

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Clinoptilolite

Clinoptilolite is the natural zeolite with the simplified formula $(\text{Na,K})_6\text{Si}_{30}\text{Al}_6\text{O}_{72} \cdot n\text{H}_2\text{O}$. It is one of the most abundant zeolites, which can be found in sedimentary rocks all over the world and can be mined with simple techniques. It has a monoclinic framework consisting of ten-membered-rings ($7.5 \times 3.1 \text{ \AA}$) and two eight-membered-rings ($4.6 \times 3.6 \text{ \AA}$, $4.7 \times 2.8 \text{ \AA}$) as shown in Figure 2.1 (Lee *et al.*, 2002). It is defined as the heulandite family with $\text{Si}/\text{Al} \geq 4$. The negative charge in the zeolite lattice is typically balanced by Na^+ , K^+ , and Ca^{2+} in nature, which makes it have a high affinity to exchange with metal cations. Therefore, clinoptilolite has received much attention to be used in wastewater treatment fields. Moreover, in Europe and North America, clinoptilolite has been used in many areas such as animal hygiene, animal feed, fertilizer, and building materials. However, there are some researchers who have studied clinoptilolite for use in catalysis and gas separation fields. Lee *et al.* (2000, 2002) studied skeletal isomerization of n-butene and 1-butene on modified clinoptilolite, and they found that clinoptilolite exhibited good activity and selectivity in isomerization reactions. In carbon dioxide reforming of methane, it has been reported that using zeolite supports are superior to amorphous supports (Chang *et al.*, 1996 and Bhat and Sachtler, 1997). Chang *et al.* (1996) reported that zeolite-supported Ni catalysts showed high performance and little coke formation. Bhat and Sachtler (1997) found that Rh supported on zeolite gave high stability along the reaction, while Rh supported on amorphous oxide support showed a decrease in activity with time on stream. Therefore, it seems to be interesting to investigate the catalytic possibility of clinoptilolite, the natural zeolite, in carbon dioxide reforming of methane reactions since it has a high affinity for carbon dioxide. Moreover, the balanced charges in clinoptilolite e.g. Na^+ , K^+ , Ca^+ are expected to promote the activity of the catalysts.

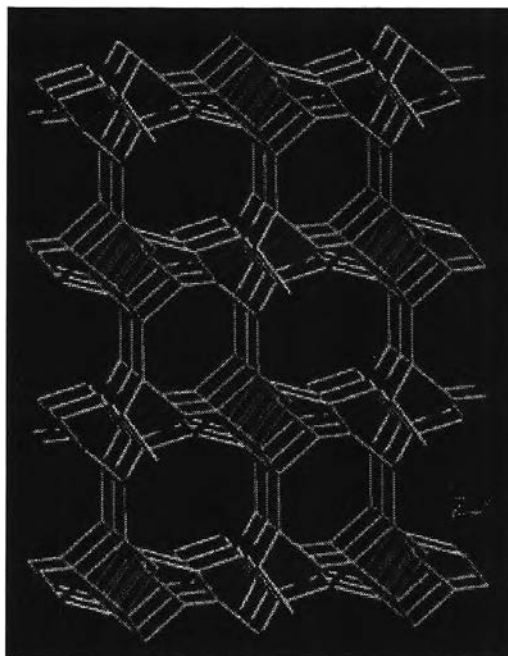


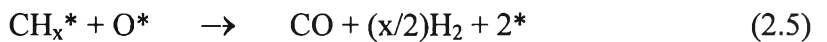
Figure 2.1 Clinoptilolite framework.

2.2 Carbon Dioxide Reforming of Methane

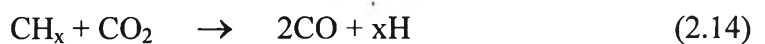
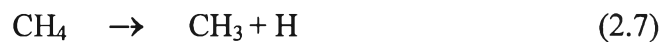
Carbon dioxide reforming of methane or dry reforming to produce synthesis gas has recently gained high attention. This reaction has important advantages over steam reforming process such as; (a) both CH_4 and CO_2 are the greenhouse gases, (b) it can produce low H_2/CO ratio, which is suitable for using as the feedstock in Fischer-Tropsch process to synthesize liquid fuel, and (c) it can be used as chemical energy transmission systems and energy storage in the form of CO and H_2 (Wang and Lu, 1996). It has been reported that using CO_2 reforming-methanation cycle instead of steam reforming-methanation cycle for solar energy application showed many advantages such as; it produced more heat of reaction, easy to operate because all the reactants and products are in vapor phase, and it gave fewer side reactions than steam reforming (Chubb, 1980 and McCrary, 1982). However, one of the major problems of using this reaction is the catalyst deactivation by carbon deposition. Therefore, it is desired to develop the catalyst, which can stabilize under the operating condition of this reaction.

