



## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

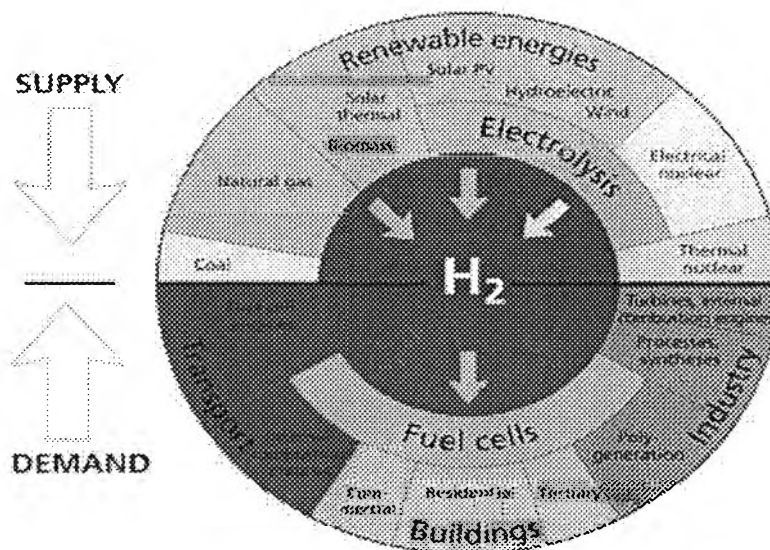
#### 2.1 Hydrogen Production from Fossil Fuels

Similar to electricity, hydrogen can be produced from many sources, including fossil fuels, renewable resources, and nuclear energy. Hydrogen production from conventional fossil-fuel feedstock is a commercial technology (on a large scale), but it results in significant CO<sub>2</sub> emissions. When hydrogen is derived from hydrocarbons (fossil fuels), the chemical energy to be stored in the hydrogen is already present in the primary fuels. Controlling in the chemical reactions and the extraction of hydrogen are the key challenges to this form of production.

Today, nearly half of the world's hydrogen production is via large-scale steam reforming of natural gas (a relatively low-carbon fuel/feedstock) because of the best hydrogen to carbon ratio of natural gas compare to other fossil fuels. The presence of hydrogen affects the efficiency and difficulty of the reforming process, more hydrogen and little other compounds make more efficient. In natural gas, methane is a main component, thus it is widely used as a feedstock in this process.

Mostly, the internal combustion engines and fuel cells are used to converse the energy which is stored in hydrogen into very useful work. Although comparatively little hydrogen is currently used as fuel or as an energy carrier, there are emerging trends that will drive the future consumption of hydrogen.

Today's economy of hydrogen is illustrated in Figure 2.1. It shows the sources and the applications of hydrogen in the world. The balance between supply and demand is required for the development of economy.



**Figure 2.1** Hydrogen's economy in the world

([http://ec.europa.eu/research/rtdinfo/42/01/article\\_1315\\_en.html](http://ec.europa.eu/research/rtdinfo/42/01/article_1315_en.html)).

## 2.2 Steam Reforming of Natural Gas (Methane)

Today, almost all hydrogen is produced via steam reforming of natural gas. The use of that hydrogen focuses on the oil refineries and petrochemical plants to refine fuel and to make industrial commodities. In industry, steam reforming of natural gas is carried out at temperatures ranging from 700 to 900°C (Levent *et al.*, 2002) and the typically pressure is 3-25 bar.

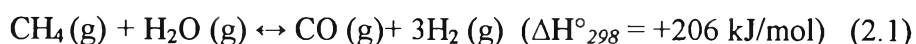
The steam methane reforming (SMR) process consists of the following two steps.

### 2.2.1 Reforming of Natural Gas

This step is a process in which a high-temperature steam is used to produce hydrogen from a methane source, such as natural gas that consists mainly of methane (CH<sub>4</sub>), mixed with some heavier hydrocarbons and CO<sub>2</sub>. The first step of the steam methane reforming process involves methane reacting with steam at 700-800°C to produce synthesis gas, a mixture primarily made up of hydrogen (H<sub>2</sub>) and

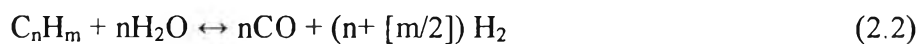
carbon monoxide (CO). And a relatively small amount of CO<sub>2</sub> and unreacted methane are also obtained.

