

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

In this chapter, background information related to this work is described. First, introduction to hydrogen production processes is provided. Next, related works in hydrocarbons partial oxidation are reviewed.

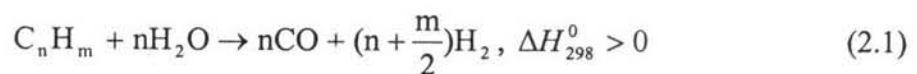
2.1 Background

2.1.1 Processes for Hydrogen Production

Several processes are used to produce hydrogen such as steam reforming, partial oxidation, pyrolysis, gasification and electrolysis. However, steam reforming and partial oxidation are important in the conversion of hydrocarbons to hydrogen.

2.1.1.1 *Steam Reforming*

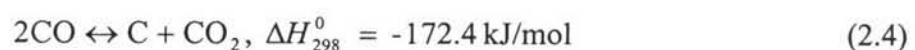
Steam reforming is the established process for converting hydrocarbons into synthesis gas (a mixture of CO and H₂). Generally, the reforming of hydrocarbons can be expressed by:

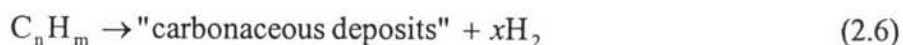
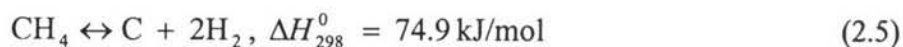


and two simple reversible reactions, water-gas shift (2.2) and methanation reaction(2.3):



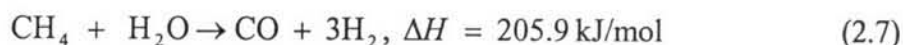
occur simultaneously. Moreover, reactions (2.1) to (2.3) may be accompanied by reactions forming carbon:



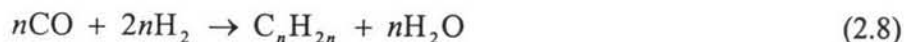


At high temperature (above 920 K), the hydrocarbons may react in parallel to reaction (2.1) by thermal cracking (called "steam cracking") into olefins which may easily form coke by reaction (2.6). The risk of carbon formation must be eliminated in operations since carbon causes serious operational troubles such as deactivation of the catalyst and increasing pressure drop. Therefore, addition of excess steam is normally used to avoid coke formation.

Currently, the most common source of synthesis gas produced by steam reforming are hydrocarbons and particularly natural gas. Since the major component in natural gas is methane, the steam reforming of methane can be expressed by:



This reaction is highly endothermic, typically has to be operated over supported nickel catalyst at pressures of 15 to 30 atm and high temperatures of 850 to 900°C. Therefore, a large amount of energy is consumed to supply this reaction. Furthermore, for Fischer-Tropsch or methanol synthesis:



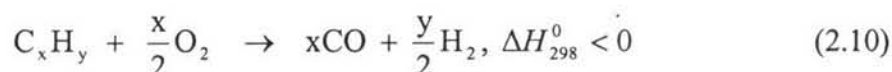
For these processes, the desired H₂/CO molar ratio is 2. Thus, the synthesis gas from steam reforming of methane must to be adjusted through the reverse water gas shift reaction (2.2).

Not only methane but also other hydrocarbons such as naphtha, butane, benzene and hexane are used as feedstock for steam reforming. However, methane is still the most popular feedstock because of its low rate of coke formation when compared with the other hydrocarbons.

As mentioned above, the disadvantages of the steam reforming process are high energy consumption, intensive capital cost, and coke deposition problem. Therefore, much research has been focused to investigate alternate processes of producing synthesis gas.

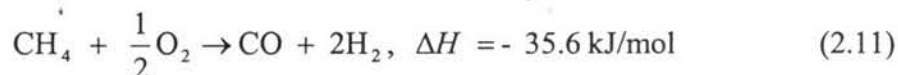
2.1.1.2 Partial Oxidation

The other major route to hydrogen is non-catalytic partial oxidation of fossil fuels, often referred as gasification. The advantage of this process is that it accepts all kinds of hydrocarbon feeds. The thermal oxidation is run at 30-100 atm with pure O₂ using a special burner inside a refractory lined vessel at about 1300°C. The general reaction is described by:



This process needs to have huge quantities of O₂ available continuously, thus requiring the substantial investment in an adjoining O₂ plant. Additional unit operations are required for gas purification and to remove soot from the waste water. Thus, the operations are quite complex and less energy efficient when compared with steam reforming. To avoid these problems, the catalytic partial oxidation of hydrocarbons is attractive nowadays, but the challenge is to avoid the runaway oxidation of hydrocarbons to CO₂ and water.

