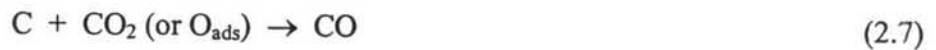## CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Carbon Dioxide Reforming of Methane

Synthesis gas (or syngas) is a mixture of H_2 and CO_2, which are important raw materials that play significant role in many chemical processes. Synthesis gas is a source of H_2 for production of methanol, ammonia, used in fuel cell, used in the processes hydrocracking, hydrotreating, and hydrodesulphurization in petroleum refining. Moreover, H_2 can be used as feed stock in Fischer-Tropsch process, which converts synthesis gas to transportation fuel and other liquid products. Nowadays many researches are interested in methane conversion to synthesis gas. CO_2 reforming of CH_4 or dry reforming (Eq.2.1) is an attractive way to generate synthesis gas since this process has the following advantages: (1) CO_2 and CH_4 are green house effect gases. The emission of these gases in the atmosphere contribute to global worming, however this process can convert two harmful gases to synthesis gas, which are useful in chemical industries. (2) This process produces low H_2/CO ratio (1:1) which is suitable for using as a feedstock for the Fisher-Tropsch reaction to produce hydrocarbon and oxygenated compounds. (3) CO_2 and CH_4 are abundant materials due to CO_2 is by product of many industrial processes, natural gas contains large amounts of CO_2, landfill gas consists of 50% CO_2, waste water can produce CO_2 (Wang and Lu., 1996).

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H_{298} = 247 \text{ kJ/mol} \qquad (2.1)$$

The main mechanism of dry reforming consists of two reactions, which are methane decomposition and carbon dioxide dissociation. Osaki $et\ al.$ (1996, 1997, 1998) have proposed the step of this reaction; CH_4 dissociation to $CH_{x,ads}$ and $(4-x)/2\ H_2$ (Eq.2.2), further dissociation of $CH_{x,ads}$ to C and $x/2\ H_2$ (Eq. 2.3), dissociation of CO_2 leading to surface oxygen and gaseous CO (Eq. 2.4), the surface reaction between $CH_{x,ads}$ and O_{ads} (Eq. 2.5), a subsequent rate-determining step (Eq. 2.6), and CO_2 reacts

with surface carbon species from CH_4 dissociation (Eq. 2.7) It seems that this step is essential for maintaining highly stable activity by the removal of surface carbon species.

$$CH_4 \rightarrow \frac{4-x}{2}H_2 + CH_{x,ads} \tag{2.2}$$

$$CH_{x,ads} \rightarrow C + \frac{x}{2}H_2 \tag{2.3}$$

$$CO_2 \rightarrow CO + O_{ads} \tag{2.4}$$

$$CH_{x,ads} + O_{ads} \rightarrow CH_xO_{ads} \tag{2.5}$$

$$CH_xO_{ads} \rightarrow CO + \frac{x}{2}H_2 \tag{2.6}$$

$$C + CO_2 \ (or \ O_{ads}) \rightarrow CO \tag{2.7}$$

Besides the above mechanism, CO_2 can also be dissociated by hydrogen species according to Eq. 2.8. This reaction is called the reverse water-gas shift reaction (RWGS), which could influence on the overall product distribution (Wang ang Lu, 1996).

$$CO_2 + H_2 \rightarrow H_2O + CO \tag{2.8}$$

The way to avoid these side reactions is to operate the reaction with short contact time. In addition, steam-carbon gasification (Eqs.2.9-2.10) can occur as the side reaction. (Gesser et al., 1994).

$$C + H_2O \rightarrow CO + H_2 \tag{2.9}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2 \tag{2.10}$$

2.2 Carbon Deposition

In the production of synthesis gas, carbon deposition is the major cause of catalyst deactivation. Especially with Ni-base catalysts, CO_2 reforming involves the risk

of carbon formation, which may cause serious operation problems and catalyst deactivation. The rate of carbon formation was found to be far less on noble metals than on Ni. This result may be explained by the fact that the noble metals do not dissolve carbon. The carbon formed on the noble metals was observed to be of a structure that was difficult to distinguish from the catalyst structure.

Shamsi and Johnson (2003) proposed that when the rate of carbon formation is greater than the rate of carbon gasificication, carbon accumulates in the catalyst bed.

