



## CHAPTER III

### EXPERIMENT

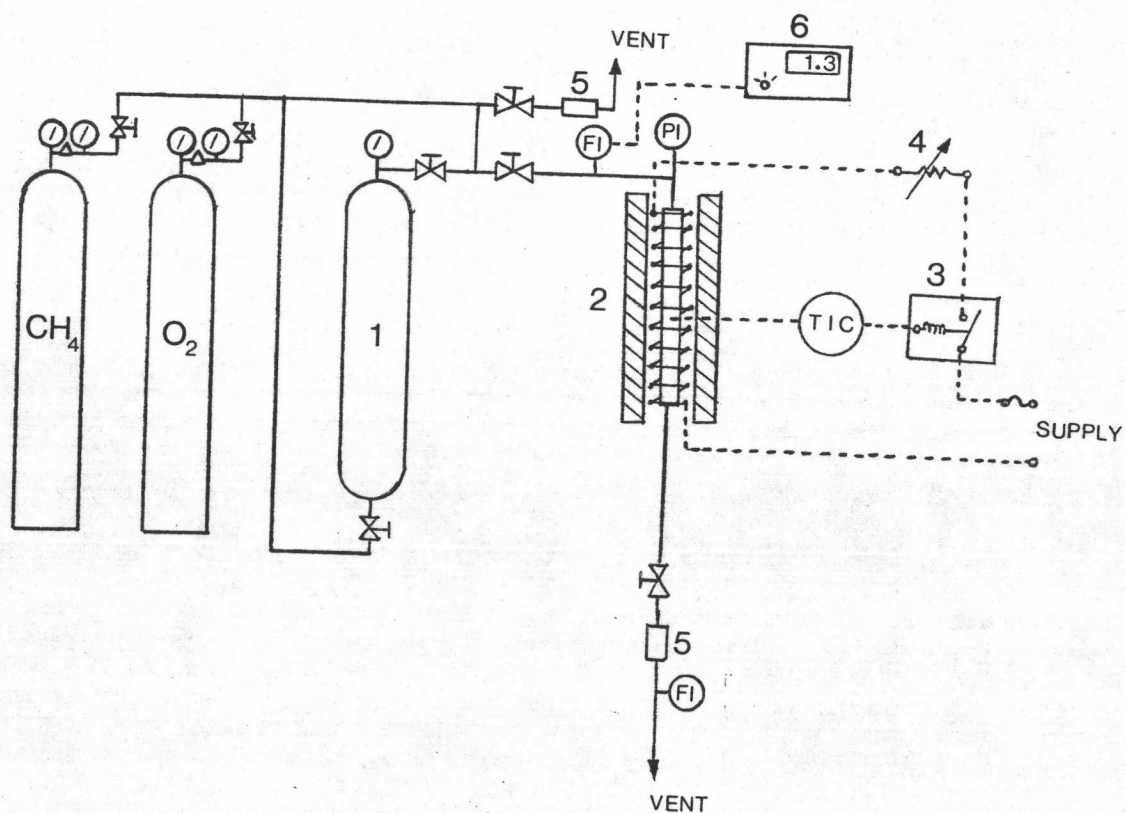
#### 3.1 Experimental Equipments

##### 3.1.1 Design and Fabrication of Reaction

##### Experimental Apparatus

##### 3.1.1 Flow Diagram

The experimental equipments used in this work were designed for heterogeneous reaction using fixed-bed catalyst. The reactant was a gas-phase mixture of methane, oxygen and nitrogen, which is used as the dilutant. The catalysts were solid-phase packing in the tubular reactor. The flow diagram of the experimental equipment is shown in Figure 3-1. It consisted of two main sections, namely, feed section and reactor section. Feed section was the preparation equipments of reactants used for mixing methane, oxygen and nitrogen and storing the mixed gas in mixing tank for feeding to the reactor after the mixed gas was homogeneous. This method was the batch-mixing of reactant gas which each reactant gas did not instantly mix. Therefore the reactant ratio in feed gas to reactor is maintained at a constant ratio



1. Mixing tank
2. Reactor and electric furnace
3. On-off temperature controller  
and display set
4. Variac
5. Sampling port
6. Mass flow meter and display set

Figure 3-1 Flow diagram of reaction experimental apparatus

through out the experiments. Reactor section consisted of a tubular reactor, electric furnace, valves, a set of temperature control and flow measurement equipments at entrance and exit of reactor.