The main steam reforming reaction is:



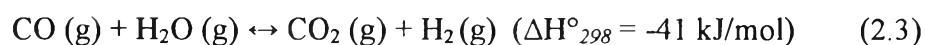
Like the steam reforming of higher hydrocarbons or alcohols such as diesel, gasoline and methanol, the above reaction is strongly endothermic (heat must be supplied) with a standard formation enthalpy of + 206 kJ/mol and can be carried out on a suitable catalyst especially Ni or noble metals on a substrate material. Due to the temperature of more than 700° C an adequate reaction rate and high hydrogen formation are ensured which, according to equation (2.1), is thermodynamically favored by high reaction temperatures and low pressures.

Moreover, the heavier hydrocarbons can also be used as a feedstock to react with steam in the process which is represented as:



### 2.2.2 Shift Reaction

Subsequently, the second step which is called as water-gas shift (WGS) reaction, CO from the first reaction is reacted with steam over a catalyst to give CO<sub>2</sub> and more hydrogen. The reaction is highly exothermic and is represented as:



This process occurs in two stages, consisting of a high temperature shift (HTS) at 350°C and a low temperature shift (LTS) at 190-210°C.

From above, steam methane reforming process gives the synthesis gas with a high H<sub>2</sub>/CO ratio (>3) because of the presence of water gas shift reaction, resulting in a low yield and selectivity of CO.

Hydrogen which is produced from steam methane reforming process involves small amounts of many impurities such as CO, CO<sub>2</sub>, and hydrogen sulfide. Thus, depending on the use, it may need additional purification. The primary steps for purification include:

- Feedstock purification: Because of their toxicity, Sulfur (S) and Chloride (Cl) are removed from the process for increasing the life of downstream steam reforming and others catalyst.
- Product purification: CO<sub>2</sub> is removed in the liquid absorption system. Then the product gas goes through the methanation step to remove the residual traces of carbon oxides. The methanation is the reverse of steam reforming reaction (Matar *et al.*, 1994). Now, a pressure swing absorption (PSA) unit is used in many new SMR plants due to a very pure hydrogen (about 99.99%) which can be produced from it.

Nevertheless, several problems from the impurities may be the causes of the requirement in the additional process steps for purification of the hydrogen to meet the industrial quality standards.

### 2.3 Steam Reforming Catalyst

High-performance catalysts are critical for synthesis gas processes technology. Due to the high temperatures and pressures involved in the steam reforming process, catalysts must be carefully shaped and formulated to ensure desired performance. The performance of the catalyst can be expressed by its properties such as the activity, stability, selectivity, and durability. Generally, the lifetime and the performance of catalysts are the key parameters of economical decision in the industrial standpoint.

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). In metal form (catalyst itself), reforming catalysts are generally supplied in an inert form which is stable under atmospheric conditions (Levent *et al.*, 2002). Industrially, a supported nickel (Ni) is most popular choice to use as a catalyst due to its inherent availability and lower

cost in comparison to other more noble metals. Some limitations of the catalyst based on noble metals restrict their favors and applications, for example cobalt (Co) and iron (Fe) which are less effective than Ni because of a rapid oxidation of Fe and a weakness in the steam partial pressure of Co, and platinum-group metals that are highly active but are too expensive for commercial operation. Although, Ni is the commercial catalyst, the large variations in the nature of the support and in the presence of promoters are interested. For the supports of the most commercial catalysts in reforming process, they are commonly based on ceramic oxide such as  $\alpha$ - and  $\gamma$ -alumina, magnesium oxide, magnesium-aluminate, or calcium-aluminate which is able to tolerate at a high temperature (Satterfield, 1991).

A catalyst is defined as a substance, which accelerates the rate of a chemical reaction without itself getting affected or changed. This definition suggests an infinite life for the catalyst. In practice, this is really not true. All catalysts deactivate, though at different rates, and have finite lives (Viswanathan *et al.*, 2002).

