

CHAPTER III

EXPERIMENT

3.1 Materials

- (1) Natural Gas Liquid (NGL) were obtained from Petroleum Authority of Thailand (PTT).
- (2) Chloroplatinic Acid 6 hydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was available from J.T. Baker.
- (3) Ammonium Fluoride (NH_4F) was available from Carlo Erba.
- (4) Industrial Hydrogen Gas was available from TIG Trading Limited.
- (5) Industrial Nitrogen Gas was available from TIG Trading Limited.
- (6) Alumina Powder Support (Alumina Catalyst AL-3912P is a powdered gamma alumina) was supplied from a dealer of Engelhard, Holland.
Surface area = $185 \text{ m}^2/\text{g}$, total pore volume = 0.50 cc/g , particle size < 90 microns = 85 wt %, density = $0.7 - 0.85 \text{ g/cm}^3$.
- (7) Molecular sieve support (4A-DG type) was supplied from Union Carbide.
BET surface area = $29.96 \text{ m}^2/\text{g}$, total pore volume = 0.096 cc/g .

3.2 Apparatus and Instruments

- (1) The condenser has a large top opening for an easy introduction of dry ice/acetone mixtures (Figure 3.1).



Figure 3.1 Condenser

(2) Tube Reactors

Annealed 316 Stainless Steel Tube ASTM A269,
O.D. $\frac{1}{4}$ in. \times Wall Thickness 0.035 \times Length 6 feet

(3) Furnace for Reaction Unit

Adapted from some units of Gas Chromatograph Instrument from Pye
Unicame GC model Pye Series 104 Chromatograph

(4) Calcinator

Carbolite Furnace model GSM

(5) Gas Chromatograph (GC)

Hewlett Packard GC model HP5890 SeriesII

3.3 Procedures

3.3.1 Preparation, Activation, Regeneration and characterization of Catalysts

(1) Preparation of Catalysts

Catalyst A : 0.3% Pt and 0.5% F/Al₂O₃

The alumina support was impregnated by an aqueous hexachloroplatinum acid solution for obtaining 0.3% platinum on the final catalyst. And then the obtained product was dried for 16 hour at 120°C, after that it was calcined for 3 hours at 500°C. The obtained product was reimpregnated by an aqueous ammonium fluoride solution. And therefore the final fluoride concentration of catalyst was 0.5 % by weight, and it was dried for 16 hours at 120°C. After that the obtained product was calcined at 150°C for 1 hour, and the temperature was raised from 150°C to 500°C in every 15 minutes then held at 500°C for 3 hours.

Catalysts B : 0.3% Pt and 1% F/Al₂O₃

For the preparation 0.3% Pt & 1% F/Al₂O₃ catalyst the alumina was impregnated using the same procedure as described for catalyst A, except the final fluoride concentration of catalyst was 1% by weight.

Catalyst C : 0.6% Pt and 0.5% F/Al₂O₃

For the preparation 0.6% Pt & 0.5% F/Al₂O₃ catalyst the alumina was impregnated using the same procedure as described for catalyst A, except the platinum concentration on the final catalyst was 0.6% by weight.

Catalyst D : 0.6% Pt and 1% F/ Al_2O_3

For the preparation 0.6% Pt & 1% F/ Al_2O_3 catalyst the alumina was impregnated using the same procedure as described for catalyst A, except the platinum concentration on the final catalyst was 0.6% by weight, and the final fluoride concentration of catalyst was 1% by weight.

Catalyst E : 0.3% Pt and 0.5% F/Molecular sieve

Catalyst F : 0.3% Pt and 1% F/Molecular sieve

Catalyst G : 0.6% Pt and 0.5% F/Molecular sieve

Catalyst H : 0.6% Pt and 1% F/Molecular sieve

To prepare catalyst E, F, G and H respectively, an impregnation procedure were the same procedure that used for the preparation of catalyst A. Except the alumina support was replaced by a 4A molecular sieve, and the remainder of the procedure still unchanged.

(2) Activation of Catalysts

Both Pt-F on alumina and Pt-F on molecular sieve catalysts had been activated under hydrogen pressure before being used. Every calcined catalysts in this research were packed in a tube reactor. The tube reactor was then installed in a furnace, which was used for a reaction unit. The temperature was gradually increased to 450°C and the hydrogen pressure was maintained at 60 psi for 6 hours to obtain the activated catalyst.

