CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Steam Reforming of Methane

The steam reforming of methane is a well-established process for the production of hydrogen or synthesis gas. This process is typically operated at temperature above 500°C. This process has two main reversible reactions. Reaction (2.1) represents the endothermic steam reforming reaction, and Reaction (2.2) represents the exothermic water gas shift reaction.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (\Delta H° = +206.2 \text{ kJ/mol}) \qquad (2.1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (\Delta H° = -41.1 \text{ kJ/mol}) \qquad (2.2)$$

From these two reactions the overall heat of reaction is a highly endothermic so, a large amount energy is necessary to heat up to reaction temperature. Steam reforming of methane produces synthesis gas with a high H_2/CO ratio (>3) due to water gas shift reaction, resulting in low selectivity and yield for CO.

Reactions (2.1) and (2.2) are reversible reactions at steam reforming temperatures meaning that thermodynamics govern the equilibrium conversion. Equilibrium favors the steam reforming reaction only at a high temperature and low pressure. Generally, the water gas shift reaction approaches the equilibrium, followed by the reaction with steam. Consequently, a mixture consisting of H_2, CO, CO_2 and unused CH_4 is obtained. The concentration of the various components depends on temperature, pressure, and the molar ratio of steam to methane (Kochloefl, 1997).

The heavy hydrocarbon also react with steam in a similar fashion:

$$C_nH_m + nH_2O \leftrightarrow nCO + \left(n + \frac{m}{2}\right)H_2 + \text{heat} \qquad (2.3)$$
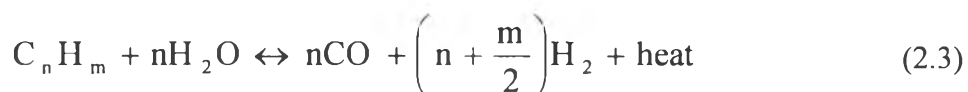
2.2 Steam Reforming Catalyst

Group VIII metals are the active metals for steam reforming catalysts. Generally, the industrial catalysts are based on nickel because of its availability and lower cost than other group VIII metals. Although other metals are active, they have drawbacks; for example, Fe rapidly oxidizes, Co can not withstand the partial pressure of steam, and the precious metals (Rh, Ru, Pt and Pd) are too expensive for commercial operation (Lee, 1997). The supports for most commercial catalysts are based on ceramic oxide. The commonly-used ceramic supports include α-alumina, magnesia, magnesium-aluminate, or calcium-aluminate which are able to tolerate high temperature (Satterfield, 1991).

Nickel steam reforming catalyst life is dependent upon several factors such as sulfur poisoning, sintering, and carbon formation. Therefore, sulfur compounds must first be removed from the natural gas feedstock to ensure catalyst life. Sintering involving the loss of surface nickel may change the nickel crystals available and cause a decrease in catalytic activity. Minimization of nickel sintering is so important, and this purpose is related to the compositions of support and the method of catalyst preparations (Satterfield, 1991). And carbon formation is the major problem for steam reforming catalysts because it causes the catalyst deactivation. In steam reforming of methane plant, carbon formation is prevented by operating at excess steam condition. From the industrial point of view, the excess steam requires a large amount of energy to vaporize water into steam, which is the cause of high operating cost.

2.3 Carbon Formation on Steam Reforming Catalyst

The high temperatures in steam reforming reaction favor the formation of carbon. Carbon formation on a metal-active site of steam reforming catalyst is the major problem in the operation of steam reforming plant. Carbon formation can lead to the deactivation of catalyst and build-up carbon deposits, which may lead to blockage of reformer tubes or the formation of hot spots. Carbon formation on steam reforming catalysts takes place in three different forms: whisker-like carbon,

encapsulated carbon and pyrolytic carbon. Three reactions can be shown for describing the formation of carbon on methane reforming catalysts (Trimm, 1997):

$$2CO \leftrightarrow CO_2 + C \qquad (\Delta H° = -172 \text{ kJ/mol}) \qquad (2.4)$$

$$CO + H_2 \leftrightarrow C + H_2O \qquad\qquad\qquad\qquad (2.5)$$

$$CH_4 \leftrightarrow C + 2H_2 \qquad (\Delta H° = +75 \text{ kJ/mol}) \qquad (2.6)$$