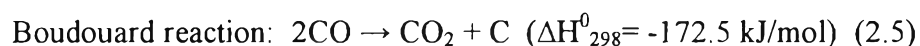
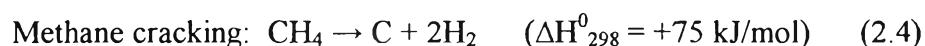
However, there are some factors of the deactivation of Ni catalyst in steam reforming. They are generally sulfur poisoning, carbon formation or carbon deposition and sintering of active metals. To ensure the catalyst lifetime, the causes of catalysts deterioration must be reduced. First factor, strong chemisorption of impurities, reactants, products or by products is a main cause of the catalytic sites poisoning. The effect of the poison will depend on its adsorption strength (at the active centre) relative to that of the reactants, the larger the strength of adsorption, the stronger the poisoning effect (Viswanathan *et al.*, 2002). Ni catalysts are very sensitive to poisoning by sulfur compounds which are the contaminants in the reactant, and the sulfur content of the feed gas must be reduced to a value below about 0.2-0.5 ppm in commercial operations (Satterfield, 1991). For the sintering that occurs because small crystallites always tend to lower their surface free energies by minimizing their specific surface areas (Viswanathan *et al.*, 2002). A physical change as the loss in total surface areas of Ni metals due to the agglomeration during the operation is accounted for the reduction of the catalyst activity and the change in the availability of Ni crystals. The rates of sintering of supported metals depend on many parameters such as the presence of impurities, the nature of the support, and the nature of the atmos-

phere. From a bad view of sintering, minimizing the sintering of Ni is also important, and this is related to support composition and method of catalyst preparation (Satterfield, 1991). Among of all deactivation factors, carbon deposition is the most serious problem and appears unavoidable, especially for Ni-based catalysts (Chen *et al.*, 1999). Therefore, it is very important to develop stable and effective Ni-based catalyst with improved resistance to deactivation caused by coking and poisoning.

#### 2.4 Carbon Formation during the Steam Reforming

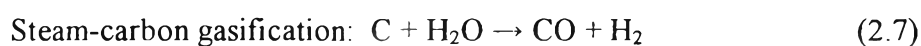
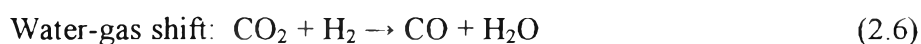
Because of a strongly endothermic reaction on reforming process, equilibrium yields of the synthesis gas require high temperatures. According to these conditions, a thin layer of inactive carbon may be formed on the catalysts surface due to the disintegration and deposition of some reactant types. It is known as a coke formation on the catalysts. Carbon formation usually takes place in the form of fibers or whiskers, with a small Ni particle at the top of fiber. Avoiding conditions leading to carbon deposition is particularly important since this can cause blockage of catalyst pores and catalyst deterioration, leading to premature reactor shutdown (Satterfield, 1991).

According to thermodynamics, there are two major reactions responsible for carbon formation. Solid carbon is expected to be formed mainly via methane decomposition and the Boudouard reaction as the following.



The tendency to form carbon on the catalyst surface depends on the reaction kinetics, process conditions, and reformer design (Anderson *et al.*, 2005).

In addition, the side reactions which are a reverse water-gas shift and steam-carbon gasification will occur, respectively.



The nature of the support may affect on the carbon properties. Carbon can be present in a form thermodynamically more active than graphite. Rostrup-Nielsen (1975) has reported that the limiting conditions at which coke formation occurred on Ni by reactions (2.4) and (2.5) seemed to be a function of the Ni crystallite size. The coke formed on the smallest crystallites showed the greatest deviation from graphite (Satterfield, 1991).

However, coke which is formed by a natural gas is generally not a significant problem in comparison to other hydrocarbons. The rate of carbon formation is largely dependent on the chemical composition of the catalyst as well as its preparation procedure.

For steam reforming of hydrocarbons over commercial Ni catalysts, three main kinds of carbon or coke species were observed. Firstly, at the temperatures above 600°C, pyrolytic carbon forms through the cracking of hydrocarbons and deposition of carbon precursors on the catalyst. Secondly, encapsulated carbon, it is formed by slow polymerization of unsaturated hydrocarbon on Ni surface at temperatures lower than 500°C. For finally, the diffusion of carbon into Ni crystals, detachment of Ni from the support, and growth of whiskers with Ni on the top of the catalyst at temperatures above about 450°C give a filamentous or whiskerlike carbon which is the most common form produced during steam reforming. Pyrolytic and encapsulated carbons encapsulate the catalyst particles and therefore deactivate the catalyst. Although the whiskerlike carbon does not deactivate the catalysts directly, it can grow on the Ni surface, causing the breakdown of the catalyst and blockage of the reformer tubes and leads to an increase in pressure drop.