### 3.1.1.2 Feed Section

The reacting feed was prepared by mixing pure methane, oxygen and nitrogen from each of the gas cylinders in a mixing tank. The mixing tank was a 1 U.S. seamless stainless steel cylinder which was able to charge the pressure up to 120 atm at room temperature. The mixing method started from the calculation of each partial pressure in mixed pressure in order to receive the required mole ratio of each component. For example, if the requirement of mixture gas,  $\text{CH}_4 : \text{O}_2 : \text{N}_2 = 10 : 1 : 11$  at 22 atm, therefore, the partial pressures of methane, oxygen and nitrogen are 10 atm, 1 atm and 11 atm respectively. Before mixing, the mixing tank must be purified by flushing with nitrogen to remove, i.e. oxygen in the tank. Then, start up at the first step by charging nitrogen into the mixing tank until the pressure in the tank raise up to 11 atm. Secondly, charge the oxygen into the mixing tank until the mixture pressure in the tank up to 12 atm. and the last, charge the methane until pressure up to 22 atm. After mixing method had been completed, the mixture must remain in the mixing tank overnight before use in experiment in order to be a homogeneous phase mixture, from experiences, two days for 50 atm mixing pressure. Take the mixture at the top and bottom of mixing tank to analyze by

using Gas Chromatograph to check the reactant ratio and uniformity.

### 3.1.1.3 Reactor Section

The fixed-bed down-flow used in the experiments was made of seamless stainless steel tube, 1/2 inch in diameter and 25 inches in length. Both ends of this tube were connected with three-way connectors, which at the top end, a thermocouple together with a thermowell was inserted into the reactor in the axial direction wherein the end of thermowell was located at a middle length of reactor where it was the highest temperature on axial temperature distribution. The mixed reactants was fed as top-down flow direction. The bottom end of reactor tube was used for changing of catalyst and the exit way of product gas. Catalyst particles having mesh number in the range of 8-16 were packed in the stainless steel basket which would be set into the reactor by fixing at the end of thermowell. The basket was supported with a stainless steel tube to ensure that it will not move down from the setting position.

### 3.1.2 Electric Furnace

#### 3.1.2.1 Construction of Electric Furnace

The constructed furnace, which was designed to ensure isothermal operation of the reactor in the heating zone, was made of

refractory bricks and heating wire.

Four bricks were divided into two side, each side consisting of two bricks longitudinally connected. Next a central hole was carved out of both sides such that the reactor tube might be placed snugly in it. Several small grooves were next carved out on inner side of the four bricks to insert the electrical heating wires. Therefore the distance between the reactor tube and the electrical heating wire was uniform around the center and a uniform heat flux occurred at the reactor wall. Finally each outer side of the bricks was cut into cylindrical shape and wrapped in a cylindrical stainless steel-tin sheet and the two sides were hinged together on one side edge, so that the furnace could be opened easily to cool-down the furnace.

#### 3.1.2.2 Temperature control

The signal from thermocouple was sent to temperature readout and control. The temperature controller was an on-off controller operated with magnetic contractor. When temperature in reactor was lower than the set point temperature, controller was turned on, the contractor closed the electric circuit of electric furnace. However, the power given to the furnace was controlled by a varied transformer namely variac, to adjust the gain value of control loop in order to prevent the overshoot of temperature.

### 3.1.2.3 Test of Axial Temperature Distribution

Measurement of the axial temperature distribution was made by placing a stainless steel tube inside the furnace and the axial temperature inside the tube was measured using a thermocouple set. To ensure isothermal operation, three sets of axial temperature distribution which covered the experimental temperature such as 450°C, 550°C and 650°C at the middle point of heating zone, each with less than  $\pm 5^\circ\text{C}$  variation, were achieved for a length not less than 5 centimeters both upper and lower sides. The observed axial temperature distribution with no gas flow are shown in Figure 3-2.

### 3.1.3 Preparation of Catalyst

The equipment for preparation of catalysts were conventional equipment used in the laboratory and with the addition of a calcinator. The calcinator used for the calcination of the catalysts was an electric furnace the same as the electric furnace of experimental reactor, but used fused-quartz as a reactor.

The catalyst powder was pressed into a pellet by using the hydraulic jack which can read and adjust the compressed force. Therefore this can control the density of the catalyst pellet constantly.