With a certain steam to carbon ratio, thermodynamics of carbon formation can be estimated from equilibrium concentrations of carbon monoxide, carbon dioxide, hydrogen, steam, and methane using Reaction (2.4). Nevertheless, the estimated carbon formation by thermodynamics data is higher than that of the actual value obtained from Reaction (2.4) with nickel catalysts, at the minimum steam to carbon ratio. According to Trimm, 1997, the key reactions were found to take place on a surface layer of nickel atoms. If filament or whisker of carbon is allowed to build up on surface of nickel atoms (e.g. because of the low steam partial pressure) that can attack to nickel atoms, such carbon filaments can generate massive forces within catalyst pellets that lead to rapid catalyst breakdown and the blocking of reactor tubes.

In the absence of air, carbon formation may also be formed by thermal cracking of methane. Reaction (2.6) leads to a pyrolytic carbon on surface of catalyst, which can encapsulate nickel particles. The formation of this carbon leads to the deactivation of catalyst and increase of pressure drop across the reformer tubes. The thermal cracking of hydrocarbon occurs at high temperatures and at low steam to hydrocarbons ratios. Higher hydrocarbons have a greater propensity for carbon formation than methane.

2.4 Catalyst Development for Steam Reforming

For the last several years, many researchers have studied on steam reforming of methane and other hydrocarbons. Most of their works were focused on steam reforming catalysts in terms of catalytic activity and stability (resistant to carbon formation) that can be operated at low steam to carbon ratios. From Section (2.2) has described that the active metal and support for steam reforming catalyst are nickel and oxide supports especially α-alumina. Therefore, most of research works have focused on improving conventional catalyst by adding promoter, changing active metals and studying new support.

The resistant to carbon 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 resistant to nickel sintering of promoted nickel alumina catalysts was improved significantly by addition of alkali or alkaline-earth metal. The promoter K was found to assist in decreasing the carbon formation rate of the nickel catalysts. The carbon formation rate of the nickel catalysts promoted with alkaline-earth metals was more extreme than that of the nickel catalysts promoted with alkali metals (Satterfield, 1991).

The influence of promoter K on the hydrogenolysis of cyclopentane and on the simultaneous carbon formation over a series of alumina-supported catalysts has been investigated (Demicheli *el al.*, 1994). They observed that the important role of K ion on the hydrogenolysis reaction and carbon formation on Ni/Al_2O_3 catalysts can be divided into three parts. The first one was that modifiers of metal support interaction reduced the adhesion strength between nickel particles and alumina matrix. Secondly, alkalinity of the promoter neutralized the acidic alumina to favor for the formation of carbon precursors but it did not affect the catalytic activity of smaller nickel crystallites. Finally, with high K/Ni ratio, a possible blockage of active sites could occur resulting in an inhibition of the hydrogenolysis reaction and carbon formation.

The influences of CeO_2 as a promoter on supported Ni and Pd catalysts for steam reforming of methane were examined by Cracuin *et al.* (1999). In comparison, a higher catalytic activity was acquired with a presence of CeO_2. It was due to the

intimate contact between either Ni or Pd and γ-Al_2O_3 supported CeO_2. This indicated a good catalytic synergism between the active metals and CeO_2. The enhancement observed catalytic activity of bulk CeO_2 as same as γ-Al_2O_3 supported CeO_2, exhibiting that bulk CeO_2 was not need for the synergism. In addition, the catalytic activity for CeO_2-supported Ni and Pd catalysts were very resembling, inferring that the catalytic activity rate limiting step involve the transfer of oxygen from CeO_2.

Kaspar $et\ al.$ (1999) found that minimization of carbon formation was 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 carbon formation by increasing carbon gasification. CeO_2 is a 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 oxygen due to the Ce^{4+}/Ce^{3+} redox couple.

There have been some studies attempting to find alternative supports for metal catalysts used for steam reforming. Hegarty $et\ al.$ (1998) investigated metal supported ZrO_2 for synthesis gas production. The catalysts containing 1wt% of Co, Cu, Fe, Ni, Pd and Pt supported on ZrO_2 were tested on the steam reforming of methane. The activity for steam reforming over metal supported ZrO_2 catalysts were found to decrease in the order: Pt, Pd>Ni >> Cu, Co and Fe. The Pt, Pd, and Ni catalysts were found the most active. In the presence of excess steam, the Cu, Co and Fe catalysts exhibited significant deactivation whereas Pt and Ni catalysts remained stable. However, the Ni catalyst was deactivated due to carbon formation, when the steam to methane ratio was 1:1. On the other hand, the Pt catalyst remained its activity. In addition, the Pt/ZrO_2 catalyst was also proven to be an active and stable catalyst for both carbon dioxide reforming and partial oxidation of methane.

