

CHAPTER I

INTRODUCTION

Natural gas is the combustible mixture of hydrocarbon gas which can be found in porous rock deep underground. It is widely used in many applications, for example, industry, electricity, residences, commercial and transportation. Natural gas consists mainly of methane which can be separated and used as a raw material for synthesis gas production.

The widely-used process to produce synthesis gas from methane is catalytic steam reforming of methane (CSR_M). This process uses methane and excess steam as the raw materials and receives the high ratio of H₂/CO. The reaction occurs at high temperatures (700-1100°C). Although SR_M process is economical and high efficiency, it still has some disadvantages. For example, it needs large amount of energy due to its highly endothermic reaction. Moreover, it required the excess steam to prevent carbon formation on catalyst. Last, the high H₂/CO product ratio is not suitable for applications of methanol and Fischer-Tropsch synthesis.

An alternative way to produce synthesis gas is catalytic partial oxidation of methane (CPOM). Stoichiometric feed of methane and oxygen with suitable catalyst can produce synthesis gas with the suitable H₂/CO ratio for further applications. Besides, the other advantages of this process are mildly exothermic and short residence time. Therefore a suitable catalyst plays an important role in CPOM.

The catalysts that have been employed in catalytic partial oxidation of methane are noble metal catalysts such as Rh, Pd, Pt and non-noble metal catalysts such as Ni, Fe, Co. Among these catalysts nickel-based catalyst has been widely studied because it is highly active, abundant and also inexpensive. However, the nickel-based catalyst is suffered from carbon deposition and sintering at elevated reaction temperatures leading to the reduction of activity (Bampenrat *et al.*, 2010). This serious problem has led many researchers to study the modification of nickel catalyst in order to improve its stability.

Carbon depositions on nickel-based catalysts occurring at elevated reaction temperatures are composed of encapsulated carbon and whisker carbon resulting in deactivation of catalyst and reactor clogging, respectively. Tsang *et al.* (1995)

reported that the carbon deposition occurred via methane decomposition and carbon monoxide disproportionation (Boudouard reaction). Such reactions are thermodynamically favorable under the reaction conditions of partial oxidation of methane.

To improve the catalyst stability, many studies have been emphasized on supports and promoters. Pengpanich *et al.* (2002) studied the effect of the ratio between ceria (CeO_2) and zirconia (ZrO_2) in CeO_2 - ZrO_2 mixed oxide solid solution on the reducibility of mixed oxides. They reported that the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ possessed the highest degree of reducibility. Moreover, Pengpanich *et al.* (2004) reported that the $\text{Ni}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ mixed catalyst exhibited the ability to resist carbon deposition due to the high degree of metal dispersion and surface oxygen mobility related to the reducibility of catalysts.

Dong *et al.* (2002) proposed that 15wt% nickel loading on CeO_2 - ZrO_2 support provided the highest performance (conversion and selectivity) and stability. At higher or lower loading of nickel the catalyst gave less stability and catalytic performance, respectively.

Pue-on *et al.* (2011) reported that $15\text{Ni}5\text{Mg}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ exhibited the high stability due to the high metallic dispersion and reduction in carbon deposition due to NiO - MgO solid solution.

Qui *et al.* (2012) reported that the partially reducible NiO - MgO solid solution seems to result in the high Ni dispersion and small Ni particles stabilizing the reduced nickel surface from carbon deposition with high activity.

Arunsingkarat *et al.* (2012) studied the effects of low Mg content and metal incorporated sequences on $\text{Ni}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ for catalytic partial oxidation of methane. They reported that adding of Mg at low content resulted in decreasing the catalytic activity but increasing the catalytic stability. For the effect of Mg incorporated sequences, they found that the $\text{Ni-Mg}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ possessed higher catalytic activity but had a lower carbon deposition resistance than the $\text{Mg-Ni}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$.

In this study, the effect of Mg content on the catalytic performance and stability to carbon formation for methane partial oxidation were investigated on the $\text{NiO}/\text{Ce}_{0.75}\text{Zr}_{0.25-x}\text{Mg}_{2x}\text{O}_2$ catalysts. The series of mixed oxide supports $\text{Ce}_{0.75}\text{Zr}_{0.25-x}\text{Mg}_{2x}\text{O}_2$ were prepared by sol-gel method via urea hydrolysis in which the atomic

mole fraction of cerium was fixed at 0.75 while that of Mg was varied in the range of 0.07-0.19 resulting in altering zirconium atomic mole fraction. Nickel loading was performed by incipient wetness impregnation method. The loading amount of nickel was fixed at 15wt%. The prepared catalysts were characterized by means of X-ray fluorescence (XRF), BET surface area measurements, H₂ temperature programmed reduction (H₂-TPR), temperature programmed oxidation (TPO), X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The catalytic activity and stability to carbon deposition for methane partial oxidation were investigated in adjusted sequentially temperature range of 400-800°C in which the temperature interval was 50°C at atmospheric pressure.