

## CHAPTER III EXPERIMENTAL



### 3.1 Materials and Equipment

#### 3.1.1 Materials

- Metal Precursors
  - Tetraamineplatinum (II) nitrate [Pt(NH<sub>3</sub>)<sub>4</sub> (NO<sub>3</sub>)<sub>2</sub>] supplied by Sigma-Aldrich (99.995% purity on trace metal basis)
  - Iron (III) nitrate nonahydrate [Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O] supplied by Sigma-Aldrich (≥99.999% purity on trace metal basis)
  - Cobalt (II) nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O] supplied by Sigma-Aldrich (98% purity)
  - Ruthenium (III) chloride [RuCl<sub>3</sub>] supplied by Sigma-Aldrich (>98% purity)
  - Potassium nitrate [KNO<sub>3</sub>] supplied by Carlo-Erba (≥ 99% - acidimetric)
- Other Chemicals
  - Glycolic acid [HOCH<sub>2</sub>CO<sub>2</sub>H] supplied by Sigma-Aldrich (99% purity)
  - Ammonium hydroxide [NH<sub>4</sub>OH]
  - Anhydrous ethanol [CH<sub>3</sub>CH<sub>2</sub>OH]
- Zeolite Supports
  - Potassium form of L zeolite supplied by Tosoh-Corporation (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 6.1, BET surface = 290 m<sup>2</sup>/g)
  - NH<sub>4</sub><sup>+</sup> form of ZSM5 zeolite supplied by SCG chemicals (Si/Al = 23 with 20% wt. of alumina binder, BET surface = 310 m<sup>2</sup>/g)
- Gases
  - Carbon monoxide in hydrogen (40% CO in hydrogen)
  - Hydrogen (99.999% purity)

- Nitrogen (99.99% purity)
- Helium ( 99.995% purity)
- Air (99.99% purity)

### 3.1.2 Equipment

- Catalyst Preparation
  - Glassware
  - Ceramic crucible
  - Magnetic stirrer with hotplate
  - Muffle furnace
  - Drying oven
- Catalyst Characterization
  - Micrometric temperature programmed reduction (TPR) equipped with TCD
  - Thermo Fannigan temperature programmed desorption, reduction and oxidation 1100 equipped with FID
  - Quantacrome Autosorb 1MP surface area analyzer
  - Pyris diamond TG/DTA instrument
  - Bruker/XAS, D8 advance x-ray diffraction instrument
  - Temperature programmed oxidation apparatus equipped with SRI model 10 detector
  - Hitachi/S-4800 scanning electron microscope with energy dispersive x-ray
- Catalyst Activity Testing
  - Continuous flow fixed bed stainless steel reactor
  - Agilent 6890N network gas chromatograph equipped with thermal conductivity detector (TCD) and flame ionization detector (FID)
  - Ritter TG 05/2 drum type gas meter
  - Brooks 0152/CC1A10 two channel mass flow controller
  - Carbolite VST 12/200 furnace for reactor heating

## 3.2 Methodology

Experimental procedures in this research can be mainly classified to three main components as catalyst preparation, catalyst characterization, and catalytic activity testing. Each step is discussed in detail in the following sections.

### 3.2.1 Catalyst Preparation

Incipient wetness impregnation (IWI) and co-precipitation (CP) techniques were used to prepare catalysts in this work. IWI is used as in many researches due to its simplicity and good composition control while CP technique is used for unsupported Fe-based catalyst for FT synthesis. Detailed procedures with process parameters are presented in next two topics.

#### 3.2.1.1 *IWI Preparation of Supported Catalysts*

Two types of catalyst supports were used in this process as KL and HZSM5 zeolite. In the test of Pt/KL zeolite catalyst, Fe, Pt or Fe and Pt together impregnated on KL zeolite with different compositions of metal. The detailed procedure is as in following steps.

- a. K-LTL-zeolite was dried at 110 °C overnight and calcined at 400 °C for 5 h.
- b. Pore volume of KLTL-zeolite was determined by Autosorb 1MP surface area and pore volume analyzer using N<sub>2</sub> adsorption/desorption method to obtain the solution volume need for IWI.
- c. Both tetraamineplatinum (II) nitrate and iron (III) nitrate nonahydrate were dissolved together in distilled water to obtain exactly a same volume of solution as pore volume of the support in co-impregnation. For physically mixed catalyst test, Fe and Pt were impregnated to K-LTL-zeolite separately.
- d. Mixture was dried at 110 °C overnight in an oven and cooled to room temperature.
- e. A thermo gravimetric analysis (TGA) test was carried out to find the proper calcining temperature for different type of catalyst to obtain the metal precursor decomposition temperatures.

- f. Calcination of the dried mixture was conducted with 100 cm<sup>3</sup>/min.g of catalyst of air flow by increasing the temperature at the rate of 3 °C/min to the temperature of 500 °C and kept for 3 h at that temperature and cooled to room temperature. The prepared catalyst was then stored in a desiccator.

### 3.2.1.2 CP Preparation of Unsupported Catalysts

FeCoK catalyst for FT synthesis was prepared by co-precipitation technique by precipitation of Fe and Co as a salt formed with alpha hydroxyl carboxylic acid. The detailed precipitation procedure is described below (Soled *et al.*, 1985).

