

## CHAPTER IV

### EXPERIMENTAL

This chapter describes the experimental systems and the experimental procedures in this research. A description of catalyst preparation method is given in section 4.1. The experimental system of non-oxidative methane conversion reaction and characterization of the catalyst are explained in section 4.2 and 4.3, respectively. Details of experimental procedures, including the materials and apparatus are as follows:

#### **The scope of this study**

The catalysts used in non-oxidative methane conversion in this study were prepared by incipient wetness impregnation.

The catalysts are as follows:

- HZSM-5
- (5-10 wt%) Mo/HZSM-5
- (8 wt%) Mo/HY

Non-oxidative methane conversion was carried out under the following conditions:

Reaction Temperature	:	600-700°C
Operation Pressure	:	1 atm
Time of non-oxidative methane conversion	:	0-300 min
GHSV of CH <sub>4</sub>	:	2000-6000 h <sup>-1</sup>

## 4.1 Catalyst preparation

Catalysts were prepared from a commercial Na-ZSM-5 zeolite (ALSI-PENTA ZEOLITE SM-55), a commercial HY zeolite (JRC-Z-HY5.5) and ammonium molybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$  (99.0%). Ammonium molybdate, analytical grade, was provided by Ajax Chemicals. The preparation of Mo/HZSM-5 and Mo/HY are described as follows:

### 4.1.1 Ammonium ion-exchange of Na-ZSM-5 zeolite

The ion-exchange step was carried out by mixing 3 g of Na-ZSM-5 zeolite with 90 ml of 1 M  $\text{NH}_4\text{NO}_3$  and heated on a stirring hot plate at  $80^\circ\text{C}$  for 40 min. After that, the mixture was cooled down to room temperature and washed with distilled water for 3 times by using the centrifugal separator (10 min for each time). The ion-exchange step was repeated 3 times. Then, the ion-exchanged zeolite was dried at  $110^\circ\text{C}$  for at least 3 h in an oven. The Na-ZSM-5 was thus changed to  $\text{NH}_4\text{-ZSM-5}$ .

### 4.1.2 Impregnation and calcination

Mo/HZSM-5 catalysts were obtained by impregnating  $\text{NH}_4\text{-ZSM-5}$  with ammonium molybdate aqueous solution (incipient wetness method), and then dried at  $110^\circ\text{C}$  overnight and calcined at  $500^\circ\text{C}$  for 5 h at a heating rate of  $7^\circ\text{C}/\text{min}$ . For Mo/HY, the HY zeolites were prepared with the same condition as  $\text{NH}_4\text{-ZSM-5}$ . Hereafter, the HZSM-5 and HY catalysts with different Mo loadings will be denoted as  $x\%\text{Mo/HZSM-5}$  and  $x\%\text{Mo/HY}$ , where x is the nominal Mo content weight percent.

The obtained catalysts were pressed, crushed and sieved to the sizes of 20-30 mesh.

## 4.2 Methane conversion

### 4.2.1 Chemicals and reagents

10%CH<sub>4</sub>/He, N<sub>2</sub>(UHP) and air zero were supplied by Thai Industrial Gases Limited were used in these experiments.

### 4.2.2 Instrument and apparatus

A flow diagram of the steady state methane conversion system is shown in Figure 4.1. The system consists of a reactor, an automation temperature controller, an electrical furnace and a gas control system. This instruments used in this system is listed and explained below:

1. Reactor: The reactor is made from a stainless steel tube. The reaction was carried out under ordinary gas flow and atmospheric pressure.
2. Automation temperature controller: This consists of magnetic switch connected to a variable voltage transformer and a RKC temperature controller connected to a thermocouple attached to the catalyst bed in a reactor. A dial setting establishes a set point at any temperature within the range between 0°C to 800°C.
3. Electrical furnace: This supplies the required heat to the reactor for reaction. The reactor can be operated from room temperature up to 700°C at maximum voltage of 220 volts.
4. Gas controlling system: Methane, air and nitrogen cylinder: each cylinder was equipped with a pressure regulator (0-120 psig). An on-off valve and a needle valve were used to adjust the gas flow rate.
5. Gas Chromatograph: The apparatus consist of flame ionization detector equipped with gas chromatographs, Shimadzu GC-14A and Shimadzu GC-14B, and thermal conductivity detector equipped with gas chromatographs, Shimadzu GC-8A. Operating condition used in this study are given in Table 4.1.