2.2 Reaction Mechanism

It has been proposed that CO₂ reforming of CH₄ consists of two simplified reactions, which are CH₄ decomposition and CO₂ dissociation (Equations 2.1-2.6) (Wang and Lu, 1996).



Moreover, it has been found that H₂ from CH₄ decomposition can facilitate CO₂ dissociation. Erdohelyi *et al.*(1995) have proposed the reaction mechanism on Rh and Pd catalysts as follows (Equations 2.7-2.16):



Stagg and Resasco (1998) proposed the cleaning mechanism on the supported Pt catalysts, which can remove the carbon deposition on the metal surface as shown in Figure 2.2. First step is CH₄ decomposition (Equation 2.17) that occurs on the metal surface and produces H₂ and carbon deposition. Then the carbon is partially oxidized by oxygen in the support to produce CO and oxygen vacancies

(Equation 2.18). The second step is CO_2 dissociation to CO and O (Equation 2.19), which can fill the oxygen vacancies and then clean the metal surface by reacting with the carbon deposition on the catalyst (Equation 2.20).

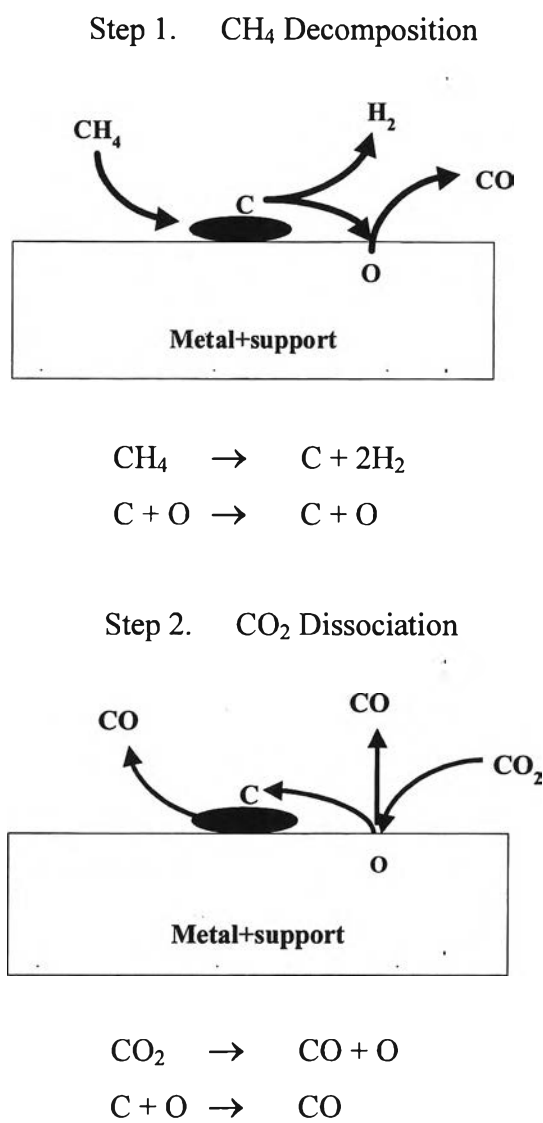


Figure 2.2 Cleaning mechanism scheme.

In this work, all of the catalysts were prepared by incipient wetness impregnation method using clinoptilolite as the support and Ni as the active metal. Ce and Zr were selected to be used as the catalyst modifiers. The carbon dioxide

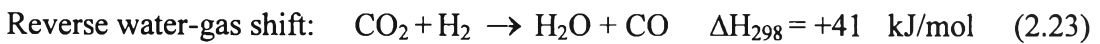
reforming of methane reaction was performed at 500-800°C, and the activity of the catalysts in terms of activity and stability were examined by gas chromatograph. Fresh and used catalysts were characterized by a number of characterization techniques. The effects of Ni loading, added promoter, and reaction temperature were also studied.

2.4 Carbon Deposition

Carbon deposition on a catalyst is the most significant problem for CO₂ reforming of CH₄. The deposited carbon is mainly from CO₂ molecular route, while the small amount is from CH₄ route (Erdohelyi *et al.*, 1994; Tsipouriari *et al.*, 1994). Matsukata *et al.* (1995) proposed that the graphitic carbon was filamentous which could be gasified by CO₂. The other form of carbon, which is mosslike carbon in the amorphous structure was difficult to be gasified by CO₂. Wang and Lu (1999) found that two carbon species, graphitic carbon and oxidized carbon species, were generally formed on the catalyst surface. The first type of carbon was originated from CH₄ cracking (Equation 2.21) and can be oxidized at low temperatures. The second type of carbon was generated from Boudouard reaction (Equation 2.22) and oxidized at high temperatures. The latter could spread over and encapsulate the nickel particles, which causes the deactivation of the catalyst. Moreover, they have found that the properties of the support affected to the carbon deposition on the catalysts. Among the catalysts that they have tested, the coking ability of four catalysts was in the following order: Ni/ α -Al₂O₃ > Ni/ γ -Al₂O₃ > Ni/SiO₂ > Ni/MgO (Wang and Lu, 1998a). Shamsi and Johnson (2003) studied carbon deposition on Pt/ZrO₂ catalyst by using Temperature-programmed oxidation (TPO). They found that there were two major peaks occurred at 380 and 830°C, respectively. They concluded that the different peaks of TPO were the result of carbon deposited at two different locations on the catalyst surface. The peak at lower temperature might be the carbon deposited on the catalyst site, which can facilitate the carbon oxidation and the peak at higher temperature from the carbon deposited on the catalyst support.



