

## CHAPTER III EXPERIMENTAL

### 3.1 Catalysts and Chemicals

Four types of commercial ZSM-5 catalysts varied in Si/Al ratios were used in this study. The Si/Al ratios of these catalysts are 20, 40, 190, and 398. The physical and chemical properties of the studied zeolite are summarized in Table 3.1.

**Table 3.1** Properties of ZSM-5 catalysts

Si/Al ratio	Chemical Composition (wt %)		Physical Properties	
	Si	Al	BET area (m <sup>2</sup> /g)	Pore Volume (cc/g)
20	88.00	4.470	290	0.148
40	97.60	2.400	305	0.155
190	99.40	0.512	360	0.167
398	97.50	0.235	420	0.180

Surface area and pore volume were obtained by a Quantachrome Autosorb-1 following the BET procedure. The Si/Al ratio was determined by using X-ray fluorescence spectroscopy (XRF).

The mixed C<sub>4</sub>, non-butadiene C<sub>4</sub>, mixed C<sub>5</sub> and mixed C<sub>6</sub> were used as feedstock obtained from Rayong Olefins Co.,Ltd., Thailand. The mixed C<sub>4</sub> has two grades used for reactivity of butadiene studied. The detailed compositions of feedstock are summarized in Table 3.2 to Table 3.4.

**Table 3.2** Compositions of Mixed C<sub>4</sub> compared with Non-butadiene C<sub>4</sub> feedstock

Components	Mixed C <sub>4</sub>	Non-BD C <sub>4</sub>
Composition (wt %)		
<i>trans</i> -2-butene	3.14	12.66
<i>i</i> -butene	25.44	59.73
1,3 butadiene	47.62	-
<i>l</i> -butene	17.10	21.33
<i>n</i> -butane	6.69	6.26
Total	100	100

**Table 3.3** Compositions of Mixed C<sub>5</sub> feedstock

Components	Mixed C <sub>5</sub>
Composition (wt %)	
<i>methyl</i> -butene	0.08
<i>cyclo</i> -pentane	0.58
isoprene	5.35
<i>l</i> -pentene	9.11
<i>cyclo</i> -pentene	0.52
<i>cyclo</i> -pentadiene	19.53
<i>n</i> -pentane	54.93
pentadiene	1.01
<i>i</i> -pentane	8.89
Total	100

