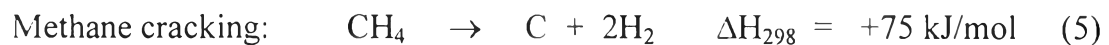# CHAPTER II
LITERATURE SURVEY

2.1 Methane Reforming Reaction

To date, no industrial technology for the reforming of methane with carbon dioxide has so far been established, in spite of potentially attractive incentives with economical and environmental benefits. The principle reason for this is carbon-forming reaction causing quick deactivation of conventional reforming catalysts. Depending on the reaction conditions and on the composition of the feed gas, carbon deposition is due to the Boudouard reaction and methane cracking (Wang *et al.*, 1996).

Boudouard: $2CO \rightarrow C + CO_2 \quad \Delta H_{298} = -172 \text{ kJ/mol} \quad (4)$

Methane cracking: $CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298} = +75 \text{ kJ/mol} \quad (5)$

The side reactions which could also have an important influence on the overall product distribution are the reverse water gas shift and the steam-carbon gasification reaction:

The reverse water gas shift reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H_{298} = +41 \text{ kJ/mol} \quad (6)$$

The steam-carbon gasification:

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H_{298} = +131 \text{ kJ/mol} \quad (7)$$

Ideally, the carbon formed in reaction (4) and (5) should be rapidly consumed by the reverse of reaction (4) and, to a lesser extent, by reaction (7). If carbon formation rate is faster than the carbon removal rate, there will be a build-up of carbon leading to catalyst deactivation and reactor blockages.

The reverse water gas shift reaction produces water which is undesirable by-product. However, Gesser *et al.* (1994) proposed a way to reduce the effect of reaction (6), a side reaction, by operating at short contact

time, narrow reactor and high temperature or a palladium membrane wall reactor.

Obviously, the role of suitable catalysts would not only be to speed up the overall reaction but also to adjust the appropriate elementary steps in such a way to prevent both net carbon deposition and water formation.

2.2 Catalyst Development

2.2.1 Active Metals

Numerous supported metal catalysts have been tested for methane reforming. Among those, nickel-based catalysts and noble metal supported catalysts (Rh, Ru, Pd, Pt, Ir) were found to have promising performance in terms of catalytic activity and selectivity. The activity trend of methane reforming is Ru, Rh > Ir > Ni, Pt, Pd, and the catalysts based on noble metals were reported to be less sensitive to coking than Ni based catalysts (Rostrup-Nielsen and Bak Hansen, 1993). However, considering the aspect of high cost that limit the availability of noble metals, it is more desirable, from an industrial point of view, to develop Ni based catalysts which are resistant to carbon deposition and exhibit more stable operation for a long period of time.

2.2.2 Supports

It is widely known that, except for %Ni loading, the supports play an important role in the catalytic activity and stability of catalysts, since the nature of the oxide support greatly affects the catalytic activity due to the various active surface area and acid-base property. Wang and Lu (1998a) studied the catalytic activity and stability of Ni on various supports. It was found that among the catalysts tested the conversions were in the following order at the same temperature: Ni/γ-alumina $\sim$ Ni/silica gel > Ni/α-alumina $\sim$ Ni/magnesium oxide powder > Ni/precipitated silica > Ni/MgO prepared by

co-precipitation technique. The last two catalysts have low activity and therefore they are not suitable for the carbon dioxide reforming reaction. The deactivation rate of the other four catalysts followed the order of Ni/MgO powder < Ni/γ-alumina < Ni/silica gel < Ni/α-alumina (Wang and Lu, 1998a).

2.2.3 Ni Precursors

The catalytic activity of Ni/Al_2O_3 prepared by three different Ni precursors namely nickel nitrate, nickel chloride and nickel acetylacetonate were compared by Wang and Lu (1998b). It was found that the catalyst based on nickel nitrate exhibited higher activity and stability than the other two catalysts because the weak interaction between Ni particles and γ-alumina resulted in more active sites on nickel nitrate-derived catalysts. Coking studies showed that carbon deposition on Ni catalysts derived from inorganic precursors (nickel nitrate and nickel chloride) was more severe than that on organic precursor-derived catalyst (nickel acetylacetonate). However, the nickel nitrate-derived catalyst was found to have the highest stability or the lowest deactivation rate due to the active carbon species of the resulting graphitic structure and their close contact with metal particles. In contrast, the carbon formed on nickel acetylacetonate-derived catalysts is dominated by inactive species, thus leading to rapid accumulation of carbon on the catalysts and a more severe deactivation (Wang and Lu, 1998b).

2.3 Reaction Conditions

It is widely known that both the CH_4 and CO_2 conversions increase with increasing temperature due to the endothermicity of the carbon dioxide reforming. In addition, the carbon formation is thermodynamically favored at low temperatures but it is easily gasified at high temperatures.