Several researchers have pointed that main cause of coke formation comes from Boudouard reaction (Eq. 2.11) and/or methane decomposition (Eq. 2.12), which leads to catalyst deactivation, plugging of the reactor, and breakdown of the catalyst.

$$2CO \rightarrow C + CO_2 \tag{2.11}$$
$$CH_4 \rightarrow C + 2H_2 \tag{2.12}$$

Stagg and Resasco (1998) proposed the cleaning mechanism on the supported Pt catalysts. The carbon deposition can be removed out by cleaning mechanism, which is the reaction of the deposited carbon and O_{ads} to produce CO (Eq. 2.13)

$$C + O_{ads} \rightarrow CO \tag{2.13}$$

Zhang et al. (1994) found that three types of carbonaceous species were found to exist on the Ni/Al$_2$O$_3$ catalyst, designated as C_α at 150-220°C, C_β at 530-600°C and C_γ at > 650°C. This results agree with the work reported by Wang and Lu (1996). They found that three types of carbon deposits formed on Ni/γ-Al$_2$O$_3$ and their amounts were dependent on the Ni loading. Moreover, surface carbon deposits consisted of –C–C– and oxidized carbon species (–C–CO, CO$_3^-$). The –C–C species is in the form of filaments and oxidized carbons are possible presented in amorphous carbon. Bokx et al. (1985) reported that amorphous carbon deposited on Ni/SiO$_2$ via CH$_4$ decomposition was more reactive for H$_2$ gasification than filamentous carbon. Shi et al. (1995) reported that most of the deposited carbon from CH$_4$ dissociated on the Ni/Al$_2$O$_3$ catalyst could be gasified

by CO_2. However, there were still some carbon that could not be gasified. It generally deposited on the support. They proposed that carbon gasification only occurred on the interface between carbon filaments and the metal particle.

2.3 Catalyst Metals

Groups VIII metals (Rh, Ru, Ni, Pt, Pd, Ir, Co, Fe) are good for this reforming reaction. Noble metal catalysts (Rh, Ru, Pt,) have been reported to be less sensitive for carbon formation. Nielsen and Hansen (1993) studied the CO_2 reforming over catalysts based on Ni, Ru, Rh, Pd, Ir, and Pt. They observed that Ru and Rh showed high selectivity for the carbon-free operation. Richardson and Paripatyadar (1990) compared the catalytic performance of $Rh/\gamma-Al_2O_3$ and $Ru/\gamma-Al_2O_3$ catalysts for the CO_2 reforming of CH_4. They found that the $Rh/\gamma-Al_2O_3$ catalyst exhibited better stability than the $Ru/\gamma-Al_2O_3$ catalyst.

Although Rh seems to be the best catalyst for this reaction, the expensive price of noble metals is strongly considered. Thus, this leads to the investigation of non-noble metal supported catalysts. Many researchers have developed Ni-based catalysts in order to obtain a catalyst having a high catalytic activity without suffering from the coke deactivation. However, the activity, selectivity, and stability of Ni catalyst varied greatly with type of supports (Gadalla and Bower, 1998).

2.4 Catalyst Supports

2.4.1 Amorphous Supports

Wang and Lu (1998) studied the catalytic activities and coking characteristics of amorphous-supported Ni catalysts. They used different types of support such as La_2O_3, SiO_2, TiO_2, Al_2O_3, MgO, and CeO_2. It is apparent that the catalyst activities of the prepared catalysts in their work showed in the order of Ni/La_2O_3 ~ Ni/SiO_2 > $Ni/\alpha-Al_2O_3$ ~ Ni/MgO > Ni/CeO_2 > Ni/TiO_2. It was found that, for Ni/MgO catalyst reduced at high temperatures (800°C), it showed the comparable conversion to

Ni/La$_2$O$_3$ and Ni/SiO$_2$ catalysts. In case of Ni/TiO$_2$, conversion decreased at temperature up to 600°C, which suggests that this catalyst showed quick deactivation. The results are similar to Swaan *et al.* (1994), they reported that Ni/TiO$_2$ catalyst completely deactivated at 400°C within 1 h of testing. For the amount of carbon deposition on catalyst after 24 h reaction at 700°C followed the order of Ni/La$_2$O$_3$ > Ni/α-Al$_2$O$_3$ > Ni/SiO$_2$ > Ni/MgO > Ni/CeO$_2$. The Ni/La$_2$O$_3$ catalyst has the highest carbon content (about 50%) due to two types of carbon formed (amorphous and graphitic carbon) on this catalyst.