The difference between the carbon formation and carbon gasification can indicate the net carbon deposition. The carbon deposition may be controlled or be eliminated by using optimal catalysts with an alkaline promoters or using high steam-to-carbon feed ratios. The presence of alkaline promoters may decrease the rate of hydrocarbon cracking which is a source of deposited carbon on the catalyst surface because the alkaline metals neutralize the acid sites of the catalyst support and poison some active Ni surface. For the method of using a sufficiently high ratio

of steam to carbon, the reduction of this ratio to the minimum consistent with adequate catalyst life is desirable for economical operation (Satterfield, 1991).

## 2.5 Catalyst Preparation Method

For zeolite-supported metal catalyst, the acid- and metal-site density and strength distribution are both important and their proper balance is critical in determining the catalyst activity (Canizares *et al.*, 1997). According to these influences on the activity of catalyst, the support and the methods of catalyst preparation are considered. For the catalyst preparation, the metal component can be loaded by various methods especially impregnation and ion exchange, which are the most widely used methods. The loading method has direct or indirect influence on several characteristics of the catalysts as metal dispersion, size and location of metal particles, metal-surface interactions or acidity. All of them are important parameters, usually with opposite effects on the catalyst activity (Canizares *et al.*, 1997). However, few researchers paid great attentions to improve the preparation techniques to obtain highly dispersed noble metal catalysts, which retained sufficient activity while suppressing carbon deposition (Wang *et al.*, 1997).

From a previous work of NaY zeolite-supported Ni catalyst with steam methane reforming, the comparison of the catalyst preparation methods was investigated. It was reported that the impregnation is the most suitable method to synthesis catalyst for steam reforming process due to its simplicity and high performance to produce hydrogen. Therefore, we focus on the impregnation method only.

### 2.5.1 Impregnation

Many catalyst types are produced by impregnation. It is a preparation technique in which a solution of the precursor of the active phase (agent) is brought in contact with the support (Anderson *et al.*, 2005). The agent must be applied uniformly in a predetermined quantity to a preset depth of penetration. This is especially true of catalysts based on noble metals. The active agent is never introduced into a porous support in its final form but by the intermediary of a precursor, the choice of which holds great importance for the quality of the final deposit, its structure, its



grain size, its distribution as a function of the diameter of the granule (Le Page *et al.*, 1978). The air trapped in the pellet pores may block the liquid that want to penetrate into the pellets.

Several techniques like pressurizing, vacuum treatment, acoustic activation etc. are used to facilitate the impregnation process. But their aspects of the high cost and the limited controlling in penetration depth and absorption are the barriers of their applications. Thus, a simple, inexpensive, conserving, precise and rapid method to impregnate catalytic supports is desired.

Two methodologies exist as dry and wet impregnations.

#### *2.5.1.1 Dry impregnation*

In dry impregnation, also referred to as “pore volume impregnation”, just enough liquid (solution of the precursors) is used to fill the pore volume of the support. The maximum loading available in each time of impregnation is determined by the solubility of the catalyst precursors and the pore volume of the support. If a high loading is needed, successive impregnations (and heat treatments) may be necessary. The impregnation is called as co-impregnation when several precursors are present simultaneously in the impregnating solution. Generally, there are three processes occur respectively in the first step of impregnation which are the transportation of solute to the pore system of the support bodies, the diffusion of solute within the pore system, and the uptake of solute by the pore wall (Anderson *et al.*, 2005).

#### *2.5.1.2 Wet impregnation*

It consists in the repeated dipping of porous support pellets into an excess quantity of precursor solution of desired catalytic agent (active phase). Then, the steps of drying, washing, calcinations and activation are followed. In the case of wet impregnation, there is another impregnation process that is different from the above three processes. A fourth process is the transportation of solute to the outer particle surface or operative.

Furthermore, the wet impregnation can be divided into two types, depending on if an interaction exists between the support and the precursors at the moment of wetting, or if there is no interaction (Le Page *et al.*, 1978).

#### *2.5.1.2.1 Impregnation with no interaction between support and catalyst*

If the support does not have its own catalytic activity, its role is to suitably present the catalytic agents; it gives the finished catalyst its form, its texture and its mechanical resistance.

#### *2.5.1.2.2 Impregnation with interaction between catalyst and support*

Impregnations with interaction occur when the solute to be deposited establishes a bond with the surface of the support at the time of wetting. Such interaction results in a near-atomic dispersion of the active species' precursor. Ion exchange, adsorption, or chemical reactions are the interactions that can be occurred.