Ideally, the partial oxidation of methane to synthesis gas:



is an exothermic reaction and yields a H₂/CO molar ratio of 2. This reaction may offer the greatest potential for fast and economical process due to the high conversion, high selectivity, suitable H₂/CO product molar ratio and very short residence time. For this reason, the partial oxidation of methane to synthesis gas has been extensively studied both in terms of its mechanism and the characterization of

the catalyst. The literature survey of this process will be reviewed in following section.

2.1.2 Ceria-Zirconia Mixed Oxide Solid Solution

Ceria plays an important role in most commercial catalytic processes in terms of economic relevance and tonnage: three-way catalysis (TWC) and fluid catalytic cracking (FCC). In addition, ceria can stabilize supports and keep high surface area, prevent the sintering of precious metal, and thus, stabilize their disperse state, promote CO oxidation and water-gas shift reaction, and act as oxygen reservoir. However, pure CeO₂ has poor thermal stability properties (Gonzalez-Velasco *et al.*, 1999).

Recently, it has been reported that the addition of zirconia (ZrO₂) to CeO₂ leads to improvements in its oxygen storage capacity, redox properties, and thermal resistance and to better catalytic activity at lower temperatures (Fornasiero *et al.*, 1995; Gonzalez-Velasco *et al.*, 1999; Vidal *et al.*, 2000). This was found to be due to the partial substitution of Ce⁴⁺ with Zr⁴⁺ in the lattice of CeO₂, which consequently resulted in a solid solution formation (Fornasiero *et al.*, 1995; Otsuka *et al.*, 1999).

Hori *et al.* (1998) reported that the beneficial effects of ZrO₂ were pronounced in solid solutions which had the oxygen storage capacity values 3-5 times higher than that of pure CeO₂. When the optimum Zr dopant concentration was 25 mol%, solid solution materials aged at 1000°C showed a higher oxygen storage capacity than that of pure CeO₂. This result could be ascribed to an occurrence of Zr promotion via an alteration of bulk properties of the CeO₂. Furthermore, the redox properties of CeO₂ have been enhanced by the addition of Zr⁴⁺ into the lattice of CeO₂ by formation of solid solutions. Nevertheless, it was also reported that CeO₂-ZrO₂ solid solutions showed a high catalytic activity, particularly for oxidation of CO, CH₄ and C₃H₆ (Bozo *et al.*, 2000; Fornasiero *et al.*, 1995; Gonzalez-Velasco *et al.*, 1999; Otsuka *et al.*, 1999). In our early study, we have also found that Ce_{0.75}Zr_{0.25}O₂ solid solution exhibited the highest reducibility (Pengpanich *et al.*, 2002).

2.2 Literature Survey

Since this work focuses on methane and *iso*-octane partial oxidation, only those works have been reviewed.

2.2.1 Methane Partial Oxidation

Methane is the major component of natural gas. It is directly used as a fuel in combustion process. The other utilization of methane for manufacturing valuable products has gained attention. An active research has been attempted in the last several years to achieve this via conversion processes of methane to either C²⁺ hydrocarbons or oxygenated compound such as methanol and formaldehyde. The conversion processes can be classified in two classes: direct and indirect conversion. The direct conversion of methane has focused on the oxidative coupling to ethylene and ethane and on the oxygenation to methanol and formaldehyde. (Hargreaves *et al.*, 1990; Chellappa and Viswanath, 1995) However, these processes exhibit either low conversion or low selectivity and have not been appreciable to commercial application. The another process is to convert methane to synthesis gas (CO and H₂) as intermediate, which can be easily produced to methanol or higher hydrocarbons by methanol or Fischer-Tropsch synthesis.

It is well-established that the partial oxidation of methane to synthesis gas occurs at very high temperatures (> 1400 K). The use of a catalyst can reduce the operating temperature necessary to achieve thermodynamic equilibrium (Tsang *et al.*, 1995). Many metals have been investigated as the catalysts for methane partial oxidation.