The reverse water-gas shift reaction (Equation 2.23) and steam-carbon gasification (Equation 2.24) occur as side reactions, which could also have an important influence on the overall product distribution (Wang *et al.*, 1996). The way to avoid these side reactions is to operate the reaction with short contact time (Gesser *et al.*, 1994). Therefore, the effective catalysts should have the properties that can speed up the overall reaction and prevent undesirable reactions at the same time.



2.5 Catalysts Development

2.5.1 Active Metal

Numerous supported metal catalysts have been studied for methane reforming. Group VIII metals (Rh, Ru, Ni, Pt, Pd, Ir, Co, Fe) are good for this reforming reaction. Noble metals (Rh, Ru, Pt) are not deactivated by carbon deposition whereas Co, Ni, and Pd are deactivated by coking (Cheng *et al.*, 1996). In order to avoid carbon formation the reactant gas should have the composition of CO_2/CH_4 ratio more than one (Wang *et al.*, 1996). Tokunaga *et al.* (1989) compared the activities of catalysts such as Ni, Fe, and Co supported on $\gamma\text{-Al}_2\text{O}_3$, and found that $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ was the most effective catalyst. Richardson *et al.* (1990) also studied catalysts based on Ni, Ru, Rh, Pd, Pt, and Ir. The deactivation test showed that the Rh catalyst was more stable than the other catalysts. Although the noble metals present high performance, but the limited availability and expensive price lead to the investigation of non-noble metal supported catalyst in order to obtain high catalytic activity and stability for carbon dioxide reforming of methane reaction.

In the past decade, many researchers have developed Ni-based catalysts, which could be the effective catalysts for CO₂ reforming of methane in terms of conversion, stability, and commercialization. It has been found that many factors influence the catalyst activity for this reaction.

2.5.2 Catalyst Preparation Method

Preparation method is one of the factors that affect the properties of the catalyst. Ashcroft *et al.* (1991) first used an improved vacuum wetness technique to obtain highly dispersed noble metal catalysts. The catalyst prepared by this technique preserved sufficient activity, and could hold back the carbon deposition. Chang *et al.* (1994) reported that Ni/zeolite catalysts synthesized by solid-state reaction gave much higher activity than that prepared by incipient wetness method. From their results, the former gave over 90% conversion at 800°C without deactivation by coking. Chen *et al.* (1996) studied the effect of catalyst preparation on the Ni/Al₂O₃ catalysts. It was found that catalysts prepared by successive impregnation of promoter oxide and nickel oxide were better than those prepared by co-impregnation process. Wang and Lu (1998a) studied Ni/MgO catalysts based on a commercial MgO and Ni/MgO catalysts prepared by co-precipitation process. The results indicated that Ni/MgO from the latter process gave little conversion for the reaction and had poor stability. However, Ruckenstein and Hu (1996) found that Ni/MgO catalyst prepared by impregnation gave high conversion of about 90% and showed high stability. The comparison of the conventional impregnation and co-precipitation methods was investigated by Potdar *et al.* (2002). They found that the surface area of the catalyst from co-precipitation was higher than the catalyst from the impregnation method. Moreover, they indicated that better dispersion and less sintering of fine NiO particles during the calcination process were observed when catalysts were prepared by co-precipitation method.

2.5.3 Modifier

Another way to improve the activity of catalyst is adding the modifier, which are supports and promoters. The role of catalyst support on the activity of Ni for reforming methane with CO₂ was first studied by Gadalla and

