CHAPTER I

INTRODUCTION

In recent years, hydrogen production is one of the most important technologies for the chemical industry, power generation, and fuel cell applications because it is being considered as an environmentally friendly source of energy. Hydrogen can be produced from a variety of feed stocks including fossil resources, such as natural gas, naphtha and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources. There are three main method for producing hydrogen namely steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). SR process is the most widely used to produce hydrogen. However, the disadvantage of SR is highly endothermic reaction. Thus, the high temperature is necessary to obtain the maximum yield of product. The POX and ATR processes are more attractive for practical applications (Pengpanich *et al.*, 2008).

Catalytic partial oxidation of methane (CPOM) to synthesis gas: (CO and H_2) has been widely investigated as an attractive alternative process to steam reforming since the reaction is mildly exothermic, efficient and economical conversion of methane to synthesis gas, due to the high conversion, high selectivity, suitable H_2/CO ratio of 2 and very short residence time. The syngas from POM reaction can be directly used as a feed for methanol synthesis or Fischer-Tropsch reaction. On the other hand catalytic partial oxidation tends to suffer from coke deactivation. Therefore, a suitable catalyst would play an important role in CPOM to reduce carbon formation.

The catalysts that have been used in catalytic partial oxidation of methane contain transition metal such as Ni, Co, Cu, Mo and Fe, noble metals such as Ru, Rh, Ir, Pt and Pd, and metal oxide. Among those, Ni-based catalyst has been widely used because it is the most excellently catalytic activity in partial oxidation of methane and low cost when compared to noble metal catalysts. However, Ni is deactivated easily by coke formation and metal sintering.

In many researches, various metallic oxides such as MgO, CaO, TiO_2, SiO_2, Al_2O_3, CeO_2 and ZrO_2 have been investigated as supports for methane partial

oxidation. Amongst these supports, Ceria (CeO_2) has been widely used as a promoter and an oxidation catalyst because of its unique redox properties and high oxygen storage capacity. However, pure CeO_2 has poor thermal stability properties. Many researchers reported that the addition of zirconia (ZrO_2) to Ceria (CeO_2) leads to improvements in its oxygen storage capacity, redox properties and thermal resistance, and to better catalytic activity at lower temperatures. Because of the partial substitution of Ce^{4+} with Zr^{4+} in the lattice of CeO_2, which consequently resulted in a solid solution formation. Pengpanich et al., (2004) reported that the mixed oxide catalyst, $Ni/Ce_{0.75}Zr_{0.25}O_2$ solid solution exhibited the highest activity for methane oxidation and with an insignificant coke formation. Furthermore, the 15% $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts exhibited the most activity in terms of c-c breakage conversion and hydrogen production (Thaicharoensutcharittham et al., 2011).

Carbon deposition on a supported Ni catalyst was found in the form of filaments. It mainly comes from methane decomposition and CO disproportionation reaction at high temperature. In general, the deposition of carbon would occur over the metallic sites as well as on the acid sites of the support. This serious problem has led many researchers to study the modification of nickel catalyst in order to improve its stability

It is well-known that catalytic activity of a metal-support catalyst is strongly dependent on surface area, active metal particle size, its dispersion over support, and interaction between metal and support. The method of preparation catalyst is one of significant factor that a important effect on properties of catalyst. Zheng et al., (2012) reported that nano catalysts exhibited excellent activity and stability than conventional impregnated catalysts and Naeem et al., (2014) studied activities of Ni-based catalyst which prepared by polyol and conventional impregnation method. They found that the polyol catalysts provided the better characteristics than impregnated catalysts. The polyol catalyst not only provided high surface area and pore volume that can offer large contact area for reactant but also presented the higher active metal particle dispersion leading to the higher interaction between metal and support, which related to high reaction activity. Moreover, the polyol catalysts presented small metal particles size in the range of 10-40 nm so the carbon deposition occured more difficult than the impregnated catalysts that are bigger

particles size. Furthermore, the most carbon species over the spent polyol catalysts are the reactive carbon species, which do not favor catalyst deactivation.

In this study, 5, 10, 15 and 25%Ni/Ce$_{0.75}$Zr$_{0.25}$O$_2$ mixed oxide catalysts are prepared via the polyol and incipient impregnation methods. Both polyol catalyst and impregnated catalyst are characterized by BET surface area measurement, X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning electron microscope (SEM), H$_2$ Chemisorption (TPDRO), H$_2$ temperature programmed reduction (H$_2$-TPR), Temperature Programmed Oxidation (TPO), and Transmission electron microscopy (TEM). The catalytic activities and stability to carbon deposition on methane partial oxidation is conducted using a fixed bed reactor to measure activity of catalysts in the temperature range of 400-800 °C at atmospheric pressure with an interval of 50 °C.