2.4.2 Zeolites

Although supported on amorphous supports show high activity for this reforming, the thermal stability of these supports is very low. Beside amorphous supports, zeolites were also used as the catalyst support because zeolites have good properties such as high thermal stability, high surface area, high affinity for CO$_2$ as an adsorbent which can increase the cleaning mechanism rate and decrease the carbon deposition (Chang *et al.*, 1996). The advantages of using zeolite as the catalyst support were studied by Bhat and Sachtler (1997) they used Rh supported on amorphous solids: Al$_2$O$_3$, SiO$_2$, TiO$_2$, and supported on zeolites: NaY, NaZSM-5. They found that the activity of Rh on amorphous oxide supports decreased with time on stream, whereas the zeolites supported Rh catalysts did not deactivate. In addition, using Rh supported on zeolites showed higher metal dispersions than using Rh supported on oxide supports.

2.4.3 KL zeolite

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 structure of L zeolite. L zeolite has 12 membered rings 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 unit. Its Si/Al ratio is typically 3.0.

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

- High thermal stability ($\cong$ 900°C),

- High surface area (280 m^2/g) enhancing metal dispersion, and
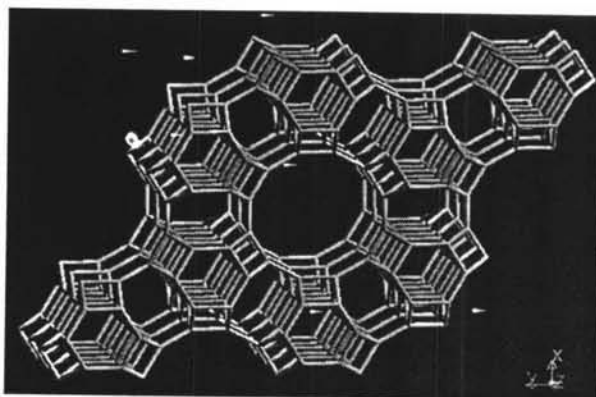- Less acidity avoiding the carbon formation.

Figure 2.1 KL zeolite structure.

2.5 Modified Catalyst

Many researchers have been attempting to reduce coke formation on Ni based catalysts. Modification of Ni based catalyst with alkali or alkaline earth oxides has been proven effective in preventing coke formation (Yamazaki *et al.*, 1992; Horiuchi *et al.*, 1996).

For alkaline earth oxide, Quincoces *et al.* (2001) investigated effect of addition CaO on Ni/γ-Al$_2$O$_3$ catalysts in order to improve the thermal stability and carbon deposition resistance of the Ni/γ-Al$_2$O$_3$ during the reforming of CH$_4$ with CO$_2$. They used concentrations of 15 wt.% Ni, and between 1 and 5 wt.% calcium salt. The results showed that catalysts containing up to 3% CaO presented higher activity and stability than that of catalyst without CaO. Moreover, the formation of whisker-type carbon decreased. They suggested that, this promoter may be attributed to an increase of basicity, which favors the CO$_2$ adsorption and/or reduce the Ni ability to dissociate the CH$_4$. The CO$_2$ adsorption makes the increase of the inverse of the Boudouard reaction, $(CO_2 + C \rightarrow 2CO)$ resulting in a decrease the amount of carbon deposited.

In same promoter, Dias and Assaf (2003) investigated influence of Ca content over Ni/CaO/γ-Al$_2$O$_3$ catalysts. The catalysts were prepared by successive impregnation of Ni and Ca on alumina. It can be concluded that it interacts with the support and has resistance to sintering when Ni is added after the Ca. When adding Ca on alumina after Ni, Ca increase in oxide granules over small pores which decreases the catalyst specific surface area of catalyst. In term of CaO contents, they found that when CaO is presented in lower contents, it increases the CO$_2$ and CH$_4$ conversions. At high contents, both CH$_4$ and CO$_2$ conversions decrease. However, at the amount of Ca is in the range of 3-3.5 wt.%, it showed the highest total CH$_4$ and CO$_2$ conversions. Chang et al. (1996) studied the catalyst activity and coke resistance in the CO$_2$ reforming of CH$_4$ over ZSM-5 zeolite supported Ni and KNiCa catalysts. They found that coke deposition on catalysts for this reforming reaction was remarkably decreased with the addition of alkaline promoter. This was attributed to the formation of carbonate species on alkaline promoters, mainly Ca located adjacent to Ni sites and the adsorption of CO$_2$ on Ni surface.

