CHAPTER II
LITERATURE REVIEW

2.1 Hydrogen Energy

The drastic expansion of global economics plays role as essential factor contributing to the increment of energy demand, especially, in worldwide transportation and industry sectors. Consequently, the world is facing energy-related problems of not having adequate energy supplies at affordable prices as shown in Figure 2.1 and environmental harm resulting from extravagant consuming of it. Concerning with that problems, the "Hydrogen Energy" has been announced and strongly pushed to be a new energy regime in the future by United States Department of Energy (DOE) and European countries.

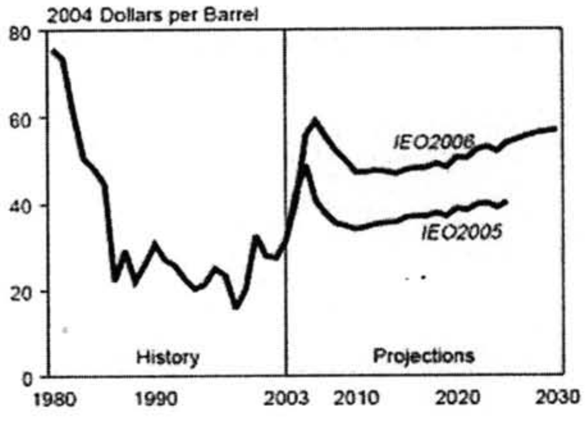

Figure 2.1 IEO 2005 and IEO 2006 world oil price projections, 1980-2030.

Hydrogen becomes a prospect as fuel for all energy-related applications. In addition, fuel cells powered by hydrogen have been continually developed and attracted the widest interest. Replacing oil used in vehicles could have major advantages for energy supply, additionally having lower emissions of pollutants and greenhouse gases (GHG) involving global warming. Hydrogen can also reduce CO_2 emissions when it is produced form renewable and nuclear energy. If natural gas or coal is the source of hydrogen then CO_2 capture and storage is essential to achieve emission saving. That of all cases, hydrogen fuel cell vehicles can obviously reduce pollution since it provides electricity more cleanly, as the only effluent is water.

In viewpoint of economics, renewable energy technologies have strong competition. It seemed like hydrogen energy more costly than conventional parts. Therefore, natural gas and coal are likely to remain the lowest-cost primary sources of hydrogen as far as meeting affordable cost of hydrogen production.

2.2 Hydrogen Production

For the chemical formula of any fossil fuel, hydrogen is mostly present in all of the formulas. In form of its pure (H_2) can be used in fuel cells and hydrogen combustion engines to cleanly release its stored energy. Its challenges are how to remove it safely, efficiently and without any other elements in the original compound. H_2 can be produced from coal, gasoline, methanol, natural gas and any other fossil fuels. Currently, hydrogen is dominantly generated from natural gas which accounts for 48 % of world's capacity. The number overcomes an account from oil which occupied capacity of 30 %.While the production from coal and the other sources such as electrolysis are less as 18 and 4 %, respectively (Figure 2.2).

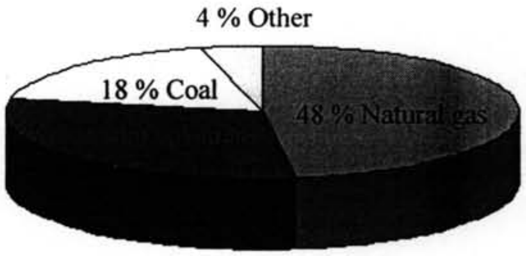

Figure 2.2 World capacity of hydrogen production source (Armor, 1999).

Some fossil fuels have high H_2 to O_2 ratio making them as better feedstock for the reforming process. The more hydrogen present and the fewer other compounds will make the reforming process simpler and more efficient. The fossil fuel that has the best hydrogen to carbon ratio is natural gas or methane (CH_4). At present, most of the world's hydrogen supply is produced via the steam reforming of natural gas. According to methane is the main composition of natural gas, thus it is often used as analog for natural gas.