Gadalla and Bower (1988) found that no carbon deposition was observed when reaction temperature is higher than 940 °C and CO_2/H_2 ratio larger than two were applied. Due to high temperatures, the support was found to change and the activity to decrease with time on stream because of reduction of surface area. Moreover, the sintering of Ni was also observed, as expected when working above tamman temperature which is about 600 °C for Ni (Zhang and Verykios, 1994).

2.4 Carbon Deposition

Rapid catalyst deactivation due to carbon deposition on supported Ni catalysts observed by Gadalla and Bower (1988). It is generally claimed that catalyst deactivation is due to carbon formation in the pores of catalyst, which leads to break up of the catalyst particles and block the active sites resulting in total loss of catalytic activity.

The carbon may be formed via different routes and each influences on the morphology of the carbon. There are three common types of carbon: whisker-like carbon, encapsulating carbon and pyrolytic carbon. The whisker carbon is formed by diffusion of carbon through Ni-crystal and causes the catalyst break-down and the increase in pressure drop. The encapsulating carbon is formed from the polymerization of C_nH_m radicals on Ni surface into encapsulating film, which causes catalyst deactivation. The pyrolytic carbon derived from thermal cracking of hydrocarbon results in catalyst deactivation as well as the increase in the pressure drop (Rostrup-Nielsen, 1984).

Wang and Lu (1998a) measured the amount of carbon by temperature programmed oxidation (TPO) on TGA for nickel supported on different supports. The amount of carbon is the difference between catalyst weight before and after oxidation. It was found that the amount of carbon formed on

the catalysts followed the order of Ni/α-Al$_2$O$_3$ > Ni/γ-Al$_2$O$_3$ > Ni/silica gel > Ni/MgO.

2.5 Catalyst Regeneration

The whisker carbon is highly reactive and may be gasified by means of hydrogen, carbon dioxide and steam with Ni as catalyst. Steam is the most effective gasifying agent. However, the whisker structure will collapse with time and be converted to a more dense layer of carbon, which may be difficult to remove under reducing conditions. Nevertheless, with the addition of small percentage of air the burn-off of carbon is easily performed at high temperatures above 720 K. The addition of air should be well controlled to minimize the local overheating of the catalyst caused by the heat produced from oxidation of the carbon (Rostrup-Nielsen, 1984).

The carbon can be oxidized at different temperatures depending on the type of catalysts and carbon formed. Wang and Lu (1998a) found the temperature of carbon oxidation by temperature programmed oxidation (TPO) for Ni on various supports. The carbon began to be oxidized at 500 °C but the maximum oxidation rate were at different temperatures. Carbon on Ni/α-Al$_2$O$_3$ showed maximum oxidation rate around 620 °C and on Ni/MgO catalyst at about 650 °C. For Ni/SiO$_2$ and Ni/γ-Al$_2$O$_3$ catalysts, the carbon was oxidized at higher temperature around 700 °C.

Several researches have shown that there is a relationship between oxidation temperature and the distance between the carbon on the support and the metal. Carbon on the metal is burned at lower temperature than the carbon on the support because the metal can catalyze the carbon combustion by oxygen spillover. For Ni/α-Al$_2$O$_3$ and Ni/MgO catalysts surface carbon deposits are close to Ni particle because Ni and carbon are all at the surface. Nickel particles were more deposited in inner pores of Ni/SiO$_2$ and Ni/γ-Al$_2$O$_3$

resulting in longer distance between surface carbon and nickel particles so that the gasification of carbon on these catalysts become more difficult.

2.6 The Application of Sol-Gel in Catalyst Preparation

Sol-gel processing in which metalorganic precursors is mixed with metal precursor to form a homogeneous solution. The metalorganic precursor is hydrolyzed through the addition of water while carefully controlling the pH and reaction temperature. As hydrolysis and polymerization occur, colloidal particles or micelles with approximate diameter of 10 nm are formed. These particles continue to increase the size until a metal oxide gel is formed (Gonzalez *et al*, 1997).
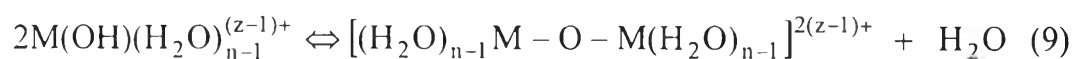
The hydrolysis and condensation reactions can be expressed as follows:
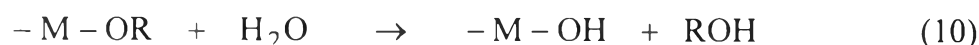
In aqueous phase:

Hydrolysis:

$$M(H_2O)_n^{Z+} + H_2O \Leftrightarrow M(OH)_{n-1}^{(z-1)} + H_3O^+ \tag{8}$$

Condensation:

$$2M(OH)(H_2O)_{n-1}^{(z-1)+} \Leftrightarrow [(H_2O)_{n-1}M - O - M(H_2O)_{n-1}]^{2(z-1)+} + H_2O \tag{9}$$

In organic phase:

Hydrolysis:

$$-M-OR + H_2O \rightarrow -M-OH + ROH \tag{10}$$

Condensation:

$$-M-OH + RO-M \rightarrow -M-O-M- + ROH \tag{11}$$

$$\text{or} \quad -M-OH + HO-M \rightarrow -M-O-M- + H_2O \tag{12}$$

The size and the degree of branching of inorganic polymer, and the extent of cross-linking have strong influence on porosity of the gel, and latter, the surface area, pore volume, pore size distribution, and thermal stability of the final oxide after calcination. In general, if the gel contains polymeric

chains with significant branching and cross-linking, the gel that has large void regions, is structurally quite rigid, and the resulting oxide after calcination has mostly macropores and mesopores. If the gel contains polymeric chains with little braching and cross-linking, the gel that has smaller void region, is structurally weak, and thus collapses readily upon calcination. The resulting oxide has mostly micropores and low surface area.

In general, in the presence of a high concentration of metal cation monomer, if hydrolysis is slow relative to condensation, long, highly branched and cross-linking polymeric chains are formed and the resulting oxide has macropores. If condensation and hydrolysis occur at comparable rates, short polymeric chains with less branching and cross-linking are formed, and the final oxide has micropores. In the case that condensation is much slower than hydrolysis, the metal cations are tightly bound together, and oxyhydroxide precipitates are formed (Kung and Ko, 1996).

Since hydrolysis and condensation are chemical reactions, their relative rates are functions of many parameters such as pH, temperature, nature and concentration of the metal ion precursor, and concentration of water. In addition, although the gel formed has the appearance of a solid, its pores contain the gelation medium, and hydrolysis and condensation continue to occur until the solid is thoroughly dried, at which stage only condensation and solid state transformation occur. Thus, the aging, drying, and calcination condition (time, temperature, atmosphere) also affect the extent of branching and cross-linking, and the properties of the final oxide (Ward and Ko, 1995).

A greater degree of control over catalyst preparation can be achieved in comparison to traditional methods of preparation. One can "tailor-made" catalysts to fit particular applications by using this method. The potential advantages of sol-gel processing include: (a) high specific surface; (b) controlled pore size distribution; (c) textural stability under preparation and reaction conditions; (d) the active phase must be at the surface, and not

homogeneously distributed into solid; (e) a good and homogeneous dispersion; (f) structural properties must be controlled in order to get the desired crystalline variety or an amorphous structure, if preferred; (g) purity of the catalyst components would be as high as possible; (h) easily controlled composition, especially for the preparation of multi-component catalysts or catalysts promoted by small concentration of additives; (i) mechanical properties must accomplish the requirement of the operation conditions (Cauqyi and Rodriguez-Iqzuierdo, 1992).

Alumina has generally been produced by pyrolysis of aluminum hydroxide prepared from various aluminum salts such as sulfates, nitrates and sodium aluminates. The alumina prepared is often contaminated with residual ions in spite of repeated washing of the aluminum hydroxide. These impurities may have undesirable effect of catalytic activity when it was used as catalyst support. It was considered that alumina prepared from alumina isopropoxide (AIP) is not only free from any impurities but is composed of finely and uniformly divided particles.

Ishiguro *et al.* (1990) prepared alumina from AIP by sol-gel technique. AIP was poured into hot water at 85 °C and then cloudy precipitates composed of boehmite and pseudoboehmite gels were formed. Then a small amount of nitric or hydrochloric acid was added to peptidize the gel-like precipitates to fibrillar aluminum hydroxide sols. The sols consist of aluminum monohydroxide associated to some extent, $(AlO(OH))_n$. The size of the fibrillar sol is determined by "n" , the extent of the association. In general, the shape and size of fibrillar sols varies with the amount of acid added to the solution and with stirring time, but they reported that the peptidization of cloudy gels is completed with small amount of acid and with a short stirring of about 1 day. The gel was dried at 110 °C for 24 hours to remove solvent. Finally, it was ground and calcined in air, and become alumina powder. To prepare the Ni/Al_2O_3 catalyst, the nickel nitrate solution dissolved in organic

solvent was added during the hydrolysis of AIP. By this method, the active component (Ni) can be incorporated into the framework of the support resulting in high dispersion catalyst.

However, the active metal of the catalysts prepared by sol-gel technique can be partially buried in the support and therefore the reactant gases can be accessible to only some of the active metal resulting in lower catalytic activity (Cho *et al.*, 1998).