The development of highly stable nickel catalyst for steam reforming of methane under low steam to carbon ratios was investigated (Yamazaki $et\ al.,$ 1996). A Ni-Mg-O solid solution with low Ni content ($Ni_{0.03}Mg_{0.97}O$) was found to be an active and stable catalyst for the steam reforming of methane at a steam to carbon

ratios of 1. The authors observed that this catalyst showed higher activity and much higher stability than a commercial reforming catalyst (Ni/Al$_2$O$_3$-MgO).

Ni/MgO catalyst (15wt.% Ni) has been utilized for the steam reforming of methane (Dong *et al.*, 2001). It was found that this catalyst had high activity and good stability in steam reforming of methane. Mainly, it showed stable catalytic performance although at a steam to carbon ratio of 1. The results from TPR and H$_2$ pulse chemisorption exhibited a strong interaction between NiO and MgO resulting in a high dispersion of Ni crytallite. Pulse reaction results showed that both CH$_4$ and O$_2$ were activated on the surface of Ni crystallite over the catalyst, and then surface carbon species reacted with adsorbed oxygen to produce CO.

Otsuka *et al.* (1999) prepared a series of CeO$_2$-ZrO$_2$ composite oxides (Ce$_x$Zr$_x$O$_2$) for the gas-solid reaction with methane in the shortage of gaseous oxidant. According to the catalyst characterization, a formation of solid solution containing fluorite structure was detected for any catalysts with Zr content below 50%. Moreover, O$_2$ desorptions and H$_2$ reductions were achieved at lower temperatures for CeO$_2$-ZrO$_2$ as compared to CeO$_2$. Selectively, similar outcome of synthesis gas with a H$_2$/CO ratio of 2 was obtained from the reaction of methane using either CeO$_2$-ZrO$_2$ or CeO$_2$. However, in the presence of ZrO$_2$, the formation rates of H$_2$ and CO were increased while the activation energy was greatly decreased. The presence of Pt catalyst could also further speed up the reaction. In addition, the conversion of methane to synthesis gas could be accomplished at temperature as low as 500°C by using Ce$_{0.8}$Zr$_{0.2}$O$_2$ in the presence of Pt.

The effect of Ni content on the Ni/Ce-ZrO$_2$ catalyst has been investigated on the steam reforming of methane (Dong *et al.*, 2002). Among the catalysts investigated, the conversion increased with increasing nickel content up to 15 wt% and then decreased with the percentage above this value. The high catalytic activity and stability of 15 wt%Ni/Ce-ZrO$_2$ were mainly due to a good balance between two kinds of active sites, i.e. one for the activation of methane and another for steam or oxygen. A strong interaction of support and metal by partial incorporation of NiO into the surface of the Ce-ZrO$_2$ supports was present as indicated by TPR results. Coupled with H$_2$ chemisorption measurements, nickel surface area, the chemical

environment of nickel, and the properties of the Ce-ZrO$_2$ support were discovered as key factors in the catalytic activity and stability of Ni/Ce-ZrO$_2$.

The support plays an importance role in steam reforming catalysts. Roh *et al.* (2002) have studied on the development of new and highly active catalysts for steam reforming of methane. They investigated the catalytic properties of Ni catalysts supported on various oxide supports. Among the catalysts examined, including Ni/Ce-ZrO$_2$, Ni/ZrO$_2$, Ni/CeO$_2$, Ni/MgAl$_2$O$_4$, and Ni/Al$_2$O$_3$. Ni/Ce-ZrO$_2$ catalysts exhibited the best activity and stability. Various advantages were found to be influenced by the catalytic performance of Ni/Ce-ZrO$_2$, including high oxygen storage capacity of ceria in Ce-ZrO$_2$ solid solution, strong interaction between Ni and Ce-ZrO$_2$, basic property, and rather high capability for H$_2$ uptake.