The way to produce hydrogen comprises of several technologies. Originally, the mixtures can generate from the reaction of steam with incandescent coke and were known as "water-gas". Regarding used first as fuel, water gas attracted attention in afterwards as a source of hydrogen and carbon monoxide, so-called synthesis gas (syngas) for chemicals production (Reyes, 2003). Ultimately, steam reforming process, which steam is reacted with natural gas (methane) or petroleum naphtha, was announced as a mature technology and found in wide applications to produce synthesis gas. Alternatively, CO_2 reforming or dry reforming has drawn attention in recent years. This catalytic reforming of carbon dioxide with methane to synthesis gas has been proposed as one promising technologies for the utilization of two greenhouse gases as carbon-containing meterials, since both methane and carbon dioxide are greenhouse gases. Unfortunately, the process is not commercial available due to the major obstacle impacts on this process is rapid catalyst deactivation by carbon deposition on catalyst surface. Additionally, catalytic partial oxidation is an alternative process for hydrogen production except for the disadvantage of the technology is highly exothermic reaction. Therefore, it is difficult to remove heat from the reaction. In point of economics, partial oxidation requires oxygen (air) to react with hydrocarbon, cost of oxygen supply make it less competitive technology comparing to steam reforming. Beside these mentioned process, steam methane reforming can be combined with partial oxidation, a process referred to as autothermal reforming. Basically, steam and oxygen (or air) are injected into the reformer, causing the reforming and oxidation reaction to occur simultaneously. The exothermic POX reaction, in which the feedstock reacts (catalytically) with oxygen in sub-stoichiometric conditions, provides heat to endothermic SMR reaction. Hence, the use of ATR allows for higher CO_2 recovery in comparison to SMR, as CO_2 emissions from the furnace at a SMR plant are relatively uneconomic to capture due to the low partial pressure in furnace exhaust. However, in view point of economics, the costs of oxygen supply make ATR less attractive than SMR even for large-scale plants.

2.3 Steam Reforming of Methane

Hydrogen production from natural gas or methane commonly employs a process known as steam reforming. The steam reforming reaction is established for converting hydrocarbon feedstock into H_2 and CO, so-called synthesis gas. Synthesis gas is essential feed chemicals for several processes like ammonia production used as fertilizer via Habor process, methanol synthesis, gas-to-liquid production (GTL) through Fischer-Tropsch process or even in refinery processes such hydrotreating process. Moreover, synthesis gas, mainly hydrogen represents as energy carrier for the future in the fuel cell utilization. Because the main fuel for fuel cells is hydrogen (Figure 2.3), steam reforming is presently the most efficient process that can provide a hydrogen-rich gas from fuels, especially methane (Liu *et al.*, 2002).

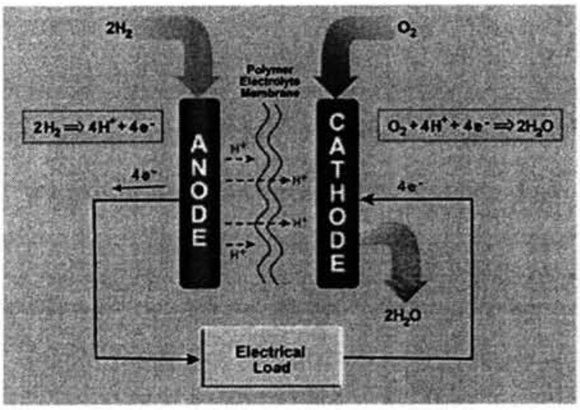

Figure 2.3 Hydrogen as dominant feed chemical for polymer electrolyte membrane chemical fuel cells.

Steam reforming involves two steps of reactions. The initial step involves rendering CH_4 into H_2, CO_2 and CO. Molecule of methane is broken down by exposing methane to high temperature steam. The second step of steam reforming consists of creating additional H_2 and CO_2 by utilizing CO created in the first step via side water-gas shift reaction.

From the above mentioned, steam reforming of methane is composed of two thermodynamically reversible reactions: the strongly endothermic reforming reaction (2.1) and the moderately exothermic water-gas-shift reaction (2.2).