Bower (1988). They found that the activity, selectivity, and stability of Ni catalyst varied greatly with different supports. Ni supported on Al_2O_3 , $\text{Al}_2\text{O}_3\text{-MgO}$, and $\text{Al}_2\text{O}_3\text{-CaO}$ gave high conversion, while the catalysts with support containing MgO and CaO were more stable. Takano *et al.* (1994) proposed that addition of MgO to SiO_2 -supported catalyst can increase the catalytic activity but decrease the stability. Wang and Lu (1998) studied the Ni-based catalysts on various supports including a silica gel, precipitated silica powder, $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and commercial magnesia prepared by wetness impregnation. The results showed that at the same temperature the conversion of CH_4 and CO_2 decreased in the following order: $\text{Ni}/\gamma\text{-Al}_2\text{O}_3 \sim \text{Ni}/\text{silica gel} > \text{Ni}/\alpha\text{-Al}_2\text{O}_3 \sim \text{Ni}/\text{commercial magnesia} > \text{Ni}/\text{precipitated silica} > \text{Ni}/\text{MgO}(\text{co-precipitation})$. These showed similar results to Takano *et al.* (1994). The deactivation rate of the catalysts caused by carbon deposition was ranked as: $\text{Ni}/\text{commercial magnesia} < \text{Ni}/\gamma\text{-Al}_2\text{O}_3 < \text{Ni}/\text{silica gel} < \text{Ni}/\alpha\text{-Al}_2\text{O}_3$. Nakamura *et al.* (1994) found that the effect of support on catalytic activity was in the following order $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{SiO}_2$. They believed that the significant effect of support might be due to a direct activation of CH_4 or CO_2 by metal oxides and the difference of particle size of the metals. Wang *et al.* (1996) proposed that adding the alkaline promoter to catalysts was effective in preventing coke formation. The alkali or alkaline-earth oxides will change the nature of support to basic catalyst that can adsorb CO_2 strongly on the surface and cover a large part of the surface at the lower CO_2 partial pressure, which will prevent carbon deposition on the catalysts. The effect of the promoters on Ni- based catalysts was also studied by Cheng *et al.* (1996). Using two groups of oxides, lanthanides (La and Ce) and alkaline earth metals (Mg and Ca) oxides as promoters for $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts. The $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts promoted with lanthanide oxides such as CeO_2 and La_2O_3 showed the product concentration two times higher than that unpromoted catalysts. The addition of alkaline earth metal oxides such as MgO and CaO also increased the product concentration, but the effect of MgO was found to be greater than that of CaO. Moreover, they found that when the promoter was impregnated prior to nickel, the result showed both enhancement of reducibility of nickel and decrease in nickel particle size, which can enhance the activity of the catalyst. However, the influence

of promoter on nickel particle size was not significantly observed when nickel was impregnated prior to promoter.

2.5.4 Ni Precursors

There were some researchers studying the effect of nickel precursors, and the results showed that the nickel precursor also played an important role in the catalytic activity for this reaction. Ruckenstein and Hu (1996) studied the activity of Ni/La₂O₃ catalysts using different precursors in the preparation, which were nickel nitrate and nickel chloride. They concluded that Ni catalyst based on nickel nitrate had a high initial CO yield but a low stability. However, for Ni catalyst based on chloride showed a high stability. The effect of nickel precursor on Ni/Al₂O₃ was also studied by Wang and Lu (1998b). Three different precursors in the process of preparing Ni-based catalysts have been used: nickel nitrate, nickel chloride, and nickel acetylacetonate. The catalyst prepared from nickel nitrate as a precursor showed high catalytic activity and high stability because of the weak interaction between nickel particle and alumina support, which created more active site than the others.

2.5.5 Ni Loading

Nickel loading also affected to the activity of the catalyst in carbon dioxide reforming of methane reaction. For noble metal catalyst, low loading of metals on supports was sufficient because of their effective performance. But, for the catalysts which metal-support interaction was strong such as Ni and Co, higher loading was required (Wang *et al.*, 1996). Potdar *et al.* (2002) proposed that 30% Ni dispersed on Ce_{0.8}Zr_{0.2}O₂ prepared by co-precipitation method showed the highest surface area and the lowest crystallite size, but it was deactivated by sintering and coke formation. They found that the optimum loading of Ni was 15% Ni catalyst that gave over 95% conversion and slowly deactivated, whereas the 5% Ni and 10% Ni loaded catalysts showed lower CH₄ and CO₂ conversion. Roh *et al.* (2002) investigated the amount of Ni loading on θ -Al₂O₃ and found that the optimum Ni loading was 9-12%.

In this work, clinoptilolite was selected to use as the catalysts support due to its micropore structure and high thermal stability that could give promotion effect to the activity of the catalysts. In order to improve the catalytic activity and stability of the catalysts, CeO_2 and ZrO_2 were used as promoters. CeO_2 is known as high oxygen storage capacity material, which can enhance the stability of the catalysts. Moreover, CeO_2 can promote the metal dispersion of the catalysts and improve the catalytic activity. For ZrO_2 , it has been reported that it can improve the thermal stability of the catalysts support that can prevent the structure collapse during the reaction and maintain the surface area of the catalysts. Consequently, the catalytic activity of Ni catalysts with various amounts of Ni loading, promoter loading and reaction temperature was investigated.