2.2.1.1 Noble Metal Catalysts

The group of noble metals is employed in the investigation of catalytic methane partial oxidation. Hickman and Schmidt (1993) found that Rh and Pt supported on monolith are excellent partial oxidation catalysts giving greater than 90% methane conversion and synthesis gas selectivity at temperature around 850°C with CH₄/O₂ feed ratio of 2 and extremely fast space time (10⁻⁴ – 10⁻² sec). Other studies have also been carried out on Ru, Pd and Pt.

A study in Ru supported catalysts was demonstrated by Elmasides *et al.* (2001). They reported that high selectivity to synthesis gas (>65%) is obtained over Ru/TiO₂ catalyst in the low methane conversion range, whereas small or zero selectivity to synthesis gas is observed over Ru catalysts supported on other materials.

Hochmuth (1992) has investigated partial oxidation of methane over Pt-Pd impregnated monolith catalyst. He found that there was initial exothermic combustion on the front catalyst bed which generated H₂O and CO₂ and then this was followed by CO₂ and H₂O reforming reactions together with the water-gas shift reaction. He also concluded that the precious metal based catalyst is extremely active driving both CO₂ and H₂O reforming reactions to equilibrium very quickly.

Among noble metals, Rh is found to be a suitable catalyst for methane partial oxidation. Mallens *et al.* (1997) reported that the methane partial oxidation over Rh showed a higher methane conversion and also higher CO and H₂ selectivities than Pt at a comparable temperature.

2.2.1.2 Transition Metal Catalysts

Although noble metal based catalysts, especially Rh-based catalysts, are found to exhibit high activity and selectivity with good long-term stability. However, the high-cost and limited availability of noble metals are the major problems to develop alternative catalysts. Thus, the transition metal group is also investigated for methane partial oxidation. Many different transition metals such as Cu, Co, Fe and Ni have been described in the literature.

Nickel based catalysts are attractive for this reaction due to their high activity and low cost. Hegarty *et al.* (1998) studied steam reforming and partial oxidation of methane over Cu, Co, Fe and Ni supported on ZrO₂ catalysts at the temperatures from 400 to 800°C. The result showed that the activity of the catalysts were found to decrease in the order Ni>Cu>Co>Fe.

Au *et al.* (1996) studied the methane partial oxidation over Ni/SiO₂ catalyst compared with that over Cu/SiO₂ catalyst. They found that methane conversion over Ni/SiO₂ was significantly higher than that over Cu/SiO₂. The main products produced by methane partial oxidation over Cu/SiO₂ catalyst are CO₂ and

H₂O while those over Ni/SiO₂ are CO₂, H₂O, H₂, surface carbon and small amount of CO.

However, Ni is easily deactivated by carbon deposition. The forms of carbon deposition presented on supported Ni catalysts during methane partial oxidation are both whisker and encapsulate forms (Takeguchi *et al.*, 2001). Tsipouriari *et al.* (1998) reported that Ni based catalysts are prone to carbon deposition and that deactivation rate is affected by the nature of the support employed. Therefore, the development of a Ni based catalyst with stable operation can be achieved. Many types of support for Ni-supported catalyst were studied for methane partial oxidation such as Al₂O₃ (Dissanayake *et al.*, 1991), CaO (Tang *et al.*, 1998; Tsipouriari *et al.*, 1998), CeO₂ (Tang *et al.*, 1998; Zhu and Flytzani-Stephanopoulos, 2001), La₂O₃ (Tsipouriari *et al.*, 1998), MgO (Tang *et al.*, 1998), SiO₂ (Au *et al.*, 1996; Looij and Geus, 1997), MgMAIO_x spinel, and ZrO₂ (Freni *et al.*, 2000).

Dissanayake *et al.* (1991) studied the partial oxidation of methane over Ni/Al₂O₃ in the temperature range of 450-900°C. They reported that carbon monoxide selectivities approaching 95% and virtually complete conversion of the methane feed can be achieved at temperatures >700°C.

Tsipouriari *et al.* (1998) studied the catalytic partial oxidation of methane to synthesis gas over various Ni-based catalysts. They found that the rate of deactivation followed the order: Ni/γ-Al₂O₃>Ni/CaO/γ-Al₂O₃>Ni/CaO. They concluded that the higher deactivation rates observed over supports of higher acidity.

Use of reducibility support could result in further activity and decrease coke deposition (Noronha *et al.*, 2001; Pantu and Gavalas, 2002). Currently, CeO₂ has been suggested for uses to store and release oxygen under lean and rich conditions. Therefore, a number of studies have been conducted to increase the stability of Ni catalysts by using CeO₂ as the support.

