

CHAPTER I

INTRODUCTION

Hydrogen (H₂), as a clean energy carrier, is one of the most important raw materials and feedstock in the petrochemical industry. Currently, hydrogen is produced commercially from natural gas, liquefied petroleum gas, and naphtha, by steam reforming (SR) or partial oxidation (POX) of heavy oil fractions which lead to the emission of a huge amount of carbon dioxide (CO₂) into the atmosphere, resulting in global warming and climate changes. For this reason, renewable sources, such as biomass, is gaining attention for a carbon dioxide neutral energy supply.

Recent developments in fast pyrolysis technologies which biomass is rapidly heated to high temperature without oxygen (O₂) in the system, it decomposes to generate a liquid product and bio-oil. Acetic acid is the one of the major components in bio-oil which can be easily converted to hydrogen with high selectivity over effective SR process. Thus, several researchers investigated acetic acid as a model compound for hydrogen production.

Another method for producing hydrogen that offers many advantages from technical and economic points of view is autothermal steam reforming (ATR). This process requires less energy due to a combination of endothermic SR and exothermic POX reaction, rendering the overall reaction being thermoneutral. Therefore, the ATR process can start quickly and continue without additional heat supply. According to Tomishige *et al.* (2004) and Simeone *et al.* (2008b), under ATR conditions, the hydrocarbon conversion take place in two consecutive steps. First, the fuel is converted through exothermic reactions with available O₂ at the top portion of catalyst bed. After O₂ is consumed, the remaining fuel is then converted through endothermic reactions down the rest of catalyst bed. It has also been observed that the type of catalytic metal will influence the reactions along the catalyst bed in ATR process. For non-noble metal catalyst such as Nickel (Ni), under oxidizing atmosphere, Ni⁰ is easily oxidized and converted into Ni²⁺ form which promotes the exothermic reaction. Then, the endothermic reaction occurs over Ni⁰ in the oxygen-depleted zone down the length of Ni catalyst bed.

Nickel-based catalysts have been mainly exploited because of high activity and low cost. However, metallic nickel is easily deactivated by carbon formation under operations of such processes. Although a previous work (Traitangwong *et al.*, 2014) employed the 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst for carbon formation resistance in ATR process, it is found that coke still occurs on the upper layer of the catalyst bed. Carbon formation over Ni has also been characterized in several works (Pengpanich *et al.*, 2004; Sehested, 2006). The morphology of the carbon species formed on Ni catalysts can be differed in many types depending on occurrence of reactions and conditions.

In this study, the main objective was to propose the acetic acid ATR over 15%Ni/Ce₇₅Zr₂₅O_x catalyst via coke characterization along the catalyst bed. Ce₇₅Zr₂₅O_x support was prepared by urea-hydrolysis followed by nickel (15 wt%) impregnation. The catalysts were characterized by BET, SEM, TEM, TG-DTA, TPO, TPR, XPS, XRD, and XRF techniques.