### 3.1.4 Analytical Instrument

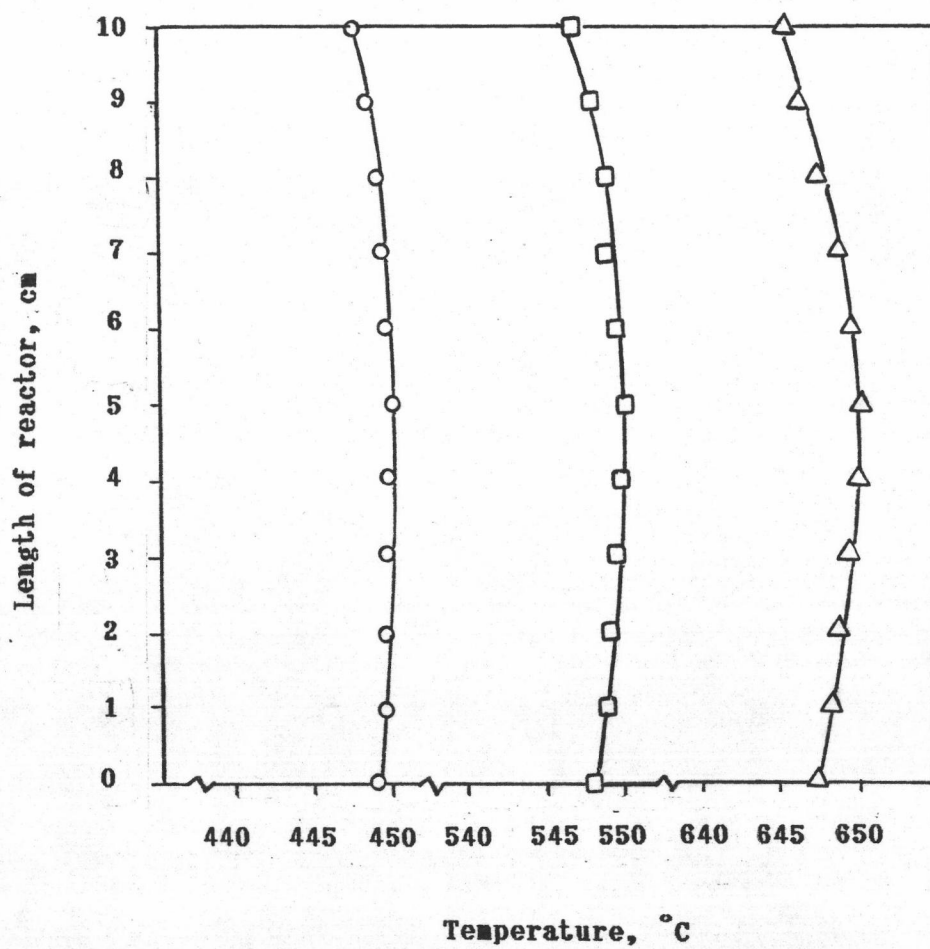


Figure 3-2 The observed axial temperature distribution  
for the reaction operating zone

#### 3.1.4.1 Gas Chromatography

A Shimadu gas chromatograph model 8 AIT with a thermal conductivity detector (TCD) was used for analyzing the components of the reactants feed and products gas. Hydrogen, oxygen, nitrogen, methane and carbon monoxide were analyzed by using column of MS-5A and those of carbon dioxide, water and the others hydrocarbon components such as ethane, ethylene, propane, propylene and methanol were analyzed by using column of Porapak Q. A recorder was used to receive signals from detector of Gas Chromatograph and plotted on continuous feeding paper. Additional details are given in Appendix A.

#### 3.1.4.2 Scanning Electron Microscopy (SEM)

For morphological study of catalysts. The pictures of catalyst surface were carried out by using SEM. This was a service of Scientific and Technological Research Equipment Centre, Chulalongkorn University. The instrument was JEOL model JSM-T220 A Scanning Microscope.

#### 3.1.4.3 Infrared Spectroscopy (IR)

To determine the functional group in catalyst, Infrared Spectroscope was used. This was using the service of Department of Science Service, Ministry of Scientific, Technology and Energy. The



instrument was PERKIN-ELMER model 1720 FTIR.