Dong *et al.* (2002) has reported that methane partial oxidation over Ni/CeO₂ catalyst yielded the synthesis gas with H₂/CO of 2. However, ceria still has some disadvantages. Ceria, by its self, has a poor thermal resistance and stability at high temperatures. It has been reported that addition of ZrO₂ to CeO₂ can improve its oxygen storage capacity, redox properties, thermal resistance and better catalytic

activity at low temperatures (Fornasiero *et al.*, 1995; Gonzalez-Velasco *et al.*, 1999; Vidal *et al.*, 2000).

2.2.1.3 Mechanisms of Methane Partial Oxidation

Two mechanisms were proposed for the catalytic partial oxidation of methane to synthesis gas. One is designated as the combustion and reforming reaction mechanism and the other one is direct partial oxidation mechanism.

The combustion and reforming reaction mechanism involves an initially exothermic methane combustion to CO_2 and H_2O followed by the strongly endothermic reforming reaction of the rest of CH_4 with CO_2 and H_2O to produce synthesis gas. Dissanayake *et al.* (1991) investigated the mechanism of methane partial oxidation over $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. They reported that the mechanism was related to the oxidation state and phase composition of the catalyst. Under operating conditions, the previously calcined catalyst bed consists of three different regions. The first of these, contacting the initial $\text{CH}_4/\text{O}_2/\text{He}$ feed mixture, is NiAl_2O_4 , which has only moderate activity for complete oxidation of methane to CO_2 and H_2O . The second region is $\text{NiO} + \text{Al}_2\text{O}_3$, over which complete oxidation of methane to CO_2 occurs, resulting in an exotherm in this section of the bed. As a result of complete consumption of O_2 in the second region, the third portion of the catalyst bed consists of a reduced $\text{Ni}/\text{Al}_2\text{O}_3$ phase. Formation of the CO and H_2 products occurs in this final region via reforming reactions of CH_4 with the CO_2 and H_2O produced during the complete oxidation reaction over the $\text{NiO}/\text{Al}_2\text{O}_3$ phase.

For the direct partial oxidation mechanism, CO and H_2 is produced directly without the formation of CO_2 and H_2O . This mechanism involves two steps, pyrolysis, followed by the oxidation of C to CO . Hickman and Schmidt (1993) claimed that CO and H_2 are the primary products of the methane partial oxidation reaction over Rh coated monolith catalyst under adiabatic conditions at very short contact times. They proposed that the mechanism involved direct formation of H_2 initiated by CH_4 pyrolysis on the surface to give surface C and H species. The H atoms dimerize and desorb as H_2 while the surface C atoms react with adsorbed O atoms and desorb as CO . A similar finding was reported by Mallens *et al.* (1997). They studied the mechanism of the methane partial oxidation over Rh

catalyst by a Temporal Analysis of Products (TAP) set-up. It was found that synthesis gas is produced as primary product. H_2 is formed via the associative desorption of two hydrogen adsorbed atoms from reduced Rh and the reaction between carbon adsorbed atoms and oxygen present as rhodium oxide results in the formation of carbonmonoxide.

Not only noble metals but also nickel catalysts are proposed for direct methane partial oxidation mechanism. Dong *et al.* (2002) proposed a mechanism over Ni/CeO₂ where CH₄ dissociates on Ni and the resultant carbon species quickly migrate to the interface of Ni-CeO₂ and then react with lattice oxygen of CeO₂ to form CO.

2.2.2 *iso*-Octane Partial Oxidation

There is currently great interest in fuel cells as a potential replacement of conventional combustion engines or as auxiliary power units in automobiles. The most promising fuel cells would seem to be the ones equipped with proton exchange membrane (PEM) using hydrogen (Avci *et al.*, 2001). However, the distribution and on-board storage of hydrogen are major hurdles. Therefore, compact and efficient devices to convert liquid transportation fuels to hydrogen are needed, either in the form of on-board reformers or in stationary facilities supplying refueling stations with hydrogen. It is very likely that for the foreseeable future, we will have to rely on the existing gasoline distribution infrastructure as source of hydrogen for fuel cell equipped vehicles. Hydrogen can be produced from natural gas, naphtha, vacuum residue, refinery off-gas, etc. In transportation, methanol, gasoline or diesel are suitable fuels (Ahmed and Krumpelt, 2001). Some studies have been focused on the conversion of methanol to hydrogen (Peppley *et al.*, 1999) but an effective distribution infrastructure for this fuel is not in place. The generation of hydrogen from the other fuels, including natural gas, liquefied petroleum gases (LPG), gasoline, and diesel represents attractive alternatives. Diesel deposits coke too easily but conversion of the other fuels is possible (Avci *et al.*, 2001). Therefore, the present studies are focused on the conversion of *iso*-octane used as a model of gasoline, to hydrogen.

