

CHAPTER I

INTRODUCTION

Apart from present strategies of methane utilization, which are generally based upon its consideration as one of the low-price fuel supplies, attempts of converting this major component of natural gas into higher hydrocarbon products like ethane, ethylene or some liquid oxygenates such as methanol or formaldehyde are now being received the increasing interests as the new upgrading route of the methane utilization.

Most of those proven technologies and efforts on the development of such methane conversion, though commercially available, still have to be based upon the multi-step reaction processes starting with the transformation of methane and water into the synthesis gas, i.e., principally the mixture of CO and H₂, via the steam reforming process before being converted further into either methanol or via the so-called Fischer-Tropsch (FT) synthesis to liquid hydrocarbons. From that natural gas or methane-based methanol, the gasoline-type hydrocarbons as well as ethylene and propylene can then be produced catalytically from the Methanol-to-Gasoline (MTG) or Methanol-to-Olefins (MTO) reactions with the aid of zeolite catalysts. The success of the MTG process is currently settled in New Zealand and the commercial FT plant was already reported to be constructed in Malaysia. (Baerns, 1992)

With the recognition of economic-intensive investments and high production costs of these processes, the direct methane conversion paths including its direct partial oxidation (POM) to methanol and its oxidative coupling (OCM) to C₂-hydrocarbons have therefore been subjected into recent

studies by many researchers. Against the principles of all those multi-step reaction processes, these two reactions are considered to be much more energy-efficient in the sense that they can bypass the highly energy-intensive step of the synthesis gas formation which is considered to be extremely endothermic reaction requiring both enormous quantities of fuel and severe reaction conditions.

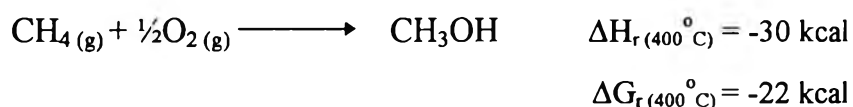
Furthermore, there is another major reason that has much influence on the increasing interest of direct methane conversion. Since most of the large deposits of natural gas (i.e., with 60-90 % of methane) are geographically located in very remote areas until precluding any economic means of its transportation to the place of consumption via the pipeline networks. This causes vast quantities of natural gas being frequently flared in those remote wells where the crude oil productions are also associated with. And it has recently been recognized during the last decade that flaring is not acceptable from an environmental point of view.

Therefore, in order to make the utilization of such remote natural gas reserves become feasible, some efficient methods will have to be employed to convert those remote gases into any transportable products, particularly in the form of liquid. Obviously, this intention will be even more applicable for the cases of those large offshore natural gas deposits which will eventually outpace the number of crude oil resources in the long-range future (Chaumette et al., 1988). This idea coupled with the substantial need to improve the current technology on the methane conversion has undoubtedly encouraged the study of the direct methane conversion into a spreading extent.

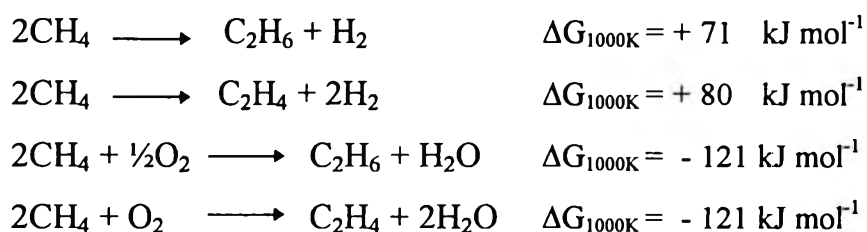
Abundant literature could be cited to illustrate the evidences of the great efforts on the attempt to develop the direct methane conversion

processes, particularly on POM and OCM reactions. (Gesser et al, 1985; Yarlagadda et al, 1987; Zanthoff and Bearn, 1990; McCarty, 1991; Bearn, 1992; Walsh et al, 1992; Periana et al, 1993; Omata et al, 1994; Casey et al, 1994; Chen and Willcox, 1994)

In almost all cases, oxygen molecule (O_2) is required to be participated in these reactions in order to activate the methane molecule (CH_4). In the direct partial oxidation of methane to methanol (CH_3OH), methane is oxidized, in the situation of O_2 deficiency, at 350-500 °C under high pressure condition according to the following exothermic reaction:



While the presence of oxygen in the case of oxidative coupling of methane to C_{2+} -hydrocarbon is required for thermodynamic reasons if the reaction is to be carried out at temperature significantly below 1,600 K. This can be illustrated by the following reactions of the methane coupling to produce either ethane or ethylene.



Unfortunately, since all these reactions would have to be operated at the elevated temperatures while all those desired products (i.e., CH_3OH , C_2H_6 , C_2H_4 , etc.) tend to be far more reactive than the starting methane molecule itself, then as long as the oxygen is introduced into the reactions, it can further

oxidize these intermediate desired products into the mixture of carbon dioxide (CO_2), carbon monoxide (CO) and water (H_2O). This undesirable reaction is sometimes referred to as “deep oxidation reaction”. Consequently, to suppress that deep oxidation reaction and to gain substantial yields from these thermal reactions, the unsurpassed catalysts as well as the proper reaction conditions are extremely desired to selectively convert the methane into those desired products. This knowledge has long been the basis for most of those studies on the direct methane conversion processes subjected to date.

Based upon the thermodynamic consideration, there has been an expectation that if the reaction between methane and oxygen can be carried out at low temperature regions, the carbon oxides formation can be substantially reduced. However, to activate the methane molecule at low temperature, active species are necessary to be provided in order to activate the methane molecule. One of the most powerful sources of such species is pronounced by the plasmas generated in the so-called electric discharges environment.

Some fundamentals about the plasmas and the electric discharges environment will be discussed in Chapter II. At this point, it is necessitated to mention clearly that it was the aim of this work to illustrate the feasibility of introducing such electric discharges environment as a new mean of activating the methane molecule to initiate and thereby carry out the direct methane conversion to produce the higher valuable hydrocarbon products.