

CHAPTER III EXPERIMENTAL

In this chapter, the materials used in this research are described. Several catalyst characterization techniques, reaction studies and regeneration will be explained. Details of catalytic life cycle investigation are also given.

3.1 Materials

3.1.1 Gases

The gases used in this research were:

1. Air zero was obtained from Thai Industrial Gas Co.,Ltd.
2. 1-butene (C₄H₈ 98%) was obtained from Rayong Olefins Co.,Ltd.
3. *i*-butene (C₄H₈ 99%) was obtained from Thai Industrial Gas Co.,Ltd.
4. *n*-butane (C₄H₁₀ 99.5%) was obtained from Thai Industrial Gas Co.,Ltd.
5. Helium (He 99.99%) was obtained from Praxair (Thailand) Co.,Ltd.
6. Hydrogen (H₂ 99.99%) was obtained from Thai Industrial Gas Co.,Ltd.
7. Mixed C₄ feedstock was obtained from Rayong Olefins Co.,Ltd.
(The detailed compositions are summarized in Table 3.1.)

3.1.2 Chemicals

The chemical reagents used in this research were:

1. ZSM-5 zeolite (Si/Al=175 without binder) was obtained from Sud-Chemie C.G.
2. ZSM-5 zeolite (Si/Al=18 without binder) was obtained from Zeochem C.G.
3. Acetone (≥99%) was obtained from Carlo Erba A.G.

4. *n*-pentane (C_5H_{12} $\geq 99.5\%$) was obtained from Lab-Scan, Analytical Sciences.
5. Gallium Nitrate ($Ga(NO_3)_3$ $\geq 99.5\%$) was obtained from Aldrich.
6. Silver Nitrate ($Ag(NO_3)$ $\geq 99.5\%$) was obtained from Aldrich.

Table 3.1 Compositions of mixed C_4 feedstock

Components	wt %
propylene	0.72
<i>n</i> -butane	8.34
<i>i</i> -butane	37.43
1-butene	15.05
<i>i</i> -butene	7.26
<i>cis</i> -2-butene	11.50
<i>tran</i> -2-butene	16.77
<i>n</i> -pentane	0.07
1-pentene	2.08
3- <i>methyl</i> -1-butene	0.18
Total	100

3.2 Experiment

3.2.1 Catalyst Preparation

3.2.1.1 *ZSM-5 Catalysts*

ZSM-5 zeolite powder was calcined in flowing air at 500°C for 8 h to remove the contamination. Then, the calcined sample was hydraulically pressed to be the pellet by using 15 tons BIO-RAD pellet maker, model. Subsequently, the pressed sample was ground and sieved to obtain the desired particle size, which are 0.71 to 1 mm (mesh No.18 and 25).

3.2.1.2 *Ag-Supported Catalyst*

Ag cations were introduced by ion-exchange into ZSM-5 zeolite. To prepare Ag supported ZSM-5 catalysts, 4 g of support was added into 500 ml of silver nitrate solution (0.001 M) and stirred for 4 h. Then, the mixture was centrifuged in order to separate the particulate and the solution. After that the catalyst was dried overnight and calcined at 550°C for 5 h in air.

3.2.1.3 *Ga-Supported Catalyst*

The catalysts were prepared by the incipient wetness impregnation method. To prepare Ga supported ZSM-5 catalysts, Ga 0.5 wt% was loaded by the incipient wetness impregnation method into the supports using its nitrate salt solution. The catalysts were then calcined at 500°C for 4 h in air.

3.2.2 Catalyst Characterization

3.2.2.1 *X-Ray Fluorescence*

The element composition of catalysts was analyzed by a Siemens SRS3400 X-Ray Fluorescence (XRF). Typically, a 0.5 g of catalyst and 4.5 g of boric acid were physically mixed and pressed to be the pellet.

3.2.2.2 *Transmission Electron Microscopy*

The morphology of carbon deposition on the spent catalysts was observed by transmission electron microscopy (TEM) with a JEOL (JEM-2010) transmission electron microscope operated at 200 kV. The samples were dispersed in absolute ethanol ultrasonically, and the solutions were then dropped on copper grids coated with a Lacey carbon film.

3.2.2.3 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) was performed to determine the nature and amount of carbonaceous deposition on the spent catalysts. TPO measurement was carried out in a quartz tube micro-reactor. The coked catalyst sample, about 15 mg, was loaded in a quartz tube (i.d. 2.0 mm). Then, the sample was heated at a constant rate (10°C/min) from ambient temperature to 950°C under the continuous flow of 2%O₂ in He (40 ml/min). The combustion product, CO₂, was passed to a methanator containing 15 wt% Ni/Al₂O₃ as a catalyst. In this methanator, CO₂ formed from the carbon was completely converted with excess H₂ into methane, to permit precise quantification by FID detector. After the TPO system reached 950°C, where all carbon had been burned off, the FID signal for methane was calibrated by injecting 100 µl of pure CO₂. By integrating the methane signal during the entire TPO run, it was possible to calculate the amount of coke removed from catalyst. Moreover, TPO profile predicted the type of coke formation. Carbonaceous with different morphologies or different locations are burnt at different temperature.

3.2.3 Catalytic Activity Test

3.2.3.1 Catalytic Cracking

The experimental procedure for catalytic cracking is done by using a small-scale flow reactor at atmospheric pressure. A quartz tube fixed-bed reactor (i.d. 6.0 mm), typically containing 50 mg of catalyst, provided with a K-type thermocouple in the center of the catalyst bed, which presented the reaction temperature. For removal of the (physisorbed) water, the catalyst was heated in He for 1 h at 120°C. C₄ (*n*-butane, *i*-butene, 1-butene or mixed C₄ feedstock) was used as 50% mixture in He. In the case of *n*-pentane, it was vaporized from a saturator at 20°C using He as carrier gas. The concentration of *n*-pentane was maintained at 50% by mole. The catalytic activity test system of C₄ and *n*-pentane are shown in Figures. 3.1 and 3.2, respectively. The reaction conditions were as follows: T=600°C, gas hourly space velocity (GHSV) = 21,220 h⁻¹. Reaction products were analyzed by gas chromatograph using a Shimadzu GC 14A with Porapak Q column and FID detector (see retention time of products in Appendix A). Yields of the products were calculated following the ASTM D 5443 standard method (Appendix B).