### 2.5.2 Metal loading

Chang *et al.*, 1996 performed CO<sub>2</sub> reforming of methane over pentasil-type zeolite-supported Ni catalysts to produce synthesis gas. The zeolite-supported Ni and KNiCa catalysts were prepared and hybridized by the solid-state reaction method. Effect of Ni loadings on these catalysts was also investigated by varying the amounts of Ni loading from 0.8 to 9.7 wt%. For Ni/ZSI catalyst, the results showed that the enough high catalytic activities were obtained from over 2 wt% of Ni loading and the activity was a function of the overall Ni content. When the Ni content was increased, the activity would increase also. But, too high of Ni content did not give any further significant increase in activity because Ni particles might sinter and reduce the surface area of catalysts as a result of lower activity and deactivation. The optimum loading was 5 wt% and the catalysts were quickly deactivated when Ni loading is more than 7 wt%.

## **2.6 Development of Catalyst for Steam Reforming**

The development of steam reforming catalysts during the last several years have been mandated mainly by considerations related to industrial requirement, high performance of catalysts, more efficient processes, more production of products, and

more applications. The terms of catalytic activity and stability (resistant to carbon formation) at a low steam to carbon ratios have been concentrated to study by many researchers. Generally, ceramic oxides and Ni are used as the commercial support and active metal in steam reforming, respectively. But, the causes of catalyst deactivation especially coke formation may lead to the improvement of catalysts. Therefore, the essential components in catalysts which play very important roles with the process are firstly accounted. According to many researchers, the improvement of conventional catalyst by finding new supports, changing active metals or adding promoters has been considered to focus.

In methane steam reforming that used Ni as a catalyst, the species of metal oxide support were varied as silica,  $\gamma$ -alumina and zirconia by Matsumura and Nakamori (2004) in order to study the effects of the supports especially in terms of activity and efficiency. These processes were operated at a low temperature of 500°C and these catalysts were prepared by an impregnation technique. Their results showed that hydrogen and carbon oxides were formed at 500°C in steam reforming over Ni catalysts. According to a high and stable activity, Ni supported on zirconium oxide was found as the most effective catalyst for steam reforming at 500°C in comparison to the others. Furthermore, the presence of hydroxyl groups on the surface was an important step in a mechanism of steam reforming to CO<sub>2</sub> because of the promptly reaction of these catalysts and methane. In the case of zirconia-supported Ni, the accumulation of water on the support assisted the formation of hydroxyl groups on the surface, resulting in the formation of hydrogen and CO<sub>2</sub> in the reaction with methane. This might be the reason why zirconia was an effective support of Ni in steam reforming at 500°C.

New supports of Ni- and Ru- catalysts with methane reforming by steam for new ICAR-process of direct nuclear-to-chemical energy conversion were explored. Gordeeva *et al.* (1994) found that porous U<sub>3</sub>O<sub>8</sub> material was a suitable support to use in this process. These studied catalysts were very active in methane steam reforming and had a high hydrogen production as 17-18 cm<sup>3</sup>/s per 1 gram of the catalyst at the conditions of pressure = 1 atm and temperature = 600-780°C. In a summary, the

catalytic activity of catalysts depended on the effects of the metal (Ni or Ru) content, temperature and contact time in non-gradient catalytic reactor.

The oxygen transfer and catalytic properties of Ni iron oxide ( $\text{NiFe}_2\text{O}_4$ ) which used as a combined catalyst precursor and oxygen transfer material in steam reforming of methane were investigated to improve the conversion of methane into synthesis gas (Sturzenegger *et al.*, 2006). According to thermogravimetric measurements with simultaneous gas analysis, it showed that Ni iron oxide had a superior behavior than iron oxide. Thus, the catalyzed steam reforming of methane became increasingly essential when the quantities of Ni-rich alloy increased. The generation of fresh Ni surfaces in the term of the reduction of metal oxide generally related to the increasing of catalytic activity.

For the studies of methane steam reforming over Ce-ZrO<sub>2</sub>-supported Ni, Pt, Ru and Rh catalysts at 500-800°C, methane conversion and CO selectivity were determined to select the highly active and stable reforming catalysts for the use in a membrane reactor. Kusakabe *et al.* (2004) compared the Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports containing 10 wt.% of Ni loading, as a result, the Ce<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>2</sub> support expressed the highest methane conversion which were maintained without deactivation for 5 hours at 500-600°C and high H<sub>2</sub>/CO ratio due to the oxidation of CO via the water-gas shift reaction, but low CO selectivity. Besides, they considered to improve the catalytic activity of Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports by adding the Pt, Ru and Rh metals into the supports. The Rh/Ce<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>2</sub> catalysts showed the highest activity that can convert methane to synthesis gas as 28.1% at 500°C.