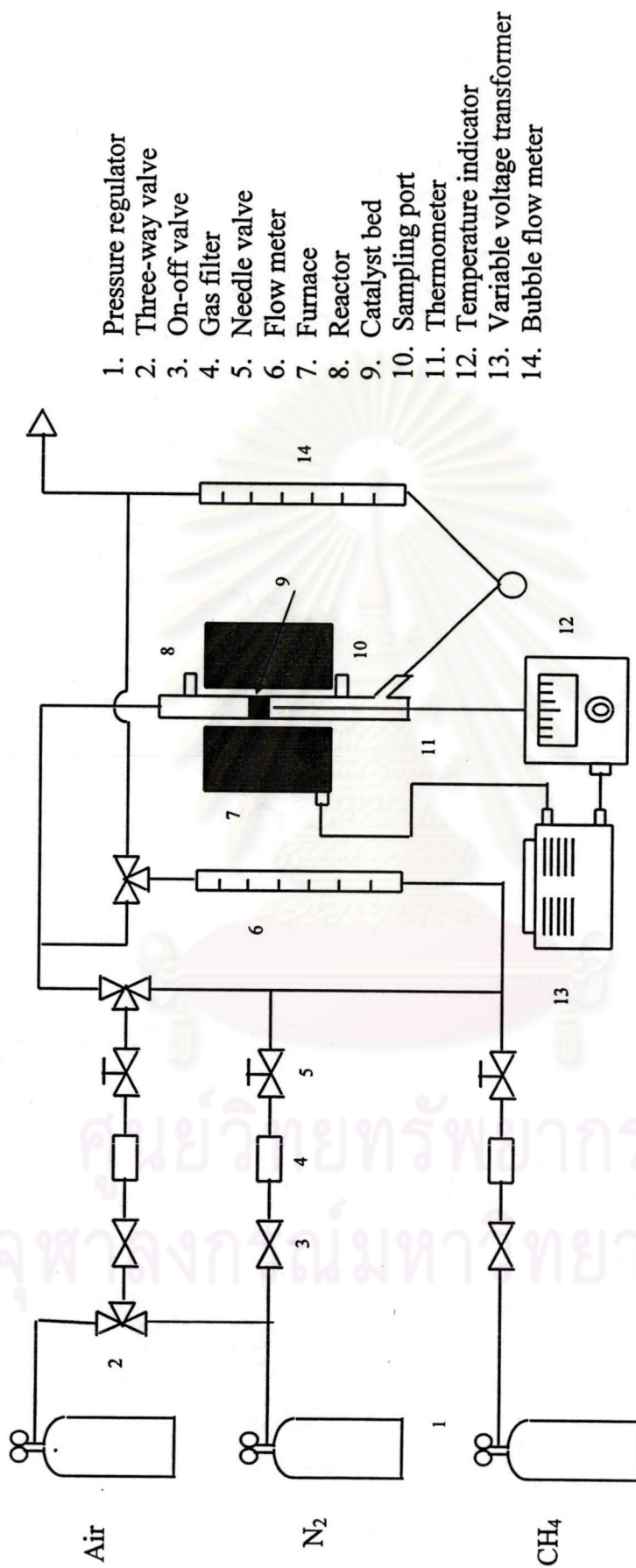


Figure 4.1 Schematic diagram of the experimental setup

**Table 4.1** Operating conditions for gas chromatograph

Gas chromatograph	Shimadzu GC-14A	Shimadzu GC-14B	Shimadzu GC-8A
Detector	FID	FID	TCD
Column	Capillary	VZ-10	MS-5A, Porapak-Q
Carrier gas	N <sub>2</sub> (99.999 %)	N <sub>2</sub> (99.999 %)	He (99.999 %)
Carrier gas flow	25 ml/min	25 ml/min	25 ml/min
Column temperature			
- Initial	40	60	60
- Final	140	60	60
Detector temperature	150	150	120
Injector temperature	150	100	120
Analyzed gas	Hydrocarbon	Hydrocarbon C <sub>1</sub> -C <sub>4</sub>	CO, CO <sub>2</sub>

#### 4.2.3 Reaction Method

The methane conversion reaction was carried out by using a conventional flow apparatus which has already shown in Figure 4.1.

The reaction was arranged as follows:

1. A 0.2g of the catalyst was packed in the middle of a stainless steel reactor. The reactor was then firmly placed into the furnace.
2. The catalyst was heated up to 500°C under air flow at a constant heating rate of 5°C/min and maintained at this temperature for 30 min.
3. Then the catalyst was heated in N<sub>2</sub> (flow rate of 50 ml/min) by raising the temperature from 500°C to the required temperature.
4. After that the catalyst was switched to a CH<sub>4</sub> stream.
5. The products were withdrawn periodically from the outlet of the reactor and analyzed by FID-type and TCD-type gas chromatographs.

### 4.3 Characterization of Catalyst

#### 4.3.1 X-ray diffraction (XRD) analysis

The crystallinity and structure of the catalyst can be analyzed using X-ray diffraction analysis. The XRD patterns of the catalysts were performed by X-ray diffraction spectroscopy D5000, SIEMENS using  $\text{CuK}\alpha$  radiation with Ni filter in the  $2\theta$  range of 5 to  $40^\circ$  at Petrochemical Engineering Research Laboratory, Chulalongkorn University.

#### 4.3.2 Morphology

The shape and the size distribution of the crystals were observed by JEOL Scanning Electron Microscope (SEM) at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC) and JEOL 5200 Scanning Electron Microscope at Centro de Ciencias de la Materia Condensada-UNAM, Mexico.

#### 4.3.3 BET surface area measurement

Surface areas of the catalysts were measured by the BET method, with nitrogen as the adsorbate using a Micromeritics model ASAP 2000 at liquid-nitrogen boiling point temperature at the Analysis Center of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

#### 4.3.4 Chemical analysis

Percentage of metals was analyzed by X-ray fluorescence spectrometer (XRF) technique. The silicon, aluminum and molybdenum contents of the prepared catalyst were analyzed by X-ray fluorescence spectrometer (XRF) at the Department of Science Service, Ministry of Science, Technology and Environment.

#### 4.3.5 Ultraviolet-Visible spectroscopy (UV-Vis)

Diffuse reflectance spectrum (DRS) was collected on a Varian Cary 300 equipped with a standard diffuse reflectance unit using a teflon reference at Centro de Ciencias de la Materia Condensada-UNAM, Mexico

#### 4.3.6 $^{27}\text{Al}$ Magic Angle Spinning Nuclear Magnetic Resonance ( $^{27}\text{Al}$ MAS NMR)

$^{27}\text{Al}$  MAS NMR spectra were recorded at room temperature in a magnetic field of 7 T at 78 MHz using a Varian Chemagnetics CMX Infinity 300 MHz spectrometer at the Department of Physics & Astronomy, Arizona State University, USA.  $^{27}\text{Al}$  spectra were measured at a spinning rate of 6.5 MHz using a 4 pulse width.



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