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (\Delta H^\circ_{298} = +206 \text{ kJ/mol}) \qquad (2.1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (\Delta H^\circ_{298} = -41 \text{ kJ/mol}) \qquad (2.2)$$

According to endothermic character, the reaction is favored by high temperature (700-1000°C) requiring large amount of energy to heat it up, including evaporation of steam. Reforming reaction is accompanied by a volume expansion so it is favored by low pressure. The typical temperatures and pressures for the process are 700-850°C and 3 to 25 bars. Steam reforming of methane is efficient to produce high ratio of hydrogen over steam (>3). Beside the reforming reaction, water-gas shift reaction (2.2) can occur resulting in higher yield of hydrogen. However, the reaction can cause of decreasing yield and selectivity of CO.

Additional hydrocarbons higher than methane can also be used as feedstock for steam reforming process as following equation.

$$C_nH_m + nH_2O \leftrightarrow nCO + (n+ [m/2])\ H_2 \qquad (2.3)$$

Nevertheless, the presence of higher molecule of hydrocarbons will enhance the effect of carbon formation leading to reduced the life of catalyst and reformer (Lee, 1997).

2.4 Steam Reforming Catalyst

The most important considerations for the catalyst are activity and durability. Firstly, the catalyst has to be able to effect on the desired reaction at acceptable rate under conditions of temperature and pressure that are typically practicable. Secondly, the catalyst has to be able to maintain the desired reaction for prolonged periods as possible. In some processes, a catalyst life of several years is economical necessary.

It is clear that the longer life time of catalyst toleration, the smaller initial cost that will be affected to overall processes. It is usually cheaper in the long run to use an expensive catalyst that can endure for a long time than a cheap one that has to be replaced frequently. The main causes of deterioration of catalyst in use are first, poisoning due to impurities in the reactants, for example, contamination of sulfur in natural gas rendering poison over Ni catalyst so purification process should be required. The others are irreversible physical changes including loss of surface area, so-called sintering and mechanical failure (Bond, 1984).

For reforming catalyst typically composed of two primary components, the catalyst itself (metal in reduced state) and the appropriate catalyst support over which the active metal can be dispersed (Rostrup-Nielsen, 1984). The metals in group VIII are considered to be active components for reforming as the noble metals (Rh, Ru and Pt). The catalysts based on noble metals have been found to be less sensitive to carbon deposition because of a smaller dissolution of the carbon into these metals. However, the use of the noble metals in large scale industrial steam reforming is not common due to it is considered to be high cost and limited availability. For example, the Pt-group metals are highly active but they are so expensive and other metals such as Co and Fe are less effective than Ni (Satterfield, 1991). Therefore, it is more practical in view point of industry to develop catalyst that come with high performance and high resistance to carbon deposition. From that point of its low cost, Ni is mostly selected to be used as reforming catalyst. However, Ni is less active and usually more prone to deactivation by carbon formation or oxidation (Rostrup-Nielsen, 1984). The supports for commercial reforming catalysts are mostly based on ceramic oxide such as Al_2O_3, MgO, $MgAl_2O_4$, SiO_2, ZrO_2 and TiO_2. The role of the support is to provide a support for the catalytically active metal in order to obtain a stable and high active surface area. Among the most common supports for the reforming are α- and γ-alumina, magnesium oxide, magnesium-aluminate. These supports have good porosity, which results in a long contact-time between reactants and catalyst (Beurden, 2004).

The combination of high temperatures and high pressure steam can create a severe environmental for Ni catalysts. The life time of catalyst depends on several factors mostly related to catalyst deactivation. There are many reasons for catalyst deactivation that are sulfur poisoning, carbon formation and sintering (Sehested, 2006). Sulfur is strong poison for Ni catalysts and blocks the active nickel sites. Thus the feedstock as natural gas must be removed sulfur contaminant through desulphurization process before entering steam reforming unit in order to extend the catalyst life. For the sintering, Ni particles in the catalyst may agglomerate during operation which leads to lose of active surface and is caused of decreasing activity. Sintering involves many factors, the metal content, initial crystallite size and size distribution, the dispersion of the metal over the support, the nature of the support material and the operating conditions such as temperature and the atmosphere in contact with catalyst which are the most important (Beurden, 2004). Nevertheless, the major serious problem for reforming catalyst is the deposition of carbon on its surface.