NiO/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared and investigated after the reduction treatment in methane-reforming reactions (Roh *et al.*, 2003). Among the different Ni loadings, Ni loading of 12 wt.% was found to be the optimum point which gave the highest catalytic activity, selectivity and remarkable stability. From TPR results, the strongly interaction between the support and Ni played a role in forming stable NiO<sub>x</sub> species. Considering, the catalytic activity and stability depended on the whole amounts of NiO<sub>x</sub> compared with NiO or NiAl<sub>2</sub>O<sub>4</sub> on the surfaces due to the metallic Ni sites reduced from NiO<sub>x</sub> species were active sites for methane-reforming reactions and presented a high coke resistance. Finally, this study also indicated that the interaction between Ni and CeZrO<sub>2</sub> had the essential effects on

preventing the formation of inactive  $\text{NiAl}_2\text{O}_4$  and producing mobile oxygen species, resulting in a high activity and stability of  $\text{NiO/Ce-ZrO}_2/\theta\text{-Al}_2\text{O}_3$  catalysts.

Dong *et al.* (2002)'s investigation also focused on the effect of Ni content on the  $\text{Ni/Ce-ZrO}_2$  catalyst in the methane conversion reactions to syngas. From this examination,  $\text{Ni/Ce-ZrO}_2$  catalyst with 15% Ni loading was the most suitable catalyst because two kinds of active sites, one for methane and another for steam or oxygen, were balanced which made not only the highest catalytic activity and selectivity but also remarkable stability. Some parts of NiO incorporated in the surface of  $\text{Ce-ZrO}_2$  support and the resulting strong interaction between NiO and  $\text{Ce-ZrO}_2$  matrix suppressed the reduction of NiO. According to assuming results, the catalytic activity and stability of  $\text{Ni/Ce-ZrO}_2$  catalysts depended on Ni surface area, chemical environment of Ni and the properties of  $\text{Ce-ZrO}_2$  support.

At temperatures of 400-800°C, 1 wt.% of Co, Cu, Fe, Ni, Pd and Pt were used as supported metals on zirconia ( $\text{ZrO}_2$ ) in order to test for the production of syngas via steam reforming of methane. The Pt, Pd and Ni metals were found to be the most active. The result from stability tests at 800°C was described as the Pt catalyst was only stable catalyst with an excess steam that can observe through the maintaining of its activity while other catalysts deactivated due to carbon deposition (Hegarty *et al.*, 1998).

Yamazaki *et al.* (1996) tried to develop a highly stable Ni catalyst for methane steam reaction under a low steam to carbon ratio. They found that Ni-Mg-O solid solution with low Ni content ( $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ ), which was reduced at the temperature over 800°C, presented high stability and activity for methane steam reforming in a steam to carbon ratio of 1.0. The terms of lower stability and lower activity of a commercial reforming catalyst ( $\text{Ni/Al}_2\text{O}_3\text{-MgO}$ ) were presented in the comparison to reduced  $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$  catalyst, suggesting in the different composition of surface carbonaceous species on the Ni metal particles and very small size of Ni particles affected on the subduing of coke formation on our catalyst.

The effect of  $\text{CeO}_2$  structure on the activity of supported Pd catalysts in the steam reforming of methane was investigated (Craciun *et al.*, 2002). Palladium (Pd) supported on  $\text{CeO}_2$ -promoted  $\gamma\text{-Al}_2\text{O}_3$  with various  $\text{CeO}_2$  crystallinities, were used as

catalysts in the methane steam reforming reaction. The terms of Pd and CeO<sub>2</sub> structure and dispersion on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support of the samples were analyzed by x-ray diffraction (XRD), FTIR spectroscopy of adsorbed CO, and x-ray photoelectron spectroscopy (XPS). A well dispersion of Pd on crystalline CeO<sub>2</sub> and the agglomeration of Pd as large clusters on amorphous CeO<sub>2</sub> were revealed by XRD. Crystalline CeO<sub>2</sub> and dispersed Pd preferred high reaction rates and low activation energy, suggesting in the effect of CeO<sub>2</sub> structure on methane steam reaction rates. A catalytic synergistic effect between Pd and CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was observed, with the reaction rates were two orders of magnitude higher on Pd/CeO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> than on unpromoted catalysts. For the activity, addition of CeO<sub>2</sub> in the alumina-supported Pd catalysts can promote their activity. Moreover, the loss of Pd sites due to encapsulation or particle agglomeration can make the reduced Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst had a low reaction rates.

