

## CHAPTER I

### INTRODUCTION

Methane (CH<sub>4</sub>) conversion to higher hydrocarbons is of worldwide interest. A possible route is the oxidation coupling of CH<sub>4</sub> reaction to C<sub>2</sub> hydrocarbons, but this reaction seems to be too difficult to reach an economical scale. Current practice of converting CH<sub>4</sub> into higher hydrocarbons proceeds by an indirect route, in which CH<sub>4</sub> is first converted to syngas, a mixture of hydrogen and carbon monoxide, via steam reforming, partial oxidation, or carbon dioxide (CO<sub>2</sub>) reforming of methane:

*Steam reforming of methane*



*Partial oxidation of methane*



*CO<sub>2</sub> reforming of methane*

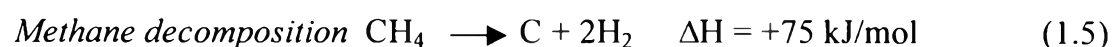
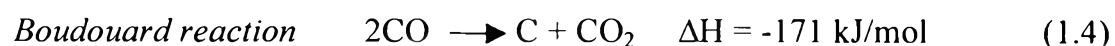


Syngas is then converted into desired products.

However, CH<sub>4</sub> reforming with CO<sub>2</sub> or dry reforming, reaction (1.3), has some advantages over the other methods. The reaction reduces both CO<sub>2</sub> and CH<sub>4</sub>, which are greenhouse gases. CO<sub>2</sub>, which is separated from exhaust gas, can also be used in reaction (1.3). This reaction is also preferred for simultaneous utilization of CH<sub>4</sub> and CO<sub>2</sub> from natural gas reservoirs with abundance of CO<sub>2</sub>. In addition, the reaction gives a lower H<sub>2</sub>-to-CO ratio, approximately one, while that of the steam reforming is 3:1, and partial oxidation is 2:1. The 1:1 ratio of H<sub>2</sub>:CO is suitable for many processes, such as hydroformylation, acetic acid production, oxo synthesis, dimethyl ether production, and Fischer-Tropsch synthesis to liquid hydrocarbons. Another advantage is reaction (1.3) and its reverse CO/H<sub>2</sub> methanation reaction have

been considered as a means to store and transfer solar energy in thermochemical heat pipe (TCHP) application (Edwards and Maitra, 1995). The TCHP application concept based on this reaction partially benefits from the absence of steam because the latent heat of steam would generally not be recoverable in a useful fashion and hence it represents a direct energy loss.

It is well known that supported group VIII metals are good catalysts for the CO<sub>2</sub> reforming reaction. And because reaction (1.3) is highly endothermic, high temperature is necessary for high CH<sub>4</sub> and CO<sub>2</sub> conversions. Operating at such high temperature causes the catalysts to deactivate by carbon deposition. Normally, carbon can be formed via two reactions:



Reaction (1.4) can be avoided by operating at 800 °C, but at that temperature reaction (1.5) is favorable.

Generally, it is necessary to regenerate the coked catalysts in the dry reforming by means of combustion with a diluted oxygen stream, or by gasification treatments involving steam, CO<sub>2</sub> or H<sub>2</sub>. Alternatively, the operating conditions can be modified to diminish the coke formation. Options to reduce the coke build up are the addition of water (coupling with the steam reforming) or the addition of oxygen (coupling with the partial oxidation) to the dry reforming. Furthermore, catalysts can be specifically designed either to give lower coking rates or to be less sensitive to the coke formation. For operating conditions, coupling the highly endothermic reaction of the CO<sub>2</sub> reforming with an exothermic reaction like the partial oxidation would also have economic advantages.

In this work, cerium will be added as promoters to the catalyst to improve its stability and activity. In addition, effects of oxygen concentration on the catalyst stability and activity will be also investigated.