



## CHAPTER I INTRODUCTION

In the era of globalization, hydrogen is forecasted to become a major energy carrier because it has been found as an ecologically-friendly fuel. Currently, hydrogen is used in several petroleum refining processes and petrochemical industries. Fossil fuel is currently the main source of hydrogen production including natural gas (mainly methane), naphtha and vacuum. Several economically available processes are used to produce hydrogen such as steam reforming, partial oxidation and autothermal reforming. More recently, catalytic partial oxidation (CPOX) has been considered as an alternative route for synthesis gas production. The principal advantages of CPOX over the others are exothermic reaction, high efficiency, and affording appropriate  $H_2/CO$  ratio of 2. (York *et al.*, 2003)

The nickel(Ni)- based catalysts are suitable for synthesis gas production via catalytic partial oxidation due to their high activity and low cost. However, the main problems of this catalyst are the carbon deposition and metal sintering which lead to the catalyst deactivation, plugging of the reactor, and breakdown of the catalyst (Huszar *et al.*, 1971) (Dissanayake *et al.*, 1991). The deposition of carbon present on supported catalyst by methane decomposition and/or CO disproportion reaction. The carbon deposition occurs over the metallic sites and acid sites of the support at high temperatures. Therefore, the development of Ni based catalysts has been achieved by modifying the support in order to decrease the carbon deposition, increase the stability of the support and extend the catalyst lifetime.

In 2004, Pengpanich and coworker reported that  $Ni/Ce_{0.75}Zr_{0.25}O_2$  mixed oxide catalysts were active and resistant to carbon formation. Nevertheless, carbon deposition over the  $Ni/Ce_{0.75}Zr_{0.25}O_2$  mixed oxide catalysts was still relatively high. Therefore, they proposed several additives used to suppress the carbon deposition for  $Ni/Ce_{0.75}Zr_{0.25}O_2$  mixed oxide catalysts such as Sn and Nb (Pengpanich *et al.*, 2006 and 2007). In addition, Yejun and coworker (2007) as well as Hu and Ruckenstein (2002) indicated that the incorporation of MgO as a promoter into the Ni-based catalysts was found to give a high specific surface area, increase basicity for supported catalysts, improve Ni dispersion at high temperatures, and suppress the growth of Ni

crystallites after reduction or catalyst sintering leading to high activity and resistance to carbon formation.

From previous studies, Pue-on and coworker (2011) studied on NiO-MgO/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> mixed oxide catalysts to investigate the effects of MgO promoter and catalyst preparation method on the catalytic performance as well as carbon deposition. The author concluded that addition of MgO into the mixed oxide catalyst caused the light-off temperatures shifted to higher temperatures indicating a less activity of the catalyst. However, the addition of MgO could diminish the Boudouard reaction and prevent the agglomeration of Ni particles on methane partial oxidation at high temperatures resulting in the stability of the catalyst. In addition, the catalysts prepared by incipient wetness impregnation method possessed slightly higher catalytic activity and lower carbon deposition than those prepared by co-impregnation method.

In this study, NiO-MgO/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> mixed oxide catalysts were investigated on the influence of low Mg loading amounts and its incorporated sequences. The used catalysts were prepared via sequential incipient wetness impregnation method by having a fixed Ni loading of 15 wt% and varying Mg loading in the range of 1-5wt%. The metal incorporated sequence was carried out in such a way that Mg was incorporated onto the Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> -base mixed oxide catalyst followed by Ni incorporation or vice versa. All the catalysts were investigated for their catalytic activities and inhibition of carbon deposition on methane partial oxidation (MPO) in the temperature range of 400 to 800°C at atmospheric pressure. The catalysts were characterized by BET surface area measurements, H<sub>2</sub> chemisorption, X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD) analysis, temperature-programmed reduction (TPR) and temperature programmed oxidation (TPO) techniques and Scanning electron microscopy (SEM).