and oil considered being depleted. Moreover, it has the highest energy content per unit of weight (52,000 BTU/lb.) of any known fuel, which makes it an extremely efficient source of energy (Freni S., 2000).

Several processes are often used to manufacture hydrogen such as steam reforming, partial oxidation, pyrolysis, and gasification. Other methods used for hydrogen production are electrolysis (using electricity to split the hydrogen from the oxygen in water), photoelectrolysis (using sunlight to split water molecules), biomass gasification (superheating wood chips and agricultural waste), and the use of sunlight on bacteria and algae under certain conditions. Such methods are only experimental and not commercially viable at this time.

The current standard process in hydrogen production is steam reforming because it is the largest and the most economical way. However, the major problem in industrial steam reforming is the coke formation. Therefore, the minimization of coke is one of the important factors that is controlled the industrial application of steam reforming. To solve the coke formation problem, several methods were investigated such as sulfur passivation, the uses of sulfide catalyst and autothermal system. Only sulfur passivation and autothermal system were forecasted to be the most economical.

1.1 Steam Reforming

Steam reforming is the established process for converting natural gas and other hydrocarbons into synthesis gas, which is a mixture of CO and H_2 (Satterfield, 1991). The reforming of natural gas utilizes two simple reversible reactions: the reforming reaction (1.1) and the water-gas shift reaction (1.2).

$$CH_4 + H_2O = CO + 3H_2 \qquad (\Delta H^\circ = 206.2 \text{ kJ/mol}) \qquad (1.1)$$
$$CO + H_2O = CO_2 + H_2 \qquad (\Delta H^\circ = -41.1 \text{ kJ/mol}) \qquad (1.2)$$

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 a similar fashion:

$$C_nH_m + nH_2O = nCO + (n+m/2)H_2 + heat \qquad (1.3)$$
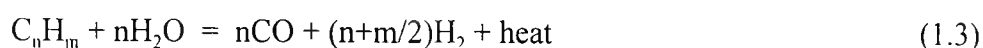
Reactions (1.1) and (1.2) are reversible and are normally at equilibrium as the reaction rates are very fast. The product gases from a traditional reformer reactor are, therefore, governed by thermodynamics. Steam is normally added well in excess of the stoichiometric requirement of reaction (1.1) so that the equilibrium of reaction

(1.2) moves towards CO_2 rather than CO. This is to avoid carbon deposition through the Boudouard reaction (2.6), which is also catalyzed by nickel

Steam may be replaced completely (or in part) by CO_2, which gives a more favorable H_2/CO ratio for some applications:

$$CH_4 + CO_2 = CO + 2H_2 \qquad (\Delta H^\circ = 247.2 \text{ kJ/mol}) \qquad (1.4)$$

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

$$CH_4 + \frac{1}{2}O_2 = CO + 2H_2 \qquad (\Delta H^\circ = -36 \text{ kJ/mol}) \qquad (1.5)$$

Several metals have been found to catalyze reactions (1.1)-(1.5), but nickel is generally preferred on the cost grounds. In commercial steam reforming catalysts, nickel 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.

In steam reforming system, heat is needed to supply to the system since the reaction is an endothermic reaction. If the steam reforming is combined with an exothermic oxidation reaction, heat will be supplied by the oxidation reaction simultaneously to steam reforming reaction in the same bed. The supplied heat is enough to run the reaction continuously, and hydrogen yield can be also increased via the addition of hydrocarbon oxidation. Coke will be removed form the catalyst in the presence of oxygen.

1.2 Partial Oxidation

The non-catalytic partial oxidation is the other major route to H_2 (Pena *et al.*, 1996). One key advantage of this approach is that it accepts all kind of hydrocarbon feeds. The general reaction is described by (1.6).

$$CH_4 + 1/2O_2 = CO + H_2 \qquad (\Delta H^\circ = -36 \text{ kJ/mol}) \qquad (1.6)$$
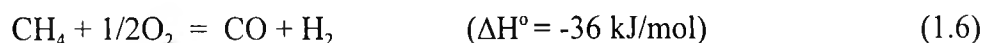
In the absence of catalyst, the reactor temperature must be high enough to reach complete CH_4 conversion. Combustion products such as CO_2 and H_2O are also formed to a certain extent. Subsequently, endothermic reactions such as steam reforming are also involved, which determine the outlet temperature of 1,000-1,100°C. At this stage, the gas composition is near a thermodynamic equilibrium. According to the stoichiometry of reaction (1.6), the ratio of O_2 should be, in the absence of combustion products, approximately 0.5 O_2/CH_4. However, actual use requires O_2/CH_4 ratio of about 0.7 (Armor, 1999). $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts have been found to be very promising catalysts in term of catalytic activity (Jundee *et al.*, 2001). However, no research has been reported on the effect of nickel loading method and percentage of nickel on catalytic behavior of $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts in autothermal system of iso-octane.

The aim of this work is, therefore, to study this dominant catalyst in autothermal system prepared with three different percentages of nickel (5, 10 and 15% by weight) and by two major loading methods: "sol-gel" and "impregnation". The effects of H_2O/C ratios, O_2/C ratios and temperature were also investigated on $Ni/Ce_{0.75}Zr_{0.25}O_2$ for autothermal system studies. Moreover, the temperature distribution in the reactor of autothermal system was studied as well.