CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Carbon Dioxide Reforming of Methane

Methane reforming reactions or dry reforming has been employed to produce hydrogen or synthesis gas. Because of the increase of hydrogen demand and the importance of synthesis gas as a major feedstock for C_1 chemistry and fuel cells, methane reforming reactions have become more important.

Methane reforming using carbon dioxide involves the highly endothermic reaction (1), which has similar thermodynamic and equilibrium characteristics to the widely employed H_2O/CH_4 reforming reaction (2), but which produces synthesis gas with a lower H_2/CO ratio.

$$CO_{2\,(g)} + CH_{4\,(g)} \longrightarrow 2CO_{(g)} + 2H_{2\,(g)} \qquad \Delta H^\circ = 247 \text{ kJ/mol} \qquad (1)$$

$$H_2O_{(g)} + CH_{4\,(g)} \longrightarrow CO_{(g)} + 3H_{2\,(g)} \qquad \Delta H^\circ = 206 \text{ kJ/mol} \qquad (2)$$

As with the H_2O/CH_4 reaction, CO_2 reforming of methane is likely to be conducted under conditions where carbon deposition is thermodynamically feasible.

2.2 Carbon Deposition

Carbon deposition is the most serious problem in CO_2 reforming of methane which causes catalyst deactivation and destruction. Erdohelyi *et al.* (1994) and Tsipouriari *et al.* (1994) found that the major route producing deposited carbon is CO_2 molecular route, while the rest is from CH_4 route. Moreover, Wang and Lu (1999) found that two carbon species were generally formed on the catalyst surface. They are grafitic carbon and oxidized carbon. The first type of carbon was originated from methane decomposition reaction (3) and can be oxidized at low temperatures whereas the second type of carbon was generated from CO disproportionation or called Boudouard reaction (4) and can be oxidized at high temperatures. The latter could spread over and encapsulate the catalyst particles, which cause the deactivation of the catalyst.

$$CH_{4\,(g)} \longrightarrow C_{(s)} + 2H_{2\,(g)} \qquad \Delta H° = 75 \text{ kJ/mol} \qquad (3)$$

$$2CO_{(g)} \longrightarrow C_{(s)} + CO_{2\,(g)} \qquad \Delta H° = -171 \text{ kJ/mol} \qquad (4)$$

Ideally, the carbon formed in reaction (3) should be rapidly consumed by the reverse of reaction (4). Thus, the CO_2 reforming of methane reaction (1) can be seen as consisting of reaction (3) and the reverse of reaction (4). If reaction (3) is faster than the carbon removal rate, there will be a net build-up of carbon to pose serious problems in the overall reaction concept which in practice would lead to catalyst deactivation and reactor blockages. Thermodynamics suggests operating the CO_2 reforming of methane at high temperatures and with CO_2/CH_4 ratios far above unity to avoid regions with a thermodynamic potential for carbon formation (Gadalla and Bower, 1998).

Other side reactions which could also have an important influence on the overall product distribution are the reverse water-gas shift (RWGS) reaction (5) and steam-carbon gasification (6) (Wang and Lu, 1996). Reaction (6) can play an important role in CO_2 reforming of methane because steam is almost formed via the reverse water gas-shift reaction (5).

$$CO_{2\,(g)} + H_{2\,(g)} \longrightarrow CO_{(g)} + H_2O_{(g)} \qquad \Delta H° = 40 \text{ kJ/mol} \qquad (5)$$

$$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2\,(g)} \qquad \Delta H° = 131 \text{ kJ/mol} \qquad (6)$$

Gesser *et al.* (1994) reported the way to avoid these reactions (5) and (6) by operating the reaction with short contact time.

2.3 Catalysts

The CO_2 reforming reaction of CH_4 on Ni and Co based catalysts was first reported by Fischer and Tropsch in 1928. Since then many researchers have investigated group VIII metals such as Ru, Rh, Pt, Ir and Pd (Ashcroft *et al.*, 1991, Vernon *et al.*, 1992, Qin *et al.*, 1994 and Nakamura *et al.*, 1994) for this reaction. The studies of catalysts based on Ni, Ru, Rh, Pd, Ir, and Pt by Richardson *et al.* (1990) and Rostrup-Nielsen (1994) showed that Rh has stability for carbon deposition resistance and selectivity for carbon-free operation higher than other catalysts. Tsipouriari *et al.* (1994) found that the performance of Rh catalysts, under conditions of CO_2 reforming of methane, strongly depends on the carrier employed to disperse the metal. Cheng *et al.* (1996) also found that noble metals (Rh, Ru, Pt) exhibit better activity and very high stability because of the less sensitivity to carbon deposition whereas Ni, Co, and Pd are deactivated by coking. Although Rh seems to be the most effective catalyst for this reaction, considering the high cost and limited availability of noble metals, Ni could be a good practical choice for industrial reason due to its inherent availability and lower cost in comparison with noble metals.

2.4 Catalyst Supports

The coke formation is the most serious problem in CO_2 reforming, especially for Ni-based catalyst. In the past decade, it has been found that many factors influence the properties and performance of Ni catalyst such as catalyst support and the promoter.

2.4.1 Amorphous Solid

According to the importance of catalyst support, many types of support have been investigated. Kuijpers *et al.* (1981) used silica (SiO_2) as support in CH_4 reforming of CO_2 but the report by Rostrup-Nielsen (1984) showed that the use of silica (SiO_2) is generally avoided as it can be volatilized under reforming conditions. Arena *et al.* (1991) and Parmaliana *et al.* (1993) studied the use of magnesia (MgO) and found that it showed an important disadvantage: as calcination temperature increased, the amount of available nickel was reduced. This was attributed to the presence of free magnesia in the support which formed a non-reducible NiO-MgO solid phase when hydrated. Therefore, α-alumina formed by the decomposition of hydrated alumina is a preferred support as it is mechanically strong at 1200°C, as required by the conditions of methane reforming (Tsuchida, 1993). However, it is also suffered serious deactivation. For that reason, zeolite seemed to be an alternative to investigate as catalyst support for carbon dioxide reforming of methane.

2.4.2 Zeolites

Zeolites have many potential properties for being a support of Ni catalysts in reforming reactions such as micropore structure, high surface area and high affinity for CO_2 as adsorbents (Chang *et al.*, 2000). McDaniel *et al.* (1984) found that faujasites have been shown to be effective in several catalytic applications. The basic building block of the faujasite is a truncated octahedron that is connected at four of the hexagonal faces by hexagonal prismatic structures of AlO^{-}_4 and SiO_4 tetrahedra. The three-dimensional framework includes elliptically shaped cavities approximately 12 Å in diameter called super cages. The Y-type zeolites with high Si/Al ratios (1.5–3.0), 300-800 m^2/g surface areas, are preferred given the thermal stability and the high catalytic activity. The use of Ni supported on zeolites in methane reforming have been studied by Gustafson *et al.* (1982) and Iwamoto *et al.* (1983) suggesting that higher activity can be attained when using zeolite supports. In addition to higher activity, zeolite supports have the potential to deliver very high metal dispersion that is stable combined with a low potential for support metal interaction. Chang *et al.* (1996) prepared zeolite-supported Ni and KNiCa catalysts by the solid-state reaction method and used ZSM-5 mixed with a 19.5% Al_2O_3 as catalyst support, which was designated as Ni/ZSI and KNiCa/ZSI, respectively. These results indicated that did not significantly affect on the catalytic activity moreover, surface area of KNiCa/ZSI catalyst is half lower than Ni/ZSI. In addition, KNiCa/ZSI catalyst showed superior coke resistance on carbon dioxide reforming of methane.