

CHAPTER I

INTRODUCTION

Methane is the major component of natural gas as well as coal mine release gas. It is also available in rather large quantities either as an undesirable by-product or as a component of an off-gas from certain processes. Hence, catalytic conversion of methane to desirable chemical products or liquid fuel is a great challenge to catalytic chemists. This conversion will utilize methane containing resources in general and natural gas resources. Moreover, methane is the most stable and symmetric organic molecule consisting of four C-H covalence bonds with bond energy of 435 kJ/mol. Accordingly, the effective activation and direct conversion of methane are also a great challenge in the science of catalysis.

Research in this field was spread over a wide range which can be arranged the tendency in three parts ; (i) new reactions of C₁ compounds ; (ii) development of efficient catalysts for such reactions ; (iii) development of the industrial processes. Various processes are either already commercial or at an advanced stage of development. There are two general types for methane conversion. One is methane derivation and the other is direct methane conversion (Figure 1.1).

Methane derivation includes conversion to synthesis gas (CO/H₂) followed by either a Fischer-Tropsch (FT) synthesis or further conversion to methanol followed by a zeolite-based methanol- to- hydrocarbon process. Some of the typical and most desirable reactions of the hydrogenation of CO are summarized in Table 1.1. Other products such as acids, ketones, aldehydes and aromatics can also be produced by similar reactions. Since water is a primary product in most of the synthesis reactions, the water-gas shift reaction can occur between this water and CO from the feed, which changes the O-containing by-products from water to carbon dioxide. As a result, considerable research into alternative direct routes has been carried out so as to avoid this necessity [Fierro (1993)].

Direct methane conversion consists of oxidative coupling of methane (OCM) and non-oxidative conversion of methane. Oxidative coupling of methane has been a great deal of work done since 1982 but this route is still far from meeting the conditions required for industrial application, unless the C_2^+ yield can exceed 25%. Furthermore, in the oxidative coupling process the combustion reaction could be occurred. Part of methane loses in this reaction. Then the non-oxidative conversion of methane has recently attracted considerable attention.

The non-oxidative conversion of methane can be divided into two methods. One is the non-oxidative coupling of methane that the methane was decomposed at high temperatures (127-527 °C) to form hydrogen and adsorbed surface carbonaceous species which were hydrogenated at low temperatures (77-177 °C), producing hydrocarbons such as ethane, propane, butane and pentane [Koerts *et al.* (1992)]. The other method is the dehydrogenation and aromatization of methane which was observed in the last few years.

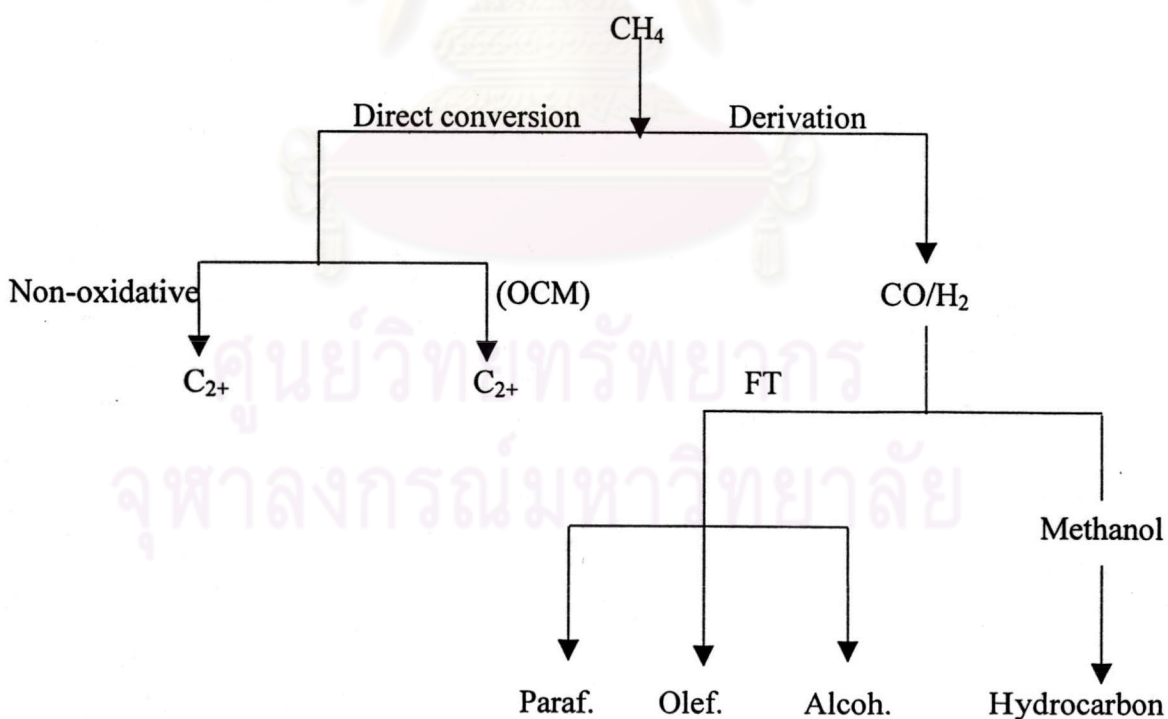


Figure1.1 Schematic representation of several catalytic developments of which the origin lies in natural gas [Fierro (1993)].

Table 1.1 Reactions which can occur during hydrogenation of CO [Fierro (1993)].

Desirable	Methanation:	$3\text{H}_2 + \text{CO} \longrightarrow \text{CH}_4$
	Hydrocarbons:	$2n\text{H}_2 + n\text{CO} \longrightarrow \text{C}_n\text{H}_{2n}(\text{C}_n\text{H}_{2n+2})$
	Alcohols:	$2n\text{H}_2 + n\text{CO} \longrightarrow \text{C}_n\text{H}_{2n+1}\text{OH}$
Undesirable	Water-gas shift:	$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$
	Boudouard reaction:	$2\text{CO} \longrightarrow \text{C} + \text{CO}_2$
	Coke formation:	$\text{CO} + \text{H}_2 \longrightarrow \text{C} + \text{H}_2\text{O}$

Recently, series of experiments were carried out using transition metals supported on silica for the non-oxidative conversion of methane. Subsequently, ZSM-5 (MFI) and Y-type zeolite were used in this reaction as a support of transition metals due to a better yield in higher hydrocarbon. There are few reports which studied the effective utilization of Mo-modified ZSM-5 and Y-type zeolite catalysts.

Therefore, this study aims to investigate the catalytic performance of Mo-modified HZSM-5 and HY catalysts in the absence of oxygen. The present work is arranged as follows:

Chapter II presents the literature reviews on investigation of the non-oxidative conversion of methane. The theory of this research, the theoretical consideration on ZSM-5 and Y zeolites and the mechanism of the dehydrogenation of methane are given in Chapter III, followed by the description of the experimental systems and the operational procedures in Chapter IV. The experimental results obtained from a laboratory scale reactor and standard measurement are reported and discussed in chapter

V. Chapter VI gives overall conclusions emerged from this work and presents some recommendations for future works.

Finally, the sample of calculation of catalyst preparation, the calibration curves of methane, ethane, ethylene, benzene, CO and CO₂ and the data of experiments are included in appendix at the end of this thesis.



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