2.5 Carbon Formation

Due to operation at high temperatures, some of the reactant species may decompose and deposit in form of a thin layer of inactive carbon on the catalyst surface, well-known coke. It may cause serious problems in operation, including deactivation of catalyst. In practical, carbon formation may cause pressure drop, block the active site of Ni catalyst, and plugging in the reactor resulting in a lower heat transfer. Coke may present in various forms: encapsulated carbon, pyrolytic coke and whisker carbon, amorphous carbon. The process of coke deposition has been mentioned by Trimm, which coke formation occurs mainly in gas phases and by these routes, deactivation of catalyst is slow. For the process, carbon may be gasified and may encapsulate the surface or may dissolve in the Ni crystallite. Then dissolved carbon diffuse into Ni and nucleate and precipitate over crystallite. Mostly, whisker carbon may take place in steam reforming process because its operation at high temperatures (Rostrup-Nielsen, 2000). It may break the catalyst pellet but the deactivation will not occur. There are two major pathways for carbon formation as following (Amor, 1999 and Trimm, 1997).

Methane cracking: $CH_4 \rightarrow C + 2H_2$ (4.1)

Boudouard reaction: $2CO \rightarrow CO_2 + C$ (4.2)

From Equations (4.1) and (4.2), cracking of hydrocarbons as methane and Boudouard reactions may produce adsorbed carbon particle over the catalyst surface. These reactions may be balanced by the utilizing carbon from carbon forming reactions. The reverse water-gas shift and steam-carbon gasification occur as side reactions, respectively.

Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$ (4.3)

Steam-carbon gasification: $C + H_2O \rightarrow CO + H_2$ (4.4)

For the feedstock, especially higher hydrocarbons are more inclined to create coke than methane corresponding to the report proposed by Rostrup-Nielsen and Tottrup, 1979. In addition, arising with traces of sulphur may be also presented in heavier feedstock. That problem can impact on the deactivation of the catalyst caused by formation of nickel sulfide. The investigation of various feedstocks unveiled that olefins and aromatics can rapidly prone to carbon formation (Trimm, 1997). To minimize the coke formation, high steam to carbon ratios is adjusted for promoting gasification of the carbon deposited on catalysts. The reaction can create carbon monoxide and hydrogen as gas products. However, pressurizing and heating a large excess of water is expensive.

2.6 Development of Reforming Catalyst

There has been a considerable amount of research in developing a catalyst for reforming process. According to industrial applications, it requires catalysts that exhibit excellent properties in activity, mechanical and thermal stability, and selectivity for desired reaction. In steam reforming process, as mentioned previously that the essential components of reforming catalysts are metal which Ni is mainly used as an active metal. The support also plays an important role for providing catalytic performance; therefore, the improvement of catalyst support in order to overcoming the problems of coke formation, thermal sintering, and including stability of catalyst is investigated.

2.6.1 Ceramic-based Supports

The conventional support for commercial reforming process is still based on alumina support. Roh *et al.*, 2002 attempted to prepare a stable Ni/θ-Al_2O_3 in order to overcome the drawback of Ni/γ-Al_2O_3 which is usually unstable at high temperatures (>727°C). The phase transformation of γ-Al_2O_3 support normally was changed into α-Al_2O_3 at high temperatures. The catalyst can be prepared by heat treatment of γ-Al_2O_3 at 900°C for 6 h to obtain thermally stable support. Comparison of TPR results between Ni/θ-Al_2O_3 and Ni/γ-Al_2O_3, the peak of inactive form of $NiAl_2O_4$ was observed on the Ni/γ-Al_2O_3 surface rather than another. It was implied that chemical interaction between Ni and γ-Al_2O_3 leads to create spinel $NiAl_2O_4$ resulting in loss of active surface.

Acidity of supports is one of important factors rendering coke deposition on catalyst surface. Roh *et al.*, 2002 carried out the development of new and highly active catalyst. It was found that Ni/$MgAl_2O_4$ showed higher activity as well as high stability compared to Ni/Al_2O_3. Due to $MgAl_2O_4$ is less acidity than Al_2O_3, less coke is formed on its surface resulting in high stability.