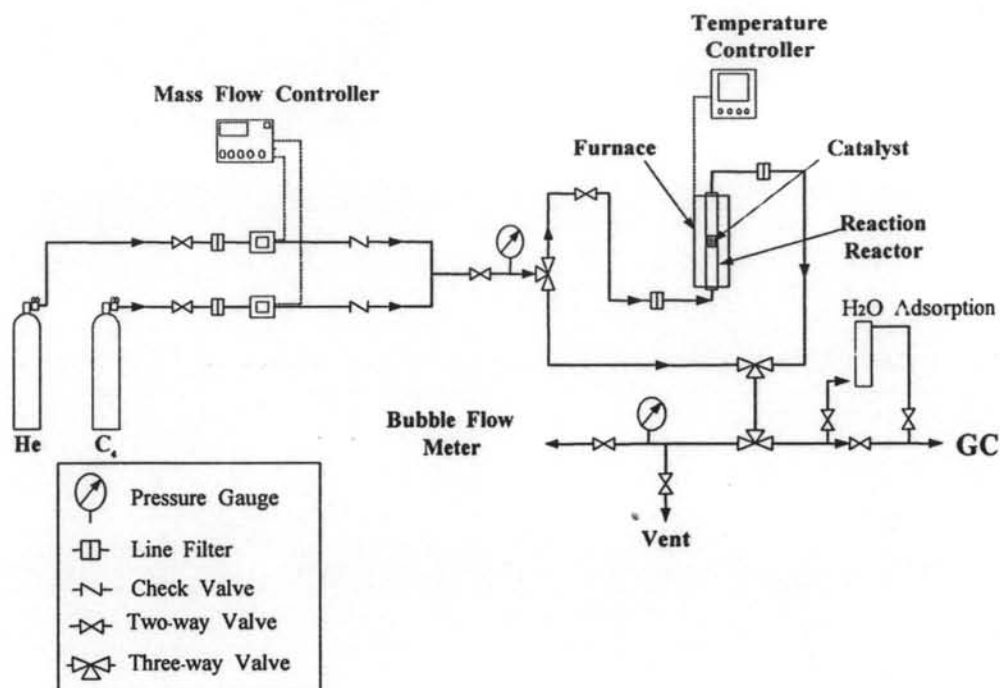


Figure 3.1 Schematic diagram of experimental setup of C_4 .

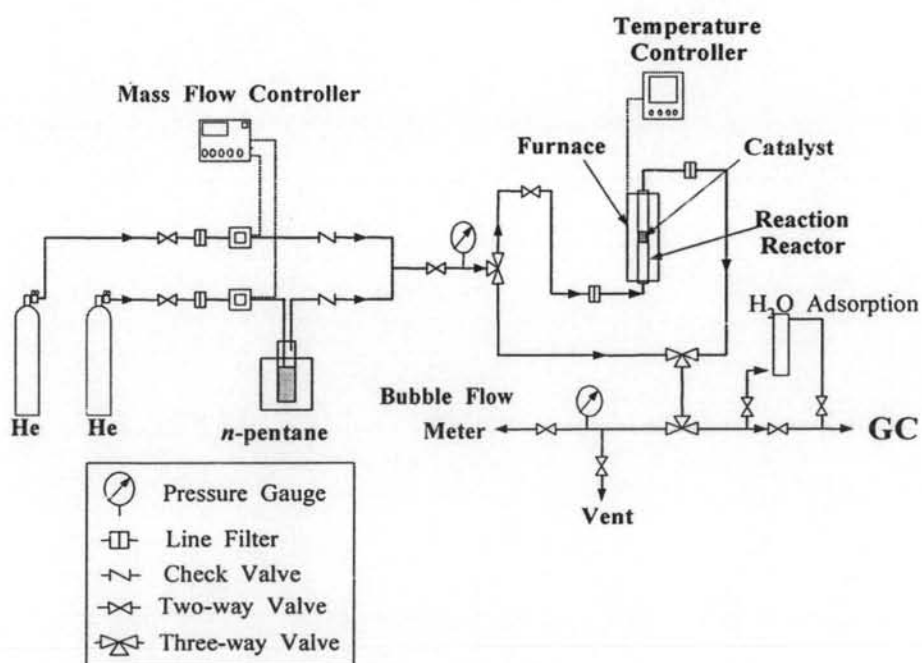


Figure 3.2 Schematic diagram of experimental setup of n -pentane.

3.2.3.2 Aromatization

The aromatization tests were carried out in the similar system to those described in cracking reaction at temperature of 460, 480, 500 and 520°C. However, only mixed C₄ feedstock was used as reactant. GHSV was used in the range 1,500-32,700 h⁻¹.

3.2.4 Regeneration

The zeolite catalyst deactivated (due to coking) in the catalytic cracking of mixed C₄ feedstock after it was on-stream for about 140 h was regenerated by TPO system measurement. Both the temperature (500, 550 and 600°C) and concentration of oxygen (2 and 10 wt%) were varied to investigate time-on-stream of regeneration. After the regeneration, the activity of the regenerated catalyst was carried out as cracking reaction. By following these catalyst deactivation-regeneration procedures, three regeneration cycles of the zeolite have been carried out.