### 3.2 Experimental Procedure

#### 3.2.1 Leak Test of Experimental Equipment

After fabrication has been finished, to make sure that the apparatus was safe to operate at the maximum design pressure, a pressurized gas test was made using nitrogen. First nitrogen at 20 atg. was introduced into the apparatus. Then a soapy solution was used to find out any connecting points by squirting the solution onto all areas susceptible to leakage. Subsequently, pressures of compressed nitrogen was raised step by step for 40 and 60 atg while carrying out the same leak test procedure as at 5 atg. Tightening the nut of leaky connector until leaky gas did not appear.

The leak testing of the experimental apparatus need to be carried out whenever the spent catalyst had to be replaced with a new one.

#### 3.2.2 Preparation of Catalyst

There were four types of supports such as zinc oxide, alumina, silica and zeolite. Zeolite was finished powder of Na-Y form which had 77.3 wt%  $\text{SiO}_2$ , 21.8 wt%  $\text{Al}_2\text{O}_3$  and 0.14

wt% of  $\text{Na}_2\text{O}$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (mole ratio) = 6.0. The preparation procedure of catalyst was as follows :

1. Adding twenty five grams of support powder and an amount of carbonate salt of doped metal which given 0.225 gram of metal ions or 0.9 wt% of doped metal ion to weight of support.

2. Adding to deionized water and evaporating the water while stirring until only a thick pate remained.

3. The paste was dried in air at  $140^\circ\text{C}$  overnight.

4. Pressed and then broken into small sizes, the catalyst

fragments were screened using 8- and 16- mesh sieves.

5. The screened catalyst was calcined at  $600^\circ\text{C}$  for 4 hrs under a flow of oxygen.

6. The calcined product was separated into two parts. One was loaded into the reactor and pretreated at  $600^\circ\text{C}$  for 1 hr under a flow of oxygen 120 ml/min (oxidizing form) before exposing to the reactant gases for reaction. The other was loaded into the reactor and pretreated at  $600^\circ\text{C}$  for 1 hr under a flow of hydrogen 120 ml/min (reducing form) before exposing to the reactant gases for reaction.

### 3.2.3 Catalyst Loading

The following steps constitute the catalyst loading procedure :

i) Two grams of the calcined catalyst was placed into a fine stainless steel basket and covered by the aluminum-wood and recovered by stainless steel screen.

ii) Insert the basket at the bottom end of reactor tube by placing the bottom of basket in the upward direction until the bottom of basket was against the thermowell. Therefore, the end of thermowell was closely placed to the catalyst bed.

iii) Close the bottom adaptor of reactor. Then carry out leak test at a pressure at least 10% higher than the operating pressure of the experiment.

### 3.2.4 Catalytic Reactions Conditions and Test

#### 3.2.4.1 Catalytic Reaction Conditions

The experiments were separated into three parts. Two parts were the study of catalysts, primary compounds or doped elements and support components. The last part was the study of reaction conditions such as methane/oxygen mole ratio, temperature

and pressure.

**i) Primary components or doped elements**

Because of proposition that methyl radicals may be an intergal part of a catalytic cycle, therefore hydrogen atom abstraction of methane by the active sites of catalysts become a critical step in the activation process and the ability of this abstraction directly involved with the doped elements. A survey was made to find out the most active elements by testing Li, Mg, V, Fe, and Cu. These elements were doped on zinc oxide at the same concentration, 0.9 wt% metal ions. The prepared catalyst were divided into three portions, the first one was used for physical characterization. The remaining 2 portions were pretreated separately with oxygen and hydrogen to form, namely, oxidizing and reducing forms respectively and both forms were used in catalytic reaction experiment in order to study the effect of redox state of catalyst. These two forms were tested at the same reaction conditions. The reaction conditions are atmospheric pressure,  $WHSV = 0.52 \text{ hr}^{-1}$  and two points of temperatures,  $450^\circ\text{C}$  and  $600^\circ\text{C}$ .

**ii) Support Components**

To study the co-operation of doped element and support. The various supports have been used at the same doped elements. A number of selected element in perious strep about 2 elements have

been tested on the other supports such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and zeolite. The experimental conditions remained the same as the investigation of primary components or doped elements.

### iii) Reaction Conditions

1. For  $\text{CH}_4:\text{O}_2$  ratio, Li, Mg, V, Fe and Cu doped over ZnO in oxidizing form were used for investigation at  $600^\circ\text{C}$ , atmospheric pressure and  $\text{WHSV} = 0.52 \text{ hr}^{-1}$ . The variation of  $\text{CH}_4:\text{O}_2$  mole ratios were 5 : 1, 10 : 1, 20 : 1, 30 : 1 and 50 : 1.