ZrO_2-supported Pt showed the highest activity over other metals (Co, Cu, Fe, Ni, Pd, and Pt) for producing synthesis gas via steam reforming of natural gas (Hegarty *et al.*, 1998). The Pt sample only exhibited excellent stability rather than others which increase a significant carbon deposition on their surface.

Methane steam reforming over Ni catalyst supported on Ce–ZrO_2 was studied at 650–900°C by Laosiripojana *et al.*, 2005. Among Ni/Ce–ZrO_2 catalysts with various Ce/Zr ratios, it was observed that the catalyst with a Ce/Zr ratio of 3/1 showed the best activity and high resistance toward carbon formation over Ni/Al_2O_3 catalyst at 900°C due to its high redox property.

Liu *et al.*, 2002 studied hydrogen production for fuel cells through methane reforming at low temperatures using $Ni/Ce\text{–}ZrO_2/\theta\text{-}Al_2O_3$ catalyst. It showed the high activity and stability, which is appropriate for SRM at low temperatures.

2.6.2 Zeolite Supports

Recently, molecular sieve has been received attention to be used as a support. Due to zeolite exhibits a well-defined structure with microporous and thermal stability.

Faujasite, Y-type zeolite, have been shown that it is effective in several catalytic applications. The basis unit of a faujasite is the typically octahedral sodalite unit consisting of 24 tetrahedra of both AlO_4^- and SiO_4 (Bond, 1987). The three-dimensional framework includes elliptically shaped cavities approximately 12 Å in diameter called supercages. The Y-type zeolites with regularly high Si/Al ratios (1.5-3.0), 300-800 m^2/g surface areas preferred given the thermal stability and the high catalytic activity (Solh *et al.,* 2001). The zeolite is usually first made in the sodium form because the sodium cation can be simply exchanged for other cations.

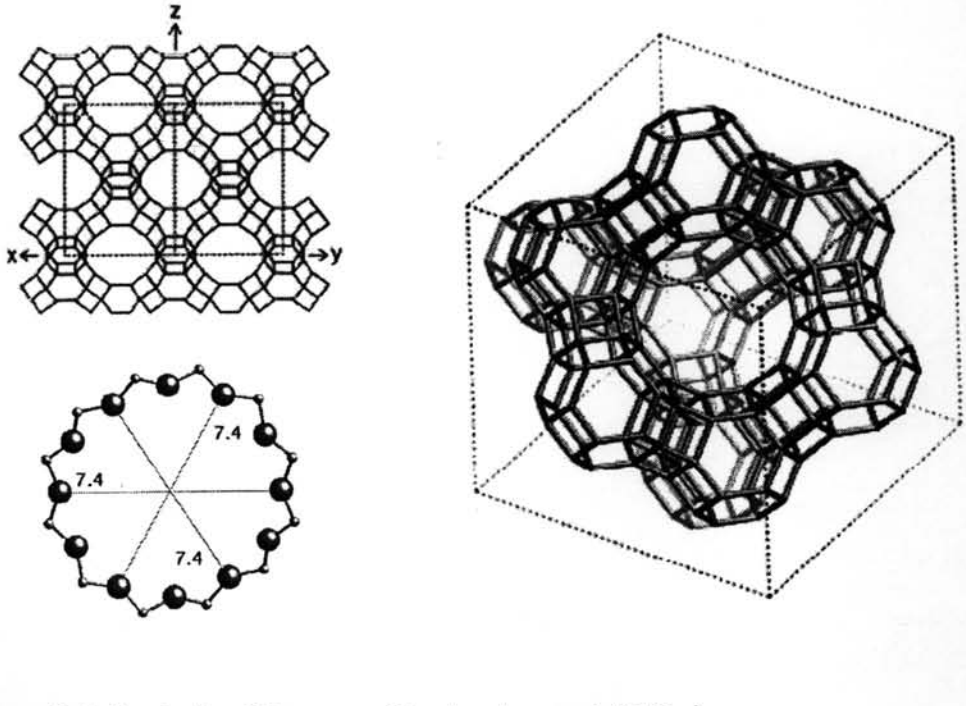

Figure 2.4 Faujasite, Y-type zeolite structure and 12 T-ring.

