



CHAPTER I

INTRODUCTION

Natural gas is defined as a combustible gas that occurs in porous rock of the earth's crust and is found with or near the accumulation of crude oil. It contains between 70-98% of methane, with higher hydrocarbons (ethane to hexane) present in quantities of up to a maximum of 16%, while diluents (N₂, CO₂) can account for a maximum of 15%, depending on the location from where it is produced (Ross *et al.*, 1996).

Currently, the main use of natural gas is the combustion for heating purposes while the only significant use in petrochemical industry is the production of hydrogen by steam reforming.



This reaction has, however, several limitations: a very high energy consumption, a poor selectivity for CO or a low CO/H₂ product ratio. Therefore, this synthesis gas or syn gas (a mixture of CO and H₂) is not suitable for methanol and Fischer-Tropsch synthesis.

In addition, hydrogen and carbon monoxide can be used separately. Hydrogen is used in ammonia synthesis and petroleum refinery while carbon monoxide is widely used in the production of plastics, paints, foams and pesticides.

In recent years, many researchers have attempted to convert methane to syngas via the catalytic partial oxidation of methane.



Although this reaction is only mildly exothermic, a small decrease in the CO selectivity due to the total combustion of methane, which is highly exothermic, results in a large increase in reaction temperature. In addition, a high methane conversion coupled with a high space velocity produces a large

amount of heat in a small region of catalyst so called ‘hot spot’. Because it is difficult to remove this heat from the reactor, particularly from a large-scale equipment, the process becomes very difficult to control (Ruckenstein and Hu, 1995).

A proposed alternative to steam reforming process and partial oxidation of methane is the reforming of methane with carbon dioxide. This reaction was first proposed by Fischer and Tropsch in 1928.



Carbon dioxide is a by-product of many industrial processes and available for utilization. For instance, power plants emit a large amount of CO₂ at relatively high temperatures and landfill gas commonly consists of 50% CH₄ and 50% CO₂ (Wang *et al.*, 1996).

Conversion of methane and carbon dioxide, which are two of the cheapest and most abundant carbon-containing materials, into useful products is an important area of current catalytic research because it produces synthesis gas with high carbon monoxide to hydrogen ratio, which enhances chain growth and increases selectivity of oxygenated compounds and liquid hydrocarbons by the Fischer-Tropsch synthesis (Zhang and Verykios, 1996).

This reaction has also very important environmental implications because CO₂ and CH₄ are substances responsible for the greenhouse effect. The contribution of CO₂ is about 50%, 24% of the effect is due to freons and N₂O and 15% is due to methane (Krylov and Mamedov, 1995). Therefore, the reforming of CH₄ with CO₂ can convert these two gases into synthesis gas simultaneously and substantially reduce their emissions to the atmosphere.

Due to the high endothermicity of the reaction (3), it can be used in chemical energy storage and energy transmission system (CETS). Figure 1.1 shows that solar energy is used to drive the endothermic forward reaction and the energy is stored in the synthesis gas which can be transported via pipeline

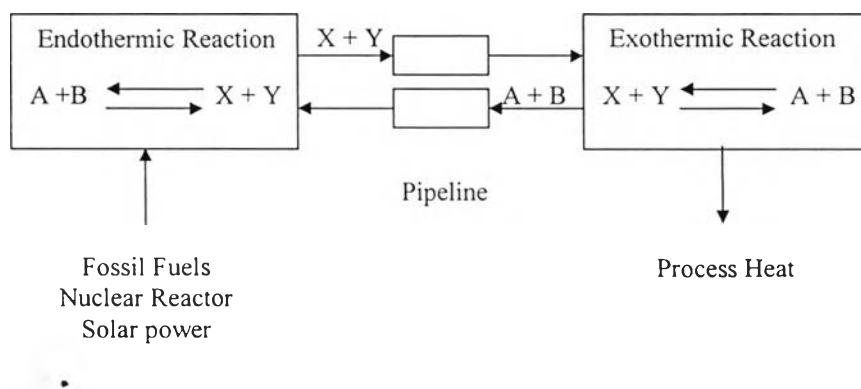


Figure 1.1 Schematic diagram of the chemical energy transmission system (CETS).

to a location where the energy is released by the exothermic backward reaction (Wang *et al.*, 1996).

Unfortunately, there is no established industrial technology for the reforming of methane with carbon dioxide because of carbon deposition, which rapidly deactivates conventional catalysts. During the past decades, the efforts have focused on the development of catalysts for methane reforming with carbon dioxide that gives high selectivity of CO and avoids deactivation by carbon deposition to display a stable long term operation.

Different methods of catalyst preparation influence the properties and activities of the catalysts. The impregnation method, the easiest method, is usually used to prepare metal supported catalysts, but the catalysts prepared by this method may have low dispersion. Adding promoters to the catalyst may improve catalytic activity and selectivity. In this case, the catalysts are probably synthesized by co-precipitation technique, in order for the metal, promoter and support to precipitate at the same time resulting in high dispersion catalysts. For instance, Chen *et al.* (1997) prepared Ni/MgO with Rh, Pt and Pd promoters by this technique. It was found that the catalyst exhibited a stable activity over 50 hours on stream.

A new approach to the preparation of supported metal catalysts is the sol-gel process, which provides a well-defined pore size distribution, purity, homogeneity, controlled porosity and a large surface area material at low temperatures. This method is not yet widely used to prepare the catalysts for CO₂ reforming.

The research objectives of this thesis were

1. To prepare 5% Ni/Al₂O₃ catalyst and alumina support by sol-gel technique and to prepare 5% Ni on commercial Al₂O₃ and on sol-gel Al₂O₃ by impregnation technique
2. To study the catalytic activity, stability, activation energy and carbon deposition for three 5% Ni/Al₂O₃ catalysts on methane reforming with CO₂