CHAPTER III

EXPERIMENTAL SECTION

3.1 Apparatus and Instruments

Hot-plate magnetic stirrer from Snijders model 34532 was used for catalysts preparation step. The calcinator from carbolite furnace model GSM was used to calcine catalysts. The prepared catalysts was packed in Annealed 316 stainless steel tubing reactors with 1/4 in. O.D. x 0.035 in. wall thickness x 6 feet length. Furnace for reaction unit was adapted from an old gas chromatograph instrument from Pye Unicame GC models Pye series 104 chromatograph. The temperature of the reaction unit was controlled by Union model PZ-6 temperature controller. To adapt the electronic power for heating coil (3000 W), the system uses Mitsubishi magnetic contractor model S-N10 for temperature support. Condenser cooled with acetone-dry ice was used to condense the major products. HPLC pump model Water 510 was used for continuously reactant injection.

The GC-MS chromatograms were recorded on a Fison Instruments (Trio 2000) GC-MS chromatograph. The quantities of aromatics and other products were measured using a HP5890 Series II gas chromatograph (GC) from Hewlett Packard.

3.2 Materials

Zeolite ZSM-5 was obtained from Nissan Company, Japan. Ammonium fluoride analytical grade, palladium (II) chloride anhydrous purum grade, n-hexane analytical grade were purchased from Fluka. Chloroplatinic acid hexa-hydrate was from Crystal Baker Analyzed. Zinc (II) chloride analytical grade was from Carlo Erba. Industrial hydrogen gas, nitrogen gas, helium gas, and air zero gas was obtained from Thai Industry Gas (TIG).

3.3 Experimental procedures

3.3.1 Continuous Aromatization Reaction Procedure

3.3.1.1 Reaction Unit

All studies in this research were performed using the reaction unit as showing in Figure 3.1. Continuously aromatization reaction was operated in tubing reactor (B) containing packed catalyst. This tube was installed in a furnace (D) that the temperature could be controlled for desired reaction temperatures. There were a thermocouple (C) in the furnace, 3000 W heating coil and circulating fan for distribution heating system. The accurate reaction temperature was controlled by the temperature control unit (E) (breaker, temperature controller and magnetic relay).

Supply of hydrogen gas was fed to tubing reactor passed inlet side of tubing reactor of injection unit. A liquid line was connected in the same

direction of hydrogen to the tubing reactor for continuous injection of hexane into the reaction unit using HPLC pump.

The condensation unit (**F**) was composed of a condenser cooled with acetone-dry ice and a reservoir set. 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 reactor, which were collected into a reservoir flask that was dipped in a bath with acetone-dry ice.

3.3.1.2 Reaction Procedure

Hexane was injected into the heated tubing reactor which packed with catalyst, under reaction condition by HPLC pump feeding. The products in the gaseous phase were condensed in cool condensation unit. For all reactions, the products in the tube were flashed out by hydrogen gas for 30 min.

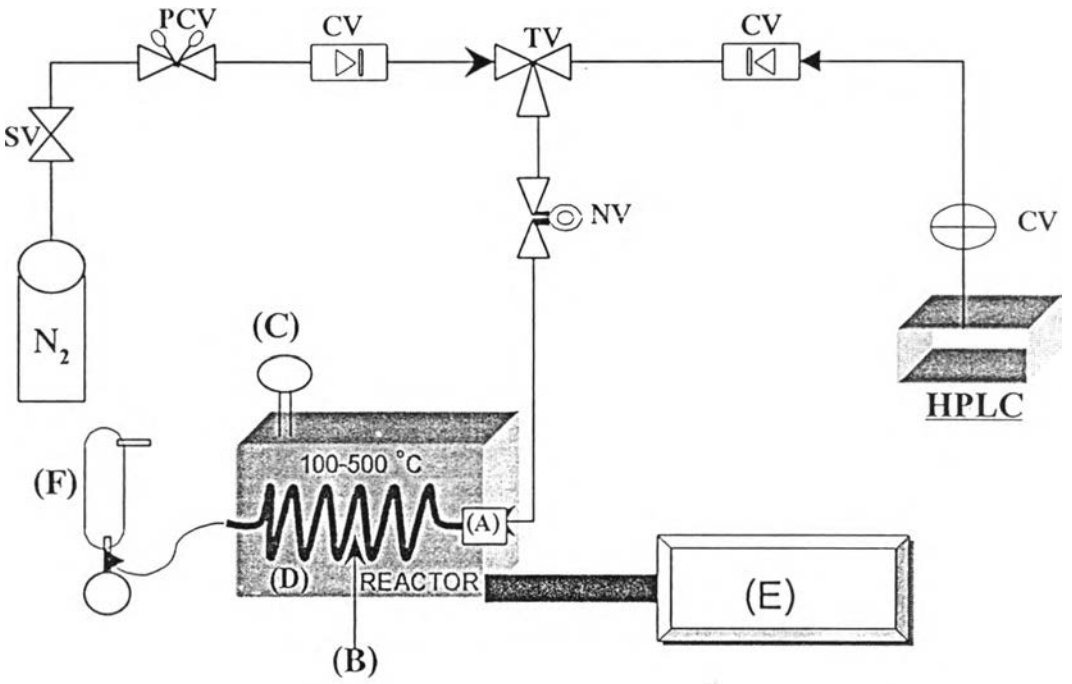

Figure 3.1 Schematic drawing of the continuous reaction unit

CV	=	check valve
NV	=	needle valve
PCV	=	pressure control valve (regulator)
SV	=	stop valve
TV	=	three-way valve
A	=	injection unit
B	=	tubing reactor
C	=	temperature gauge
D	=	furnace
E	=	temperature control unit
F	=	condensation unit