The performance of Rh catalysts under reaction conditions, Rh/NaY zeolite, was studied by Portugal *et al.*, 2002. The catalysts were prepared by ion-exchange technique. Other oxide-supports were used to compare the activity and the stability with zeolite supports. From the influence of the support on the catalyst activity observed, the results showed that an increase of the metal dispersion leads to an increase of the activity. It was proposed that the zeolite and oxide-supported Rh catalysts differ in two main aspects; firstly the H_2/CO ratio is significantly higher for zeolite catalysts compared to that of amorphous support under dry reforming. Secondly, the zeolite-supported catalysts exhibit a significant stability with time on steam due to theirs strong thermal stability.

Jeong *et al.*, 2006 studied the Ni/HY catalysts promoted by Mg, Mn, K and Ca using co-impregnation technique in methane reforming with CO_2. Among the catalysts tested at 700°C, it was observed that Ni-Mg/HY catalyst showed the highest carbon resistance and the most stable catalytic performance with only slight catalyst deactivation. It is also noticeable that methane conversion was similar to CO_2 conversion with time-on-stream; therefore, it implies that addition of Mg promoter suppressed the reverse water-gas shift reaction. Besides, it may cause reducing the particle size of Ni species and promoting highly dispersion resulted in retarding the sintering of Ni species over catalyst surface.

2.7 Preparation Method

Beside the chemical composition, structural properties of catalysts also influence the activity and stability of them. To utilize effectively the precious metal should be very small metal particles having uniformity of distribution on the surface. The uniform distribution of the active component over the surface of support is important to achieve a high active surface area rendering the catalyst performance. The distribution of the active component will be achieved when the active precursor and the support are brought together, followed by treatments to deteriorate the original one. The preparation method plays an essential role for catalyst distribution.

For the distinction of method or even a few procedures can affect on the physical properties contributed to different results. In practical, there are several techniques used for preparing catalyst, such as impregnation, precipitation, sol-gel, including ion-exchange. But only two common methods will be addressed here, impregnation and ion-exchange.

(a) Impregnation

Generally, the catalyst is mostly prepared by impregnation method because of the simply technique for catalyst preparation. Especially the Ni catalyst preparation, this method is done by adding support such as alumina into the solution of the metal precursor, i.e. nitrate salt (Joeng *et al.*, 2006, Pompeo *et al.*, 2005). The metal salt will diffuse into porous of the support, followed by drying and calcining impregnated supports. Therefore, the catalyst consists of fixing the chemical structure of the precursor prior to final activation (reduction) in the reactor before start-up. Additional impregnation method can be divided into wetting and drying impregnations (Limido, 1986).

(1) Wet impregnation

Wetting consists of adding the precursor solution in contact with the support, due to the effect of the capillary forces the solution is introduced into the pores of the support and distributed there. The procedure occurs rapidly, although it is slowed down by the presence of air occluded in the support after that the pores are filled with solution. The wet impregnation method can be done by the two dissimilar amount of solution, with an excess solution and repeated impregnation.

(2) Dry impregnation

Dry impregnation consists of adding the supersaturated precursor in order to crystallization in the pores of support, generally, by means of simply evaporization.

(b) Ion-exchange

The ion-exchange is generally produced by simple contact between the support impregnated and the precursor solution that is distinctly larger than the total porous volume of the support. The ion-exchange consists of two stages, the diffusion of solute to be exchanced at the surface and the ion-exchange itself. For the zeolite support, on type X, Y, L, etc., molecular sieves, sodium, potassium and possibly calcium ions are exchanged for more active promoter ions, such as H_2, Ca, Cd, Ce, La, and other rare earths (Limido, 1986).

The different methods of preparation, the different results will be performed. Park *et.al.*, 2001 prepared the Ni/NaY catalyst by impregnation and ion-exchange techniques. It was observed that the Ni metal particles associated with the impregnated zeolite gave narrower distribution of smaller diameters compared to the ion-exchanged catalyst.