2. For temperature, Li and Mg doped over ZnO in oxidizing form were used for investigation at atmospheric pressure,  $\text{CH}_4:\text{O}_2 = 10:1$  and  $\text{WHSV} = 0.52 \text{ hr}^{-1}$ . The variation of temperature were from  $450^\circ\text{C}$  to  $650^\circ\text{C}$  with  $50^\circ\text{C}$  stepping. However, in the study of primary compounds and support components, the investigation of temperature have been done on two points of temperature,  $450^\circ\text{C}$  and  $600^\circ\text{C}$ .

3. For pressure, only Li-doped ZnO in oxidizing form was used for investigation at  $\text{CH}_4:\text{O}_2 = 10:1$ , volumetric flow rate = 1 ml/s and two points of temperatures,  $450^\circ\text{C}$  and  $600^\circ\text{C}$ . The variation of pressures are atmospheric pressure, 10 and 30 atg.

#### 3.2.4.2 Catalytic Reactions Test

The experimental procedure after catalyst loading and mixing gas as a reactant feed is as follows :

i) First, nitrogen was used to purge the system before the start of each experimental run.

ii) Next was the catalytic pretreating, feed oxygen gas for oxidizing form of catalyst or hydrogen gas for reducing form. Adjust the required flow rate by needle valve and mass flow meter.

iii) Turn on the temperature control system and set the temperature selector to 600 °C.

iv) After 1 hr of pretreating step. Turn off the temperature control system and open the electric furnace. Shut off the pretreated gas and purged the reaction section with nitrogen.

v) After 30 minutes of nitrogen purging, sampling the purged nitrogen to ensure that had no oxygen or hydrogen gas remained in the system.

vi) Shut off the nitrogen gas and wait until no nitrogen flow out of the system using exit soap-film meter.

vii) Feed reactant gas to the reactor and set the required

flow rate at entrance of reactor at 1 ml/s by using mass flow meter.

viii) Close the electric furnace and turn on the temperature control system and set the temperature selector to the reaction temperature.

ix) For reaction at atmospheric pressure, the exit valve of reactor was fully opened and the outlet flow rate of gas was carried out by soap-film meter. For pressurized reaction, the inlet and outlet valve of reactor must be adjusted until the required pressure and feed flow rate both taken at the same time.

x) A sample of the product gas mixture was taken and then analyzed with the Gas Chromatograph.

xi) After the experimental run had been finished, the temperature control system was turned off and feed gas shut off. Nitrogen was sent to purge the remaining gas in the reactor.

### 3.2.5 Measurement and Analytic Method

When each sample of the outlet gas mixture was taken for analysis, the following information was recorded :

- i) Catalyst bed temperature.
- ii) System pressure (at the reactor inlet).

- iii) Temperature of feed and sampling port.
- iv) Flow rate of reactant.
- v) Flow rate of product gas.

In addition to the results from the Gas chromatograph, all informations were used for calculation of methane and oxygen conversion, carbon compounds selectivity and products distribution. The calculation methods are presented in Appendix A (Analytical method of Gas chromatograph) and Appendix B.

### 3.3 Characterization of the Prepared Catalysts

The prepared catalysts before and after using for catalytic reaction test have been characterized the physical properties of the catalysts by using scanning electron microscope (SEM) and infrared spectroscopy (IR).

#### 3.3.1 Scanning Electron Microscopy (SEM)

For morphological study of catalysts. The photograph of catalyst surface were carried out by using SEM. All primary compounds such as Li, Mg, V, Fe and Cu which doped over ZnO supports and Li-doped  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and zeolite supports were checked. All supports without doped compounds were also checked in order to compare the difference before and after doping. The catalysts had two forms, oxidizing and reducing forms, the study by SEM also has



been done in both forms of catalysts in order to investigate the effect of redox state to the morphological character of catalysts.

### 3.3.2 Infrared Spectroscopy (IR)

To find out the functional group in catalyst, Infrared Spectroscope was used to characterize the chemical nature of catalysts. Li-doped ZnO before and after using of both oxidizing and reducing forms were examined by this method. Pure ZnO used as support was also examined in order to be the reference for comparison of the catalysts before and after doping and reaction. This characterization was also used to observe the functional group of hydrocarbon of coke in catalysts after using in the experiment.