**Table 3.4** Compositions of Mixed C<sub>6</sub> feedstock

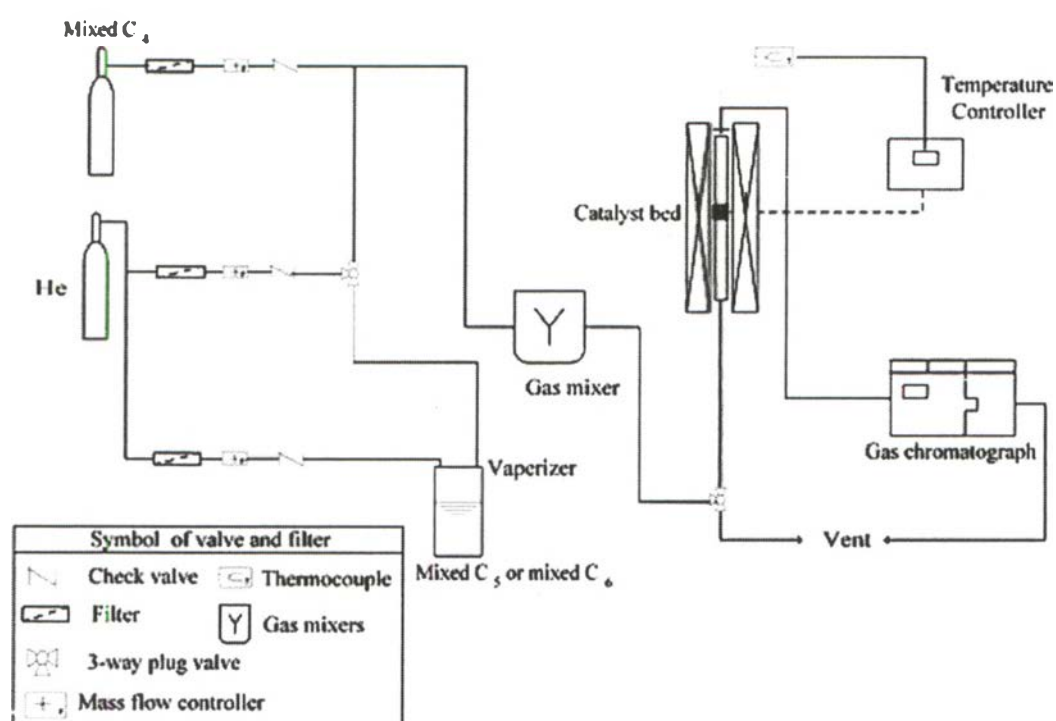
Components	Mixed C <sub>6</sub>
Composition (wt %)	
<i>n</i> -pentane	0.84
<i>i</i> -pentane	0.78
<i>cyclo</i> -pentane	24.77
<i>i</i> -hexane	12.68
benzene	3.10
<i>n</i> -hexane	13.42
<i>cyclo</i> -hexane	31.34
<i>i</i> -heptane	3.76
<i>n</i> -heptane	5.83
<i>di-methyl-cyclo</i> -pentane	3.49
Total	100

### 3.2 Reaction Procedure

All ZSM-5 were tested directly for the cracking of mixed C<sub>4</sub>, non-butadiene C<sub>4</sub>, mixed C<sub>5</sub>, and mixed C<sub>6</sub>. The reaction experiments were performed in a fixed bed micro activity test (MAT), which is a quartz glass tube micro reactor (internal diameter 6 mm) typically containing 100 mg of catalyst particles was used. Samples were collected on-line using an 8-port sample valve. The products were analyzed by a gas chromatography (Shimadzu, GC-14A with C-R4A Chromatopac) with a two-column system in series and analyzed with flame ionization detector (FID) and thermal conductivity detector (TCD). Helium (He) was used as carrier gas. Yields of the products were calculated following the ASTM D 5443 standard method.

Single-pass flow experiments were performed at atmospheric pressure. The experiments were done at any types of feed. The mixed C<sub>4</sub> and non-butadiene C<sub>4</sub> (gases formed) were individually injected directly to the reactor with feed/He ratio about 1:4 (v/v) or feed concentration about 20% by volume. In case of mixed C<sub>5</sub>

(liquid formed), in order to obtain liquid-vapor equilibrium constantly, the temperature of feed in the vaporizer was kept constant at 10°C in the water bath. Helium was used as a carrier to carry the vapor to the reactor, in addition, another helium was injected to mix with the vapor for diluting the feed concentration as same as the mixed C<sub>4</sub>. For mixed C<sub>6</sub>, it was done the same manner as mixed C<sub>5</sub> but the temperature in the vaporizer was changed to 20°C. The reaction flow diagram was shown in Figure 3.1.



**Figure 3.1** Reaction flow diagrams.

The cracking reactions were tested with different flow rates, which are 5, 12.5, 25, 50, and 100 ml/min (that gave retention times about 3.4, 1.36, 0.68, 0.34 and 0.17 seconds) for finding the best condition. In each experiment, the cracking reaction was performed at four temperatures, which are 500, 550, 600, and 650°C for mixed C<sub>4</sub> and up to 700°C in case of mixed C<sub>5</sub> and mixed C<sub>6</sub>. The reactor was heated to the desired temperature with helium at a rate of 20°C/min and kept at those temperatures for 15 minutes in order to remove the water. Afterwards, the feed was

injected to the reactor for performing the reaction. The products were sampling to analyze by GC after 5, 30, and 60 minutes on stream. The operating conditions were used for testing all of ZSM-5 zeolite and the without catalyst system was performed to test the amount of thermal conversion.

