



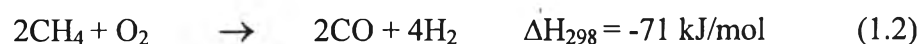
CHAPTER I

INTRODUCTION

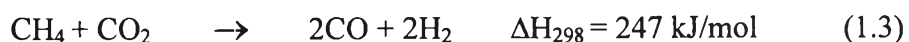
In the present, the demand of H₂ or synthesis gas (H₂+CO) increases rapidly. Because H₂ and/or synthesis gas is the major feedstock for C₁ chemistry and fuel cell applications. In addition, H₂ can be used for synthesizing ammonia and petroleum refinery while carbon monoxide (CO) is widely used in the production of plastics, paints, foams, and pesticides. Currently, synthesis gas is produced mostly by steam reforming of methane (CH₄) (Equation 1.1). However, this reaction has many limitations such as it produces high H₂/CO ratio (>3) resulting in poor selectivity for CO which is not suitable for methanol synthesis and Fischer-Tropsch process, high-energy requirement because of the highly endothermic reaction, and it needs to introduce excess steam to prevent carbon formation.



Thus, many researchers turned to study about the alternative way that is the partial oxidation reaction of CH₄ (Equation 1.2), which can produce greater selectivity to synthesis gas and more desirable CO/H₂ ratio of the product. But the disadvantage of this process is difficult to remove heat from the reactor because of the highly exothermic reaction that makes the process become very hazardous and difficult to control and still has carbon formation.



Therefore, the carbon dioxide reforming of CH₄ (Equation 1.3), which offers several advantages over the process of steam reforming and partial oxidation reactions, becomes more attractive route to produce synthesis gas.



Fisher and Tropsch firstly proposed this reaction in 1928. This reaction can produce high CO/H₂ ratio that is effective for the synthesis of valuable oxygenated chemicals such as alcohol and aldehyde. It also has very important advantage to the environment because both CH₄ and CO₂ are the green house gases. This means that it can reduce the atmospheric emission of CO₂ and CH₄. Moreover, both CO₂ and CH₄ are the most abundant carbon-containing materials that can be obtained from many sources such as landfill gas which consists of 50%CH₄ and 50%CO₂ or from digestion of industrial wastewater. Because CO₂ reforming of CH₄ reaction is highly endothermic reaction, so it can be used in energy transfer from solar energy to chemical energy, energy storage in the form of CO and H₂, and transporting nuclear energy.

Up to now, carbon dioxide reforming of methane has not been commercialized to produce synthesis gas because of quick deactivation of the catalyst by carbon formation. The carbon formation can cause plugging in the reactor and destroy the catalyst. The main routes of the carbon formation are CH₄ decomposition and CO disproportionation. In addition, it was known that sintering of metallic particles on a catalyst also caused catalyst deactivation. Many materials have been studied as the potential catalysts for this reaction, group VIII metals are mostly catalytically active for this reaction. Although the carbon deposition usually occur and cause the deactivation to the catalyst, noble metals were reported to be less sensitive for coking compared to the Ni-based catalysts. But due to the higher cost of noble metals and the limited availability of these noble metals, therefore, several researchers have been developed the Ni-based catalysts which have little or no coking deactivation and display a stable long-term operation. There are many ways to develop the Ni-based catalysts for methane reforming with carbon dioxide. Methods of catalyst preparation such as the impregnation method and co-precipitation method can also influence the properties and activity of the catalysts. Another way is the addition of a modifier, including support and promoter that can enhance the effectiveness of the catalyst.

The main purpose of this work was to develop the Ni-based catalysts for methane reforming with carbon dioxide reaction. The catalysts were prepared by using incipient wetness impregnation method. Ce and Zr were selected to be used as

the promoters. Then, the properties of the catalysts in terms of activity, coking resistance, and catalyst stability was studied by operating the reforming reaction in the appropriate condition.