## CHAPTER I INTRODUCTION



## **1.1 Introduction**

Synthesis gas or syngas is the name given to a mixture of carbon monoxide and hydrogen. The production technology of syngas plays an important role in petrochemical industries. It is a valuable feedstock for the production of high-quality liquid transportation fuels, petrochemicals, and oxygenated compounds. Traditionally, syngas has been produced by the gasification of coal or steam reforming of methane. Partial oxidation of methane is another possible route. Recently, renewed attention in both academic and industrial research has been focusing on methane reforming with carbon dioxide (dry reforming). This process has been of interest for a long time, but in recent years that interest has experienced a rapidly increase due to environmental and industrial advantages. It has very important environmental implications since both CH<sub>4</sub> and CO<sub>2</sub> contribute to the greenhouse effect. In addition, another advantage of this process over the conventional steam reforming and partial oxidation is the resulting 1/1 ratio of  $H_2/CO$  whereas the other two processes give 3/1 and 2/1  $H_2/CO$ , respectively. This 1/1 ratio is well suited to produce CO-rich synthesis gas for productions of bulk chemicals, such as acetic acid, dimethyl ether, and alcohol via oxoalcohol synthesis. Excess H<sub>2</sub>, formed by the conventional steam reforming, can suppress chain growth and decrease the selectivity to higher hydrocarbons in the Fischer-Tropsh reaction. The dry reforming is also possible for energy storage or Chemical Energy Transmission Systems (CETS). Furthermore, the CO<sub>2</sub>/CH<sub>4</sub> reforming has a definite economic advantage, both investment costs and operating costs over the steam reforming and partial oxidation.

However, a major limitation of the dry reforming is the endothermic nature of the process:

$$CO_2 + CH_4 \longrightarrow 2CO + 2H_2, \quad \Delta H^{o}_{298K} = 247.0 \text{ kJ/mol}$$
 (1.1)

According to the reaction (1.1), at low temperature operation, low equilibrium conversion is received. Although operating at higher temperature yields higher equilibrium conversion, catalysts used for the reaction suffer from rapid deactivation. Generally, deactivation can be caused by a solid reaction of the active metal with the support, carbon deposition on the catalyst surface, or sintering of the active metal. However, the deposition of carbon is the most serious problem and seems to be unavoidable. Therefore, the biggest obstacle preventing commercialization of the  $CO_2/CH_4$  reforming is the lack of suitable catalysts capable for operating at high temperature and pressure. However, there are several methods that can be used to solve this problem.

The addition of water, oxygen, or the use of suitable catalysts are a few examples on how to reduce the deactivation (Bitter *et al.*, 1997). To use the first or second method, dry reforming is simply coupled with steam reforming or partial oxidation, respectively. In the present work, the last method will be used to achieve 1/1 ratio of  $H_2/$  CO. In recent years,  $Pt/ZrO_2$  catalysts have been found to be very stable for dry reforming reaction at moderate temperatures. However, when operating at higher temperatures, some modifications to the catalysts are needed. One possibility is to add promoters to enhance the catalyst stability. It has been believed that the addition of promoters helps to stabilize the catalyst surface area for high temperature operation. Based on the cleaning mechanism, the promoters increase the density of CO<sub>2</sub> adsorption sites near the metal particle and reduce particle growth under the reaction condition (Stagg and Resasco, 1998).

## 1.2 Research Objectives

1.2.1 To investigate effects of promoters (Ce and Y) and their concentration to Pt supported with  $ZrO_2$  for the methane reforming with carbon dioxide.

1.2.2 To investigate the effects of mixed-promoter catalysts.