Horiuchi et al. (1996) studied the carbon deposition in the CO$_2$ reforming of CH$_4$ over Ni/Al$_2$O$_3$ catalyst by adding basic metal oxides (Na, K, Mg, Ca). They used 10 wt.% metal loading. They suggested that the surface of Ni catalyst with basic metal oxides was abundant in adsorbed CO$_2$, while the surface without them was abundant in adsorbed CH$_4$. The abundance in adsorbed CO$_2$ on Ni surface was considered an unfavorable condition for CH$_4$ decomposition and as a result carbon deposition was suppressed.

Moreover, several studies reported the activity of many type of metals, such as Co, Cu, Ce, Zr, Mn, Mo, Ti, Ag and Sn, as a promoter to suppress the deposition of coke and increase the useful life and the stability of catalysts.

Cheng et al. (2001) used Ni/γ-Ai$_2$O$_3$ catalyst in CO$_2$ reforming of CH$_4$. They found the formation of inactive NiAl$_2$O$_4$ during the reforming reaction caused the catalyst deactivation. The same catalyst was also studied by Wang and Lu (1998) but they added CeO$_2$ as a promoter. It seems that Ni/CeO$_2$-Al$_2$O$_3$ catalyst showed higher CH$_4$ conversions than Ni/Al$_2$O$_3$ at all temperatures. The carbon deposition and stability

with time were investigated at 700°C. The addition of CeO_2 promoters to Ni/Al_2O_3 system increased the catalytic stability and coking resistance. It has been reported that higher CeO_2 loading decreased the carbon deposition but large amounts of promoters generally decreased the catalytic activity due to the coverage of active sites. A weight loading of 1-5% CeO_2 was found to be the optimum loading.

Role of chromium (Cr) in Ni/Al_2O_3 was studied by Gonzales et al. (2000). Ni-Cr/Al_2O_3 showed the better catalytic activity levels, which is account its higher metallic dispersion. The bimetallic sample showed a notably higher stability and the lesser carbon content deposited. However, the Ni-Cr alloy was formed by reduction at high temperatures (800°C).

Role of vanadium (V) on Ni/Al_2O_3 catalysts for CO_2 reforming was investigated by Valentini et al. (2003). The H_2 chemisorption, X-ray diffraction, and X-ray photoemission spectroscopy analysis showed that low wt.%V suppresses the $NiAl_2O_4$ formation. Moreover, a low carbon deposition and the surface area (BET) increased upon the addition of 0.8 wt.%V. On the other hand, the sample presented the highest carbon deposition with high wt.%V.

Cheng et al. (1996) studied the effect of promoters over Ni/Al_2O_3 on this reaction. They prepared the catalysts promoted with alkaline earth (Mg and Ca) or lanthanide (La and Ce). For alkaline earth oxide, the promotion effect was dramatically sensitive to the methods of catalyst preparation. When promoter was impregnated prior to nickel onto alumina surface like in MgO-Ni/Al_2O_3 and CaO-Ni/Al_2O_3, a large promotion action were found. For La_2O_3 and CeO_2 as promoters, the ways to introduce a promoter did not lead to a large difference of promotion action. The activity of these catalysts decreased in the order of Ni-La, Mg-Ni > Ce-Ni > Ca-Ni, La-Ni, Ni+La > Ni+Ce > Ni-Ce > Ni+Mg > Ni-Mg.

2.6 Metal Loadings

Metal loadings also affected to the activity of the catalyst in CO_2 reforming reaction. For noble metal catalyst, low loading of metal on support was sufficient

because of their effective performance (Nimwattanakul, 2004). For the catalysts which metal-support interaction was strong such as Ni and Co, higher metal loading was required (Wang et al.,1996). Nimwattanakul (2004) showed the effect of Ni loading on Ni/Clinoptilolite. Amount of Ni loading, 1, 3, 5, 8, 10, and 15 wt.% were tested. It is clearly seen that the CH_4 and CO_2 conversions increase with increasing amounts of Ni loading from 1 to 8 wt.%. In addition, the H_2 selectivity increases with increasing the amounts of Ni loading on the catalysts from 3 to 8 wt.%. When the Ni loading is more than 8 wt.%, the H_2 selectivity decreased. In other hand, it was found that the Ni dispersion tends to decrease with the amount of nickel loading. This can be concluded that higher amount of Ni loading resulted in higher metal sintering.