### 3.3 Catalysts Stability Test

All ZSM-5 were tested for finding the life times in each feed. The cracking conditions were used at the point, which gave the best yields of propylene there were 500°C for non-butadiene C<sub>4</sub> cracking on ZSM-5 ratio 190, 600°C for non-butadiene C<sub>4</sub> with other ZSM-5, also 600°C for mixed C<sub>5</sub> and 650°C for mixed C<sub>6</sub>. The concentration of feed was increasing to 50% by volume in all tests for reducing the total time on stream. The products were collected every one hour and stop when yield of propylene reduce by 30% from the maximum yield.

### 3.4 Catalysts Characterization

#### 3.4.1 Surface Area Analysis (BET)

The surface areas of the catalysts were determined by Brunauer Emmet Teller (BET) method, using Quantachrome Autosorb-1 measuring the physical adsorption of liquid nitrogen at 77 K, which has cross section area of 16.2 Å<sup>2</sup>/molecule. Before performing the adsorption the sample must be degassed by flowing of He at 200°C for 6 hours in order to eliminate the adsorbed species at the surface. The surface area of the catalysts calculated from twenty-one point adsorption isotherms. The average radius and pore volume were calculated at P/P<sub>0</sub> ratio close to unity.

#### 3.4.2 X-ray Diffraction

Structural characterization of catalysts was investigated by X-ray Diffraction technique to analyze the peak pattern of the zeolite, which obtained by using a Rigaku X-ray Diffractometer system equipped with a Cu tube for generating

CuK $\alpha$  radiation with the wavelength of 1.5406 Å. The goniometer parameters were divergence slit = 1° (2 $\theta$ ), scattering slit = 1° (2 $\theta$ ), and receiving slit = 0.3 mm. A scan speed of 5° (2 $\theta$ )/min and a scan step of 0.02° (2 $\theta$ ) were applied for the continuous run in the 5 to 90° (2 $\theta$ ) range. The sample powder was packed on the glass slide specimen holder. The signal was sent to an online computer to record and analyze.

#### 3.4.3 Temperature Programmed Desorption (TPD)

The acidity of ZSM-5 zeolite was tested by the isopropylamine TPD technique developed by Gorte (1996). The test was conducted in the following method. First, 100 mg of sample was pretreated at 500°C in a flow of He for 1 hour. After the pretreatment, the sample was cooled in He to room temperature and then 3 ml of isopropylamine was injected over the sample and wait for 24 hours until the adsorption of isopropylamine reach equilibrium. After removing the excess of isopropylamine by flowing He overnight, the sample was linearly heated to 700°C at a heating of 10°C/min by using TPDRO/MS 1100, Thermo Finnigan. The Mass signals 44, 41 and 17 from MS, were monitored to determine the evolution of isopropylamine, propylene and ammonia, respectively.

#### 3.4.4 Temperature Programmed Oxidation (TPO)

This technique was performed to studying the reactivity of carbon deposits in the zeolite by oxidizing sample under the continuous flow of O<sub>2</sub>/He with a flow rate of 40 sccm. The flow was passed to the quartz tube with contained the zeolite sample about 20 mg was packed between quartz wool, meanwhile the temperature was linearly increased with a constant rate of 12°C/min. At the oxidation temperature, carbon deposited was oxidized in the reactor to carbon dioxide (CO<sub>2</sub>), which was converted again to methane (CH<sub>4</sub>) in methanator using Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Consequently, methane was detected with Flame Ionization Detector (FID SRI model 110) and shows the signal in the monitor. The area under the curve determines the total of carbon deposits in the catalysts. Moreover, the

shape of the curve predicted the type of carbon formation. In other words, carbons with different morphology or different locations are burnt at different temperature.