CHAPTER I

INTRODUCTION

1.1 Significance of Research

Hydrogen is forecasted to become a major energy carrier in the future. It is currently used in petroleum refining processes and petrochemical industries such as hydrotreating, hydrocracking, production of methanol, ammonia and hydrocarbon synthesis via Fischer-Tropsch process. In addition, hydrogen has been found to be very attractive as clean alternative to fossil fuels. It can be directly combusted in combustion engines or converted to electricity in fuel cell system.

Hydrogen can be produced from natural gas, naphtha, vacuum residue, refinery off-gas, etc. The natural gas reserves in the world provide a low cost source of light hydrocarbons. These large amount of inexpensive, easily attainable raw material are attractive for the chemical industry. Methane is the major component of natural gas. Methane is not only used as fuel for direct combustion, but also as feedstock for conversion to higher value chemicals. These conversion processes can be classified in two classes, direct and indirect conversion. With regard to direct conversion of methane, the oxidative coupling to ethylene and ethane and on oxygenation to methanol and formaldehyde have been investigated (Hargreaves *et al.*, 1990; Chellappa and Viswanath, 1995). However, the process yields for these reactions are not appreciable to commercial application. In indirect conversion, methane is first convert to synthesis gas (CO and H_2 mixture) as intermediate, and subsequently to methanol or higher hydrocarbons by methanol or Fischer-Tropsch synthesis.

For 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 deposites coke too easily but conversion of the other fuels is possible (Avci *et al.*, 2001).

There are three main methods for producing hydrogen from hydrocarbons, namely steam reforming, partial oxidation, and autothermal reforming. Steam reforming is the largest process to produce hydrogen. However, the disadvantage of this process is that it entails a highly endothermic reaction. Thus, high temperatures are necessary to obtain high yields of product. The partial oxidation and autothermal reforming processes are more attractive for small scale and portable applications. This research is focused on the partial oxidation process.

Partial oxidation is an exothermic reaction. Therefore, it does not need an external supply of energy. With the extreamly fast oxidation reaction, it offers the potential of much shorter contact time than steam reforming. Many catalysts containing transition metals (Ni, Cu and Fe) (Au et al., 1996; Chellappa and Viswanath, 1995; Lu et al., 1998), noble metals (Ru, Rh, Pt and Pd) (Hickman and Schmidt, 1993; Mallens et al., 1997; Otsuka et al., 1999; Pantu et al., 2000) and metal oxides (Otsuka et al., 1998; Ruckenstein and Hu, 1999) were employed in investigations of methane partial oxidation. Among those, Ni-based catalysts show an excellent catalytic activity in this reaction compared to noble metal catalysts, and also have low cost (Zhu and Flytzani-Stephanopoulos, 2001). However, Ni is deactivated easily by coke deposition and/or metal sintering (Montoya et al., 2000). Hence, there has been emphasis on the development of highly active and coke resistant catalysts for partial oxidation.

Carbon deposition on a supported catalyst mainly comes from hydrocarbon decomposition and CO disproportionation reaction at high temperature.

$$CH_4 \leftrightarrow C + H_2 \qquad (1.1)$$
$$2CO \leftrightarrow C + CO_2 \qquad (1.2)$$
$$CO + H_2 \leftrightarrow C + H_2O \qquad (1.3)$$
$$C_nH_{2n+2} \leftrightarrow nC + (n+1)H_2 \qquad (1.4)$$

These reactions are in equilibrium and the formation of coke via reactions (1.2) and (1.3) becomes less favoured with increasing temperatures whilst coke formation via reactions (1.1) and (1.4) becomes increasingly important at higher temperature

(Trimm, 1999). In general, the deposition of carbon would occur over the metallic sites as well as on the acid sites of the support. In order to minimise coke formation over catalysts, various approaches were investigated.

The use of Ni on different supports such as CaO, SiO_2 and MgO was reported (Au *et al*, 1996; Tang *et al.*, 1998). It was reported that the use of supports in the presence of basic sites such as MgO resulted in enhanced activities and lower carbon deposition (Tang *et al.*, 1998). On the other hand, use of reducible supports could result in better activity and decrease coke deposition (Noronha *et al.*, 2001; Pantu and Gavalas, 2002). Recently, Otsuka *et al.* (1999) has reported that CeO_2 could be able to convert methane to synthesis gas with H_2/CO of 2 and shown that adding Pt black could promote the syngas formation rate. This finding is similar to results on Ni/CeO_2 reported by Dong *et al.* (2002). They also proposed a mechanism over Ni/CeO_2 where CH_4 dissociates on Ni and the resultant carbon species quickly migrate to the interface of $Ni-CeO_2$ and then react with lattice oxygen of CeO_2 to form CO. However, ceria still has some disadvantages. Ceria, by itself, has poor thermal resistance and stability at high temperatures. It has been reported that addition of ZrO_2 to CeO_2 can improve its oxygen storage capacity, redox properties, thermal resistance and catalytic activity at low temperatures (Fornasiero *et al.*, 1995; Gonzalez-Velasco *et al.*, 1999; Vidal *et al.*, 2000). It was demonstrated that CeO_2-ZrO_2 mixed oxides produced synthesis gas with a H_2/CO ratio of 2 and the formation rates of H_2 and CO were increased due to the incorporation of ZrO_2 into CeO_2. The oxygen desorption and reduction by H_2 of $Ce_{1-x}Zr_xO_2$ solid solution with $x \leq 0.5$ took place at lower temperature as compared with pure ceria. In our earlier study, we have also found that $Ce_{0.75}Zr_{0.25}O_2$ solid solution exhibited the highest reducibility (Pengpanich *et al.*, 2002).

Many additives were found to reduce carbon deposition for Ni supported catalysts. It has been reported that Ni/Al_2O_3 doped with alkali metal such as Li, La, K and Na showed excellent performance for partial oxidation, along with good stability and carbon deposition resistance (Miao *et al.*, 1997). The use of tetra- and penta-valent p metals such as Ge, Sn and Pb could also reduce coke formation. It would seem possible that tetra- or penta-valent p metals could also interact with Ni 3d electrons, thereby reducing the chance of nickel carbide formation (Trimm, 1999).

1.2 Outline of Thesis

This thesis reports the development of catalysts for hydrogen production from methane (model hydrocarbon for natural gas) and *iso*-octane (model hydrocarbon for gasoline). The catalysts used in this dissertation are based on Ni supported on CeO_2-ZrO_2. The following chapter gives a very brief background of processes for hydrogen production and a review of related litteratures.

Chapter 3 describes the various experimental techniques utilized in the catalyst preparation, characterization, and reaction studies. Details of the catalytic activity test system are also given.

The methane partial oxidation over Ni/CeO_2-ZrO_2 catalysts is described in Chapter 4. This Chapter includes the activity, selectivity and stability of Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst compared with Ni/CeO_2 and Ni/ZrO_2 catalysts for this reaction. The role of reducible support on decrease of coke formation is discussed. In Chapter 5, the *iso*-octane partial oxidation over these catalysts is investigated. Furthermore, in order to better understand the role of the support in catalytic partial oxidation reactions, the iso-octane partial oxidation over Ni/β''-Al_2O_3 catalyst is examined in this chapter and compared to the results on Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst.

In an attempt to lower carbon deposition, the effect of addition of Sn into Ni supported Ce-ZrO_2 catalyst on methane and iso-octane partial oxidation was investigated and described in chapter 6. The results of adding Nb into the Ni supported catalyst are reported in chapter 7.

An overall summary and the conclusions of these research projects are given in chapter 8. Future possibilities and research directions in the area of hydrogen production are also discussed.