CHAPTER I
INTRODUCTION

Hydrogen as clean energy source is widely used in many industries. The use of hydrogen for petrochemicals and as energy carrier in connection with renewable energy production increases substantially in the present because many countries concern more about environment. There are many processes to produce hydrogen including steam reforming (SR), partial oxidation (POX), gasification of coal, and water-splitting. The steam reforming of methane (mostly in natural gas) is the most economic and efficient technology for hydrogen production. Methane steam reforming (MSR) consist of two steps; first is steam react with methane under high temperature (750 – 800 °C) to synthesis gas ($CH_4+H_2O \rightarrow CO+3H_2$), and second is using a water-gas shift reaction to form hydrogen and carbon dioxide from the carbon monoxide produced in the first step ($CO+H_2O \rightarrow CO_2+H_2$) (Padro, 1999).

MSR reaction is an effective way to produce syngas and to utilize green house gases simultaneously. The reaction produces syngas with low H_2/CO ratio therefore several supported transition metal catalysts (Ni, Ru, Rh, Pd, etc.) have been used for MSR (Rostrup-Nielsen *et al.*, 1993; Inui *et al.*, 1997). Nickel is well-known as an active catalyst for this highly endothermic reaction and mainly used in industry due to its low cost. A major problems found for this reaction are catalyst deactivation due to the methane decomposition, which is mainly generated from the following catalytic cracking of methane ($CH_4 \rightarrow C+2H_2$) (Kim *et al.*, 2003) and/or CO disproportion ($2CO \rightarrow C+CO_2$).

The coking resistance of nickel catalysts can be increased by modifying the type of the support (Gadalla and Bower, 1988; Bradford and Vannice, 1996) or introducing promoters and additives (Rostrup-Nielsen, 1984). Catalytic materials based on CeO_2-ZrO_2 have been demonstrated in methane steam reforming with high stability, high conversion, and hydrogen yield. The ability of these catalytic materials to resist carbon deposition was also found to provide them attractive in reforming reaction (Angeliki A. Lemonidou et al., 2010). Various modifiers, such as Co, Cu, Zr, Mn, Mo, Ti, and Sn, were tested. The best effect in securing stability much activity was obtained when manganese was used as a modifying additive (St. Christoskova *et al.*, 2003; Bampenrat *et al.*, 2010).

By aforementioned rationales, the addition of MnO_x to $Ni/Ce_{0.75}Zr_{0.25}O_2$ based catalysts via the co-precipitation and multi-step incipient wetness impregnation methods of MnO_x and NiO preparation methods. The loading amount of Ni will be fixed at 15 wt%, and that of Mn loading amount will be varied with 5, 10, and 15 wt% in each prepared method. All sample catalysts were investigated for catalytic activities and inhibition of carbon deposition on methane steam reforming (MSR) in the temperature range of 600 to 800°C at atmospheric pressure. The catalysts were characterized by X-ray diffraction (XRD) analysis, Hydrogen temperature-programmed reduction (H_2-TPR), BET surface area measurements, H_2-pulse chemisorption, temperature-programmed oxidation (TPO), and scanning electron microscopy (SEM).