

CHAPTER I INTRODUCTION

Nowadays many researchers have dedicated to the chemical transformations of methane (CH₄) because it can be converted into synthesis gas or “syngas” as any mixture of hydrogen (H₂) and carbon monoxide (CO). Syngas is an important raw material for converting natural gas into more versatile chemical feedstocks. It can be utilized for hydrocarbon, methanol and diethyl ether production and oxo-synthesis. Due to the increase of hydrogen demand and the important of syngas as a major feed stock for fuel cells, methane reforming reactions have been developed and separated into three main routes as shown in Table 1.

Table 1.1 Three reactions to produce syngas from methane

Reaction	Equation	ΔH°_{298} (kJ/mol)
1. Steam reforming	$\text{CH}_4 \text{ (g)} + \text{H}_2\text{O (g)} \rightleftharpoons \text{CO (g)} + 3\text{H}_2 \text{ (g)}$	206
2. Partial oxidation	$\text{CH}_4 \text{ (g)} + 0.5\text{O}_2 \text{ (g)} \rightleftharpoons \text{CO (g)} + 2\text{H}_2 \text{ (g)}$	-36
3. CO ₂ reforming	$\text{CH}_4 \text{ (g)} + \text{CO}_2 \text{ (g)} \rightleftharpoons 2\text{CO (g)} + 2\text{H}_2 \text{ (g)}$	247

Among three main route steam reforming is the most widely used process for syngas production from methane but this process is highly energy intensive because the reaction is highly endothermic and a great amount of energy is consumed to vaporize excess water and heat it up to the reaction temperature. Moreover, it produces syngas with a high H₂/CO ratio (>3) due to the water gas shift reaction, resulting in low selectivity and yield to carbon monoxide. As an alternative, partial oxidation of methane is another way to convert methane to syngas with a H₂/CO ratio of 2 in the presence of oxygen. However, this reaction has several problems e.g. explosion dangers because of highly exothermic reaction. Carbon dioxide reforming of methane is a very attractive alternative way that offers several advantages over steam reforming or partial oxidation of methane. First, the formation of suitable H₂/CO product ratio for using in a Fischer-Tropsh synthesis to

liquid carbons. Second, reducing of CO₂ and CH₄ emission as both gases are contributors to the greenhouse effect and third, better use in the chemical energy transmission. However, the major obstacle preventing commercialization of this process is that, due to the endothermic nature of the process, high temperatures are required to reach high conversions. These conditions are conducive to carbon deposition or coking and catalyst deactivation. For this reaction, a number of studies have been focused on the development of coke-resistant catalyst for CO₂ reforming of methane. Nickel (Ni), palladium (Pd), platinum (Pt), ruthenium (Ru), rhodium (Rh), and iridium (Ir) have been found to be effective catalytic component for this reaction. Noble metal-based catalysts have been reported to be less sensitive to coking compared to Ni-based catalyst. However, due to the availability and cost of noble metals, Ni-based catalysts are often preferred. The catalyst support is also an important parameter that has to be mechanically strong, stable under steam atmospheres and high temperatures (750–850°C) and resistant to metal support interactions. Amorphous solids, such as Al₂O₃, SiO₂, TiO₂, MgO, ZrO₂, CeO₂, La₂O₃, clays, and crystalline solids, such as zeolites, were used as metallic catalyst supports. Several studies have shown that the nature of support employed influences the catalytic activity. Among amorphous solid supports, Al₂O₃ catalyst showed the highest initial activities but high sensitive to coke formation. Therefore, it is interesting to investigate the Ni is supported on zeolite for development of Ni-based catalyst with little or no coking deactivation. Moreover, it is great interest as the development of industrial application of carbon dioxide reforming of methane.

The main purpose of this work is to develop the nickel-supported catalysts for methane reforming with carbon dioxide reaction. The catalysts were prepared by incipient wetness impregnation method. The effect of support was the primary focus on the present work. Then, the properties of the catalysts in terms of activity, catalyst stability and coking resistance were studied by operating the CO₂ reforming of methane reaction at the reactant molar ratio of 1:1 (CH₄:CO₂), temperature is 700°C and under atmospheric pressure.