CHAPTER 1
INTRODUCTION

Methane is the major component of natural gas. It's advance in commercial use is liquid fuel and as the raw material to produce synthesis gas. The processes of the conversion of methane to synthesis gas are:

1. Steam reforming

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

2. Partial combustion

$$CH_4 + 1/2\ O_2 \longrightarrow CO + 2H_2$$

$$CO + 1/2\ O_2 \longrightarrow CO_2$$

$$H_2 + 1/2\ O_2 \longrightarrow H_2O$$

3. Water - gas shift

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The alternative reaction for synthesis gas production, namely partial oxidation using oxygen and dry reforming with carbon dioxide, both give lower H_2/CO ratios and thus received much less attention. The mildly exothermic partial oxidation of methane to synthesis gas gives occurrence of carbon formation on the metal catalysts which depend on methane-to-oxygen ratios. Such undesired carbon formation cannot be avoided by increasing the oxygen-to-methane ratio or by increasing the operating temperature.

Reaction of methane with oxygen at high temperature gives principally CO, CO_2 , H_2O and H_2. The composition of the product gas depends on temperature, pressure, input gas composition, and also on the kinetic factors.

For example of Fischer-Tropsch technology, Mobil process requires steam reforming of methane to produce synthesis gas which is then converted to methanol. Finally methanol is reacted to form gasoline. Analysis of economics of these processes reveals that a majority of the costs are associated with synthesis gas producing. Obviously, direct methane conversion to higher hydrocarbons seems to be one reasonable way to overcome economic problem. The difficulties in direct conversion is the high stability of methane molecule and the thermodynamic disadvantages.

$$2CH_2 \longrightarrow C_2H_6 + H_2 \qquad \Delta G^o = 71\ kJmol^{-1} \quad \text{at } 1000\ K$$

However, the thermodynamic disadvantage can be overcome by introducing an oxidant as

$$2CH_4 + 1/2\ O_2 \longrightarrow C_2H_6 + H_2O \quad \Delta G^0 = -121.6\ kJmol^{-1} \quad \text{at } 1000\ K$$

This is called the oxidative coupling of methane (OCM).

The OCM in the presence of catalysts are carried out by using redox type metal oxides with a feed of methane only, where lattice oxygen is use as an oxidant, and by using non-reducible metal oxides with co-feed of methane and oxygen. A large number of catalysts which have been reported are co-feed reaction system, compared with the redox type catalysts.

The OCM is a method of utilization of methane or natural gas for the synthesis of ethane and ethylene. it has been widely accepted that the reaction involves the initial formation of methyl radicals ($^{\cdot}CH_3$) which undergo coupling to form ethane, with further oxidation of ethane producing ethylene. Due to the observation of and isotropic effect (K_H/K_D) over many catalyst systems. the initial step in the methane oxidation to produce the methyl radical has been identified to be the rate-determining step in the reaction. Concerning about the catalysts, a catalyst is a substance that affects the rate of a reaction, it changes only the rate of a reaction, but it does not affect the equilibrium. Almost the catalyst systems of the OCM consists of metal oxides. These metal oxides used as catalyst are divided broadly into three groups: (1) alkali and alkaline earth metal, (2) lanthanide and actinide metal, (3) the other metal oxides such as transition metal compounds. These oxides effect differently on conversion of methane and selectivity of C_2. Other condition however, can not be ignored for the OCM reaction, such as temperature, mole ratio of methane/oxygen, and the space velocity.

The purpose of this study is then to investigate the catalytic performance of different catalyst systems on the conversion of methane and selectivity of ethylene with the following conditions.

1. Catalyst systems of Li/Mg/nM, Li/Mn/nM with or without Al_2O_3 (n = atomic ratio o M, where M are the Ce, Pr, Sm)
2. Temperature in the range 600-750° C
3. Mole ratio of CH_4/O_2 in the range 1-5
4. Space velocity in the range 2000-8000 h^{-1}

Objectives of this study

1. To study preparation method of catalysts for methane conversion to ethane and ethylene by oxidative coupling.
2. To study the characterization of the preparaed catalysts.
3. To determine the suitable conditions for oxidative coupling reaction over the catalysts.