Similar catalysts as CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-supported Pd catalysts in the process of steam reforming of methane were examined again, but in the different effect of ceria that used as a promoter. Feio *et al.* (2007) studied the effect of CeO<sub>2</sub> loading on the surface properties and catalytic behaviors of these catalysts. The catalysts were characterized by S<sub>BET</sub>, x-ray diffraction (XRD), temperature-programmed reduction (TPR), UV-vis diffuse reflectance spectroscopy (DRS), and FTIR spectroscopy. They found that the reduction temperature and CeO<sub>2</sub> loading lead to a great change of the superficial structure of Pd particles. And the catalytic activities of Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts depended strongly on the CeO<sub>2</sub> content. High CeO<sub>2</sub> loading ( $\geq 12$  wt.%) in catalysts induced a higher catalytic activity. Furthermore, the formation of Pd-CeO<sub>x</sub> interface related to the higher activity of 1Pd/12CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. The Pd sites with high coordination were partially blocked to decrease the carbon formation on Pd surface, whereas the sites with lower coordination had the jumping of oxygen from ceria to Pd surface that can give the increasing activity also. Consequently, the accessibility of methane to metal active sites increased with the rise of CeO<sub>2</sub> loading which specific reaction rates would increase too.

Nevertheless, the deactivation of catalysts may come from many reasons. Effects of the conditions such as temperature, pressure and feed ratio were considered to be another mainly factors.

## **2.7 Effects of the Conditions during Steam Reforming Process**

In the past, the equipment that used to control conditions in the process were very difficult and not sure to use or measure. So, some defected conditions may affect on the catalytic activity of catalysts. The shorter lifetime of catalysts will occur consequently. For example, the condition effects with a study of catalyzed steam methane reforming in an automatic catalytic microreactor (Levent *et al.*, 2002) were described as the following.

### **2.7.1 Effect of temperature on exit gas composition, and on the reaction velocity coefficients**

In this study, as the temperature decreased, the amounts of unreacted methane were found to be increased while the amounts of CO and hydrogen were found to be decreased. It showed that the quantities of CO and hydrogen related to the change of temperature directly. For reaction velocity coefficients, the Arrhenius equation was used to describe as the function of temperature.

### **2.7.2 Effect of pressure on exit gas composition, and on the reaction velocity coefficients**

An increased reaction pressure was found to increase the conversion of methane in the pressure range investigated of 2.5-9 bars. The increased residence time between the catalyst and reactant gas was the cause of the increase in methane conversion. As a result of increased methane conversion, CO, CO<sub>2</sub> and H<sub>2</sub> which presented in the exit gas would increase also. On the other hand, the reaction velocity coefficients were found to decrease as the pressure was increased.

### 2.7.3 Effect of hydrogen to methane ratio on exit gas composition, and on the reaction velocity coefficients

A study showed that an increased ratio of hydrogen to methane in the feed was found to enhance the catalyst activity and to increase the velocity of the reaction in the experimental range. From the suppression of steam in the catalytic activity and the reaction velocity, an increased ratio of steam to methane in the feed found to act in the opposite sense to the hydrogen and the catalytic activity was decreased with the increase of steam in the feed.

These are some effects on the process, but not at all. Other effects may be considered in the same way if they also concern with the reforming process or make the disadvantages to catalysts during the operation.

## 2.8 Zeolite Catalyst Support (ZSM-5)

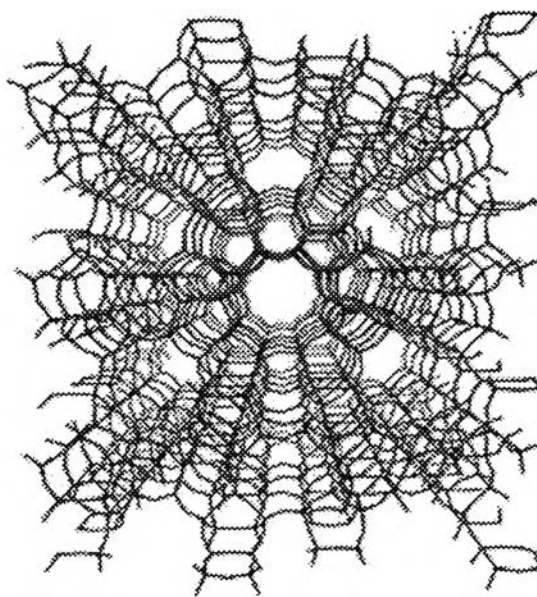
The influence of the support has been one of the issues most investigated for the search of stable catalysts. The requirement to support the active metal is evident when supported catalysts are compared with physical mixtures of components.