Ni/NaY catalyst was studied via steam reforming of methane by Al-Ubaid *et al.*, 1987. It was proposed that the different preparation affect on the catalytic activity and dispersion of the catalysts. The Ni impregnated on NaY zeolite is more active than the H-Y zeolite, as well as on silica and alumina support. The higher activity of the catalyst is related to higher metal reduced state. It was proposed that zeolite support provided sites for water adsorption, but it did not provide the stability for deactivation due to surface oxidation.

2.7.1 Metal loading

Nimwattanakul *et al.*, 2006 selected clinoptilolite as a zeolite-based support because it was expected that its microporous structure and high thermal stability could promote the activity of the catalyst. The catalysts were prepared by incipient wetness impregnation with various loadings of Ni, 1, 3, 5, 8, 10 and 15 % using $Ni(NO_3)_2 \cdot 6H_2O$ as a precursor. The results showed that the highest activity and stability were obtained from 8 wt % Ni/clinoptilolite. Too high % loading of Ni presented large crystallite sizes due to sintering resulted in lower activity or loss of surface area of catalysts which contribute to catalyst deactivation.

2.8 Reaction Condition

2.8.1 Temperature Effect

Liu *et al.*, 2002 studied hydrogen production for fuel cells through methane reforming at low temperatures using $Ni/Ce–ZrO_2/\theta-Al_2O_3$ catalyst. It showed high activity and stability for SRM at low temperature. SRM provides the highest percentage of H_2 of any reforming type. Thus the effect of temperature was investigated. It was found that both conversion of CH_4 and H_2 yield increase with increasing temperature. It was noticeable that H_2 yield increased rapidly at low temperatures; however, increment of the yield was observed to be slowly increased at higher temperature. This is due to the inhibition of the water-gas shift reaction at higher temperatures. Consequently, the lower H_2 content was obtained from water-gas shift reaction. The effect of pressure was investigated which showed that SRM is greatly suppressed under higher pressures. Therefore, it was concluded that efficient operation of SMR at low temperatures can be performed by operating at high temperature, high steam to carbon ratio and low pressure.

2.8.2 Feed Composition Effect

Steam to carbon ratio affected to CH_4 conversion or H_2 yield. Among various ratios, a steam-to-carbon ratio of 3 showed the highest conversion. For high steam-to-carbon ratios (>6), it indicated that the water-gas shift reaction occurred providing a great extent of H_2 simultaneously with steam reforming reaction (Liu *et al.*, 2002).

2.8.3 Gas Hourly Space Velocity (GHSV) Effect

Roh *et al.*, 2002 developed Ni catalysts supported on various supports via steam methane reforming at high GHSV condition in order to investigate a suitable catalyst for a compact system of hydrogen production. Among the catalysts supported on $Ce-ZrO_2$, ZrO_2, CeO_2, $MgAl_2O_4$ and Al_2O_3, they were found that $Ni/Ce-ZrO_2$ exhibited the best activity and stability. Moreover, it showed the highest yield of H_2 which its quantity obtained exceeds the limit is obtainable from steam reforming of methane reaction with H_2O/CH_4 = 3. It is believed that the side reaction, water-gas shift (WGS) reaction, had occurred resulting from excess steam supply corresponding to low CO yields. To study the influence of GHSV, the reaction catalyzed over Ni/ Ce-ZrO_2 was carried out by adjusting two-fold velocity. The results showed the higher GHSV exposed, the higher H_2/CO ratio obtained. It implies that high GHSV enhanced the water-gas shift reaction resulting in low CO yield.

In previous work, Tosiri, 2006 found that Ni/KL catalyst exhibited the high activity and stability for dry reforming with 7 wt% Ni content. The catalyst was also observed the high activity and thermal stability for steam reforming of methane reaction by Senathipbordee, 2004. Furthermore, Y-type zeolite or Faujasite was reported that it has potential to be utilized as reforming catalyst. Jeong *et al.*, 2006 reported that the Ni/HY showed the good performance for CO_2 reforming. In this work, NaY zeolite was employed in steam reforming process since its features are high thermal stability and surface area.