Praharso *et al.* (2003) studied *iso*-octane partial oxidation over Rh based catalysts. They reported that the reaction involved the total oxidation of *iso*-octane and followed by reforming of *iso*-octane to produce hydrogen. The catalytic activity did not show any difference when alumina, ceria-alumina, ceria-zirconia were used as support. However, they claimed that ceria-zirconia was the most suitable support for *iso*-octane partial oxidation over Rh based catalysts since methanation did not occur.

2.2.3 Promoters

A promoter is a substance that is added in relatively small amounts into the catalyst to improve activity, selectivity or stability. The common additives are alkali metals, and transition metals. In some cases, the precious metals such as Pt, Pd and Rh have been used. In this work, the effect of tin (Sn) and niobium (Nb) used as promoter will be reviewed.

2.2.3.1 Tin (Sn)

Sn is well known as a promoter against carbon deposition in many processes such as aromatization and dehydrogenation of paraffins. For example, bimetallic Pt-Sn catalyst has shown a much higher rate of hydrogenation of unsaturated aldehydes and furthermore a very high selectivity towards the formation of the unsaturated alcohols when compared with monometallic platinum (Neri *et al.*, 1994).

Recently, the effects of Sn in the Ni-Sn supported catalysts have been investigated in steam reforming, CO₂ reforming, and partial oxidation of hydrocarbons (Ferreira *et al.*, 2003; Hou *et al.*, 2004; Nichio *et al.*, 2000). Hou *et al.* (2004) studied Ni supported on α -Al₂O₃ and reported that small amount of Sn loadings can be effectively used as promoter to reduce the amount of carbon deposition during CO₂ reforming of methane by improving the dispersion of Ni and retarding the sintering of active Ni particles during the reaction. This result is in agreement with Nichio *et al.* (2000). It was found that there is a range of tin concentrations (Sn/Ni atomic ratios < 0.05) for which the stability of the bimetallic catalysts is markedly enhanced with respect to monometallic nickel catalyst without affecting either the activity level or the selectivity to synthesis gas of methane partial

oxidation and CO₂ reforming. The authors also concluded that the promoting effect of Sn atoms in intimate contact with nickel would be similar to what is proposed by Rostrup-Nielsen and Alstrup (1999) for the case of partly sulphur poisoned nickel catalysts.

2.2.3.2 Niobium (Nb)

Recently, the promoting effects of oxides on supported catalysts have been widely investigated. Niobium was particularly of attention because it exhibits a pronounced effect as a support, and is also active as metal oxide catalyst. Niobium-based materials are effective in many catalytic applications: pollution control, selective oxidation, hydrocarbon conversion reactions, hydrogenation, dehydrogenation, photochemistry, photo-oxidation, electrochemistry, and polymerization (Wachs *et al.*, 1996). One of the significant properties of niobium oxides is its high acidity, especially in amorphous form. It easily reacts with other oxides to form mixed metal oxide phases (Wachs *et al.*, 1996; Ushikubo, 2000). Niobia can be present in a two-dimensional structure overlayer (surface niobium species) or as an oxide support (niobia supported surface redox sites) or as a mixed oxide (solid solution) (Wachs *et al.*, 1996). As an additive, niobium oxide enhances the catalytic activity and selectivity of several reactions. It has been reported that Sb-Nb-V oxide materials can act as an appropriate promoter to improve the catalytic activity of the oxidative dehydrogenation of light alkanes, especially in the conversion of propane to propene (Barbieri *et al.*, 2000).

Not only was the promoting effect of Nb observed but in some cases there is also a retarding effect. Nb doped on ceria significantly retarded the reaction rate of direct oxidation of methane to synthesis gas (Ramirez-Cabrera *et al.*, 2002). This might be due to segregation of Nb to the ceria surface. Although a number of mixed metal oxides containing niobium have been reported, the role of niobium as a promoter has not been fully understood.