Zeolites are alumino-silicate, three-dimensional and crystalline compounds which are built from  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedron. They have a highly regular structure of pores and chambers that allows some molecules to pass through, and causes others to be either excluded, or broken down. Generally, cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and others can accommodate with an open structure of zeolites. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Under hydrothermal conditions, the solutions of sodium aluminate, sodium silicate, or sodium hydroxide can be used to synthesis zeolites. Such conditions are typical of those found in the earth's crust where some zeolites are found naturally.

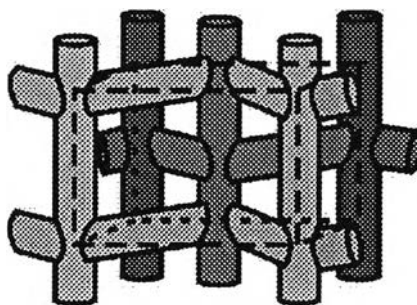
Nowadays, due to the high concentration of active acid sites, high thermal or hydrothermal stability, and high size selectivity, zeolites are considered to be a good choice for the industrial catalysts. Zeolite-based heterogeneous catalysts are commonly used in the interconversion of hydrocarbons and the alkylation of aromatic compounds. One of the zeolites which is very commercial for this industrial requirement is ZSM-5 type.



ZSM-5 is a zeolite and an industrially important catalyst. It is an aluminosilicate zeolite with a high silica and low aluminum content. In silicate and ZSM-5, the tetrahedra are linked to form the chain-type building block. The chain can be connected to form a layer (Gates, 1992). It was named as pentasil group zeolites due to the rings consisting of five oxygen atoms that are evident in its structure. These five-ring building units lead to lattice structure that is arranged in a ten ring. These are important because they provide openings in the structure large enough for passage of even rather large molecules (Gates, 1992). Its structure is based on channels with intersecting tunnels. Linear channels are perpendicular arranged to zig-zag channels. Its unique two-dimensional pore structure is illustrated in Figures 2.2 and 2.3.



**Figure 2.2** Representation of model structure of ZSM-5  
(<http://www.3dchem.com/molecules.asp>).



**Figure 2.3** Schematic representation of the intracrystalline pore structure (<http://www.uni-leipzig.de/~pdfhome/zsm1.html>).

The aluminium sites in this zeolite are very acidic. When  $\text{Al}^{3+}$  substituted in the place of the tetrahedral  $\text{Si}^{4+}$  silica, the addition of a positive charge is required. If this positive charge is  $\text{H}^+$ , the acidity of the zeolite will increase to a high level.

Typically, the ZSM-5 catalyst is used in petroleum industry for hydrocarbons interconversion. Moreover, the zeolite ZSM-5 is resistant to coke formation because of steric constraints on the transition states, and this is one of the reasons why it finds wide industrial application (Gates, 1992).

From the previous work, Senathipbordee (2004) performed Ni/KL catalyst with 7 wt% of Ni catalyst that showed the best catalytic activity and stability. Due to the suitable properties of KL zeolite, the high activity and thermal stability of Ni/KL catalyst were presented and focused for the steam reforming of methane. But the steam reforming of methane on Ni/KL catalyst had the lower performance than the reforming of methane by  $\text{CO}_2$ . However, the study of methane steam reforming on Ni/NaY was investigated as many effects that would occurred (Chankham, 2007). The development of catalysts for steam methane reforming will go on and on. The idea of this work comes from the combination of other concepts which mainly investigates the performance of Ni/ZSM5 catalyst as the function of activity and stability (resistance to coke deposition). The catalysts were prepared with various Ni loadings in order to study the effect of Ni loading on the catalytic activity and to find a suitable catalyst for methane reforming by steam. Moreover, the parameter of this reac-

tion, the addition of a promoter, and  $H_2/CO$  ratio were studied also. And the characterization of both fresh and spent catalysts was investigated.