(3) Regeneration of Catalysts

The used catalyst was taken out of the tube reactor and brought to decoke in a furnace at 550°C for at least 10 hours minimum. Then it was activated, following the activation procedure mentioned, before reusing.

(4) Characterization of Catalysts

The platinum content of catalysts were characterized by X-ray Fluorescence (XRF) spectroscopy at the Instrument Center of Chulalongkorn University (their compositions and percentage were calculated by this instrument with the library search program).

The XRF chromatograms of catalysts are shown in Figure E1-E4. The percentages of platinum are presented in Table 4.1.

3.3.2 Aromatization Reaction Procedure [33]

(1) Reaction Unit

Aromatization reaction was operated in a 316 stainless steel tube which were packed with catalysts. This tube was installed in a furnace that was adapted from some GC units and it could control the temperature to reach a desired reaction temperature. There was a temperature gauge over the furnace for checking the accuracy of reaction temperature which was controlled by the temperature control unit.

A hydrogen tank was connected to the inlet side of injection port and was used for supplying hydrogen gas into the tube through out the reaction operation.

The condensation unit was composed of an ether condenser, which has a large top opening for easy introduction of dry ice/acetone mixtures. These coolants provided rapid condensation of the volatile product. The condenser was connected to the outlet terminal of the tube for condensing the products from reactions. This made it possible to condense the products from the condenser, which were collected into a round bottom flask that was dipped in a bath with acetone-dry ice.

(2) Reaction Procedure

NGL (as the feed) was injected into the heated tube that packed with catalysts, under reaction condition during flowing of hydrogen gas. The products in the gaseous phase were taken out by hydrogen carrier gas, and then were condensed with a condenser at the condensation unit. In every reaction operation of this research, hydrogen gas was used for about 30 minutes to flush out the rest of the remaining products in the tube and to completely collection of all the products.

3.3.3 The Various Effects on Aromatization Reactions

(1) Effect of Hydrogen Pressure

The effect of hydrogen pressure in aromatization of NGL was studied at different hydrogen pressures (20, 40, and 60 psi) on 0.6% Pt & 0.5% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ catalyst.

(2) Effect of Temperature

The temperature effect in aromatization of NGL was studied at various reaction temperatures (350, 370, 400 and 430°C) on 0.6% Pt & 0.5% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ catalyst. All runs were performed in 40 psi hydrogen pressure.

(3) Effect of Catalyst Concentration

(a) Study of Hydrogenation-Dehydrogenation Center Effect

The effect of hydrogenation-dehydrogenation center (Pt-concentration effect) was performed by using 0.3% Pt & 1% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ catalyst under experimental conditions.

(b) Study of Acidic Center Effect

The effect of acidic center (F-concentration effect) was studied by using 0.6% Pt & 0.5% F/Al₂O₃ and 0.6% Pt & 1% F/Al₂O₃ catalyst under experimental conditions.

(4) Effect of Solid Support

The effect of solid support in aromatization of NGL was studied by using different support between alumina and 4A molecular sieve support. The experiments were done under 60 psi hydrogen pressure and on the catalysts below:

- 0.3% Pt & 0.5% F/4A catalyst
- 0.3% Pt & 1% F/4A catalyst
- 0.6% Pt & 0.5% F/4A catalyst
- 0.6% Pt & 1% F/4A catalyst
- 0.6% Pt & 0.5% F/Al₂O₃ catalyst

(5) Reproducibility and Activity of Used Catalyst

The reproducibility and activity of used catalyst were studied on the 0.6 % Pt & 0.5 % F/Al₂O₃.

3.3.4 Analysis of Reactant and Products

NGL and its conversion products were characterized by PIONA GC of Petroleum Authority of Thailand (PTT) following the ASTM D5443-93 [34] (their compositions and percentage were calculated by this instrument with the library search program).

The GC chromatogram of NGL is shown in Figure A1 in Appendix A. The compositions and its amount are presented in Table 4.2. The GC chromatograms of the important products are shown in Appendix A. All the data concerning the percentages of compositions, percentages of conversion and percentage of yield of aromatics were are in Appendix B, C, and D respectively.