Souza et al. (2004) tested the effect of Ni contained on the stability for the CO_2 reforming of CH_4 at 800°C. They used 2, 4, 6, and 14 wt.% Ni loadings on γ-Al_2O_3. Initially, the conversion increased with time on stream for 2 and 4 wt.% Ni loadings, showing an induction period of 5 and 2-3 hours respectively, but this phenomenon disappeared at higher metallic loading. With increasing Ni loading, the deactivation rate decreased and the 14 wt.% Ni remained stable up to 40 hours on stream. Thermogravimetric analysis experiment showed weight losses of about 28 and 12% for the 14 and 6 wt.% Ni loadings. This results indicated that, higher wt.% Ni loadings showed higher amounts of carbon deposition during 40 hours on stream ($\cong$ 2 mg coke/mg-Ni).

2.7 Preparation Methods

Wang and Lu (1998) investigated the effect of catalyst preparation methods on the catalytic activity. Ni/MgO catalysts were prepared by impregnation and co-precipitation techniques. The catalysts were tested at various temperatures from 500 to 800°C. The results indicated that Ni/MgO prepared by impregnation technique showed higher activity than Ni/MgO prepared by co-precipitation at all range of temperature.

The effect of preparation method on the modified catalysts also investigated. The preparation procedure on promoted Ni/Al_2O_3 catalysts activity for CO_2 reforming

was studied (Cheng *et al.*, 1996). It was found that catalyst preparation by successive impregnation of promoter oxide and nickel oxide was better than catalyst preparation by co-impregnation process.

Dias and Assaf (2003) prepared the $Ni/\gamma Al_2O_3$ modified with Ca catalysts by successive impregnation of Ni and Ca on alumina. It was found that when the Ni was added after the Ca, it interacts with the support and lowers its resistance to sintering. In this interaction it competes with Ni and favors the formation of reducible species of Ni. When deposited on alumina after Ni, Ca agglomerates in oxide granules over small pores, blocking them, which, in association with the sintering, decreases the catalyst specific surface area of the catalyst.

2.8 Reaction Conditions

2.8.1 Reactant Molar Ratios

The effect of reactant ratios were reported by Chang *et al.* (1996). CO_2 and CH_4 were passed over the KNiCa/ZSI catalysts with different ratios, while keeping the other conditions constant. Their results showed that the H_2/CO ratios of synthesis gas became higher ranging from 0.62 to 1.5 as the CO_2/CH_4 ratio in the reactant feed increased from 0.24 to 3.44. At a CO_2/CH_4 ratio of 1.0, the yields of CO and H_2 were maximized and the ratio of H_2/CO was equal to about 1. It appeared that the optimum ratio of CO_2 to CH_4 for the highest yields on synthesis gas was 1. However they found that the coke deposition decreased when ratio of CO_2/CH_4 increased due to the oxidizability of CO_2 on the surface carbon.

2.8.2 Reaction Temperatures

The suitable reaction temperature is important for CO_2 reforming of CH_4 in order to give high catalytic activity and stability. In general being characteristic for reforming reaction, when the reaction temperatures were raised, the conversion and yield increased. Nimwattanakul (2004) studied the effect of reaction temperature at 600, 700, and 800^oC on the catalytic activity. The results showed that the activity increase with the

reaction temperature. However at 800°C the CH_4 and CO_2 conversion were decreased rapidly so that the suitable reaction temperature is 700°C. This effect was also studied by Cheng *et al.* (1996), they found that a small amount of water was formed together with CO and H_2 produced from the CO_2 reforming below 700°C. Water was formed by the reverse water gas shift reaction. It was clear that the reaction temperature more than 700°C produced equimolar amount of CO and H_2. In term of reaction temperature to amount of coke deposition, Nimwattanakul (2004) found that the amount of coke decreased with decreasing the reaction temperature.

According to the literature surrey mentioned earlier, a non-acidic support has potential to be used as the catalysts support in order to reduce the coke formation. In this work, KL and KH zeolites were selected to be used as the catalyst supports due to high thermal stability and non-acidic zeolites. In addition, earth alkaline metals such as Mg and Ca are frequently used in the catalyst to improve stability (Quincoces *et al.*, 2001, Dias and Assaf, 2003, Chang *et al.*, 1996, Horiuchi *et al.*, 1996). Therefore, in this work, the effect of the addition of Mg and Ca to Ni/KL catalysts will be investigated for dry reforming of CH_4.