3.3.2 Preparation, Activation, Regeneration and Characterization of Catalysts

3.3.2.1 Preparation of Catalysts

3.3.2.1.1 Impregnation of Platinum on Alumina Support prior to Fluoride doped

A: Catalyst containing 0.6% Pt and 0.5% F on Alumina Support

The alumina support (9.89 g) was impregnated by an aqueous hexachloroplatinic acid solution (4 ml, 0.0769 M) to obtain 0.6% platinum on the final catalyst. And then the obtained product was dried for 16 hours at 120°C and then calcined for 3 hours at 500°C. The calcined product was re-impregnated by an aqueous ammonium fluoride solution (2.4 ml, 1.097 M). The final fluoride concentration of catalyst was 0.5% by weight, and it was dried for 16 hours at 120°C. Finally, the product was calcined at 150°C for 1 hour, and then temperature was raised from 150°C to 500°C in 15 minutes and then held at 500°C for 3 hours.

3.3.2.1.2 Ion Exchange of Zinc on Zeolite

B: Catalyst Containing 10% Zn on ZSM-5 Support

The Na/ZSM-5 zeolite (4.5 g) was stored in saturated ammonium chloride solution (50 ml) desicator at least 4 day for fully hydration. The fully hydrated Na/ZSM-5 zeolite was subjected to cation exchanged by an aqueous zinc chloride solution (50 ml, 0.1528 M) to obtain 10% zinc on the final catalyst. This

composition was added to distillated water (1000 ml) and then stirred for 8-15 hours. The cation exchanged zeolite was filtrated and then washed with deionized water (~2 x 1000 ml) to remove chloride ion (test by $AgNO_3$ solution) and then dried at 120-140 °C for 2-3 hours. Finally, the zeolite Zn/ZSM-5 was calcinated at 500 °C for 3-5 hours to obtain the calcined 10% Zn on ZSM-5 zeolite support catalyst.

3.3.2.1.3 Ion Exchange of Palladium on Zeolite

C: Catalyst Containing 2% Pd on ZSM-5 Support

Catalyst containing 2% Pd on ZSM-5 support was prepared by the same ion exchange procedure of Zn/ZSM-5 except that the palladium chloride solution (50 ml. 0.0188 M) was use as cation. The final palladium concentration of catalyst was 2% by weight and was stirred in distillated water was for 15 hours.

D: Catalyst Containing 0.5% and 1% Pd on ZSM-5 Support

For 0.5% and 1% of Pd/ZSM-5, the catalysts were prepared by the same procedure as described for catalyst C, except that the final palladium concentration of catalyst was 0.5% and 1% by weight, respectively, which can also be prepared from $PdCl_2$ solution (50 ml, 0.0047 M and 50 ml, 0.0094 M, respectively).

3.3.2.2 Activation of Catalysts

In the aromatization reaction, the Pt-F on alumina, Zn on ZSM-5 support and Pd on ZSM-5 support catalysts were activated under hydrogen pressure before using. Each calcined catalyst in this research was packed in a tubing reactor. The tubing reactor was installed in a furnace, which was used in a reaction unit. The temperature was increased to 450°C while maintained the flow of hydrogen at 60 psi for 6 hours to obtain the activated catalysts.

3.3.2.3 Regeneration of Catalysts

The used catalyst was taken out of the tubing reactor and decoked in a furnace at 550°C for the minimum of 10 hours, and then was activated again, following activation procedure mentioned above, before reuse.

3.3.2.4 Characterization of Catalysts

The percentages of zinc and palladium in the catalysts were characterized by X-ray fluorescence (XRF) spectroscopy (their composition and percentage were calculated by this instrument with the library search program).

3.3.3 The Various Effects on Continuous Aromatization Reactions

3.3.3.1 Effect of Temperature

Various reaction temperatures (200, 250, 300, 350, 400, and 450°C) were studied for the temperature effect on continuous aromatization of

hexane over 2% Pd/ZSM-5 catalyst under feeding rates of 0.2-1.0 ml/min to find the optimum reaction temperature in aromatization of hexane.

3.3.3.2 Effect of Feeding Rate

The effect of feeding rate on continuous aromatization of hexane was studied at 0.2, 0.4, 0.6, 0.8, and 1.0 ml/min for all of reaction temperatures and concentrations of catalyst to obtain the optimum feeding rate.

3.3.3.3 Effect of Catalyst Concentration

The effect of hydrogenation-dehydrogenation centre (Pd-concentration effect) was performed using 0.5% Pd, 1.0% Pd, and 2.0% Pd ion exchange on Na-ZSM-5 catalyst under the optimum feeding rate (0.4 ml/min) and several reaction temperatures (300, 350, 400, and 450°C) to find the optimum concentration of palladium for continuous aromatization of hexane.

3.3.3.4 Effect of Metal and Support on Catalyst

The effect of metal and support of catalyst on continuous aromatization of *n*-hexane was studied using different metal (platinum, zinc and palladium) and support (Al_2O_3 and ZSM-5). The experiment was done under the optimum reaction temperatures (400 and 450°C) and several feeding rates (0.2-1.0 ml/min) to find the best metal on catalyst.

3.3.3.5 Activities of Used Catalyst and Reproducibility

The reproducibility and activity of used catalyst were studied on 2% Pd/ZSM-5 catalyst under 0.4 ml/min feeding rate at 300-450°C.

3.3.4 Analysis of Reactant and Products

Gas chromatograph model HP5890 was used for characterization of *n*-hexane and its conversion products. Their hydrocarbon compositions were identified by GC-MS. Quantitative analysis were studied using gas chromatograph and then the calculations of percentages of conversion in the aromatization reactions were studied from percentages of compositions represented by peak areas of the reactant, the product and internal standard.