2.5 KL Zeolite Catalyst Support

Generally, L zeolite is an effective support of catalyst in the aromatization reaction of *n*-alkane (Jacobs *et al.,* 2001). Typically, L zeolite is in K-form with a large pore molecular sieve consisting of small cylinders arranged in one-dimensional channel system. Figure 2.1 shows the details of its structure. KL zeolite has 12-ring main channel, one-dimensional pore of about 0.75 nm aperture leading to cavities of about 0.48 x 1.24 x 1.07 nm., small hexagonal and cancrinite units (Ko and Ahn, 1999). Its Si/Al ratio is typically 3.0.

The other properties of KL zeolite have shown as the followings:

⊕ High thermal stability ($\approx$ 900°C),

⊕ High surface area (280 m^2/g) enhancing metal dispersion and increasing water adsorbed capacity, and

⊕ Less acidity avoiding the carbon formation during steam reforming reaction.

According to Roh *et al.* (2002), supports for steam reforming catalyst must have low acidity to prevent carbon formation and high thermal stability. Therefore, these excellent properties enable the use of KL zeolite as a catalyst support in steam reforming reaction.
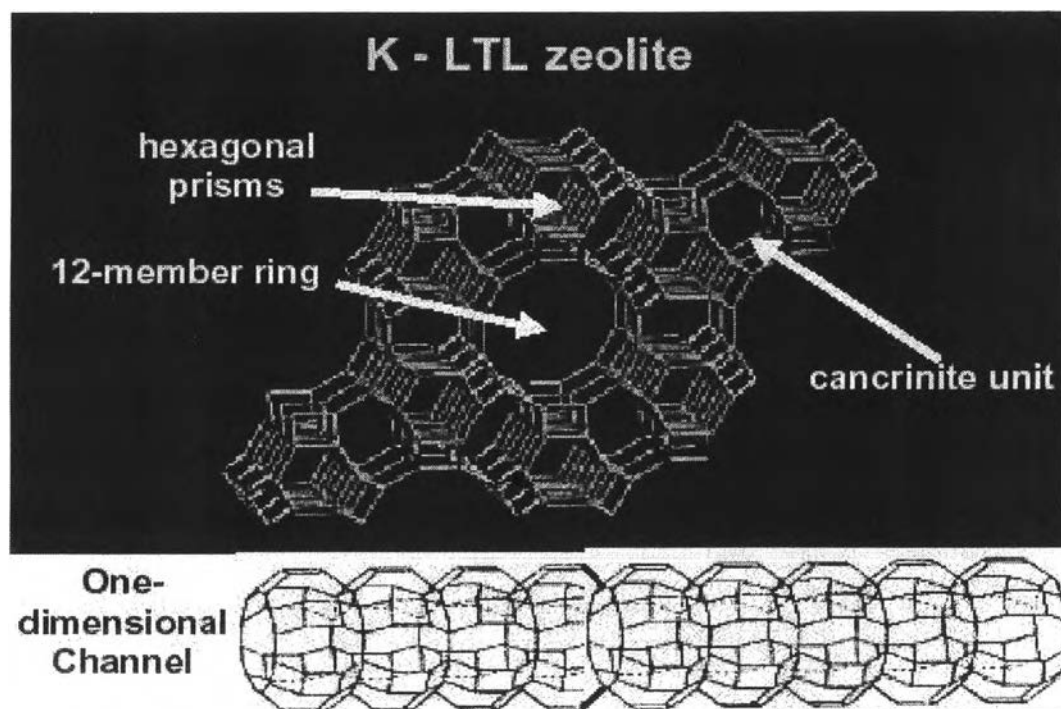
Figure 2.1 KL zeolite structure (Jacobs *et al.*, 2001).

In this work, the series of Ni catalysts supported on KL zeolite were prepared with various nickel contents (3, 5, 7, 10 and 15 wt %). The prepared catalysts were tested on steam reforming of methane to determine the optimum Ni content. The catalyst with optimum Ni loading was promoted with various contents of ceria (1, 3, 5 and 7 wt%) and these catalysts were also tested on steam reforming of methane. The best catalyst was compared with commercial one. The catalysts were also characterized by a number of techniques which are BET, XRD, TPR and TPO in order to understand the relationship between the characteristics of the catalysts and their performances on steam reforming of methane.