- a. Iron (III) nitrate nonahydrate and cobalt (II) nitrate hexahydrate were dissolved in distilled water with relevant precursor weights to form an unsaturated solution to prevent salt crystal formation. All solution preparation was done at room temperature and atmospheric pressure.
- b. Two cubic centimeters of ethanol per 50 cm<sup>3</sup> of solution were added to the solution to improve the solubility of the organic salt formed in the next step.
- c. Stoichiometric quantity of glycolic acid with 5 % excess related to both Fe and Co in the solution was added to the Fe and Co salt solution step wise with sufficient amount of ammonium hydroxide to maintain the solution pH in the range 5 -7.
- d. Then, the solution was evaporated at 80 °C to obtain solid and then dried at 80 °C overnight.
- e. The dried catalyst was then calcined at 350 °C with 2 °C/min heating rate and holding for 2 h and cooled to room temperature.
- f. Addition of K was done by impregnation of potassium nitrate solution on Fe and Co oxides.
- g. The impregnated mixture was then dried at 110 °C overnight followed by calcining at 350 °C with 2 °C/min heating rate and holding for 2 h and cooled to room temperature.
- h. The prepared catalyst is then stored in a desiccator.

A total list of catalysts synthesized for the experiment with preparation technique and notation used for each catalyst is presented in Table 3.1.

**Table 3.1** List of catalysts synthesized for FT synthesis and syngas aromatization

Catalyst	Preparation Technique	Notation
0.5% Pt on KL	Incepient Wetness Impregnation	0.5Pt/KL
9.5% Fe on KL	Incepient Wetness Impregnation	9.5Fe/KL
FeCoK	Co-precipitation	FeCoK
9.5%Fe0.5%Pt/KL	Co-impregnation	9.5Fe0.5Pt/KL
4.5%Fe0.5%Pt/KL	Co-impregnation	4.5Fe0.5Pt/KL
9.5%Fe/KL + 0.5%Pt/KL	Physical Mixing	9.5Fe/KL + 0.5Pt/KL
33% HZSM5 in FeCoK	Physical Mixing	33ZFeCoK
44% HZSM5 in FeCoK	Physical Mixing	44ZFeCoK
67% HZSM5 in FeCoK	Physical Mixing	67ZFeCoK
75% HZSM5 in FeCoK	Physical Mixing	75ZFeCoK
80% HZSM5 in FeCoK	Physical Mixing	80ZFeCoK

### 3.2.2 Catalyst Characterization

Characterization of catalyst was done in different stages depending on their importance for several objectives such as determination of calcining and reduction temperatures, surface composition, crystalline form of catalyst, and characterization of coke deposited after reaction. Techniques used for each measurement are presented below.

- Thermogravimetric analysis (TGA) to find the metal precursor decomposition temperature.
- Temperature programmed reduction (TPR) for catalyst reducibility test.
- Temperature programmed oxidation (TPO) for spent catalysts to analyze the amount and characteristics of coke deposited.
- Brunauer-Emmett-Teller (BET) method with Autosorb IMP instrument to find surface area of the catalyst.
- X-ray diffraction(XRD) to identify different phases available in catalyst
- Scanning electron spectroscopy with energy dispersive x-ray (SEM-EDX) to observe the morphology of catalysts and composition of surface

### 3.2.3 Catalyst Activity Testing

Activity and selectivity were measured for CO hydrogenation with H<sub>2</sub> to form hydrocarbons. Several variables including catalyst composition, process parameters and preparation technique were investigated. Activity and selectivity calculations were conducted based on formulae given below to compare the different systems.

Activity is determined by percentage of injected CO converted by the reaction by measuring the unconverted CO in the products and conversion can be illustrated as in the following formula.

$$\text{Conversion, \%} = \frac{(\text{CO moles in feed}) - (\text{CO moles in product})}{\text{CO moles in feed}} \times 100\%$$

Selectivity is determined in C atom basis as percentage of C atoms in each product from the total C atoms in converted CO in the reaction and can be represented in following formula.

$$\text{Selectivity to product } i, \% = \frac{(\text{Moles of product } i) \times (\text{C atoms per mole of } i)}{\text{C atoms in CO converted}} \times 100\%$$

Activity tests were carried out in a stainless steel continuous down flow isothermal fixed bed reactor (0.402" ID) with 0.5 g of catalyst in the middle of the reactor. The reactor will be kept on isothermal condition by heating with a furnace and the bed temperature was maintained at required value with external thermocouple fixed inside the bed. Figure 3.1 shows the way the catalyst was packed in the middle of the reactor (catalyst loading diagram) and the flow scheme for the catalyst testing is shown in Figure 3.2.

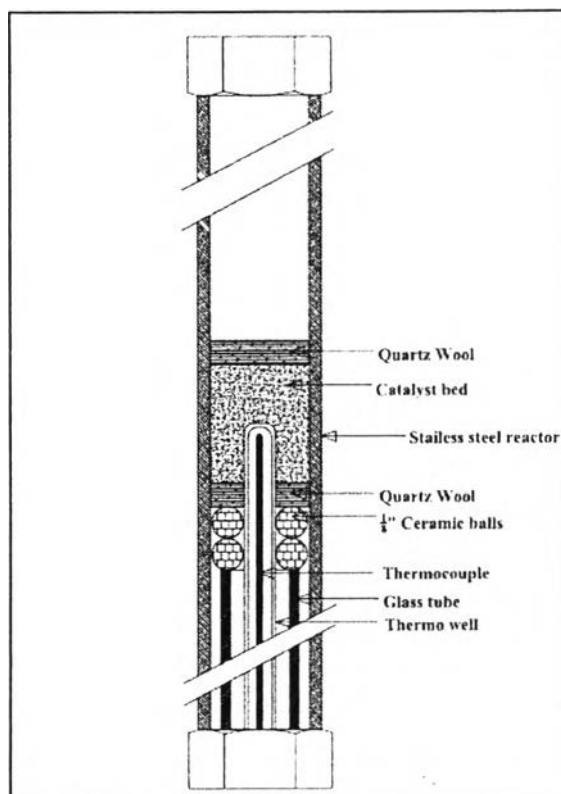


Figure 3.1 Catalyst loading diagram.

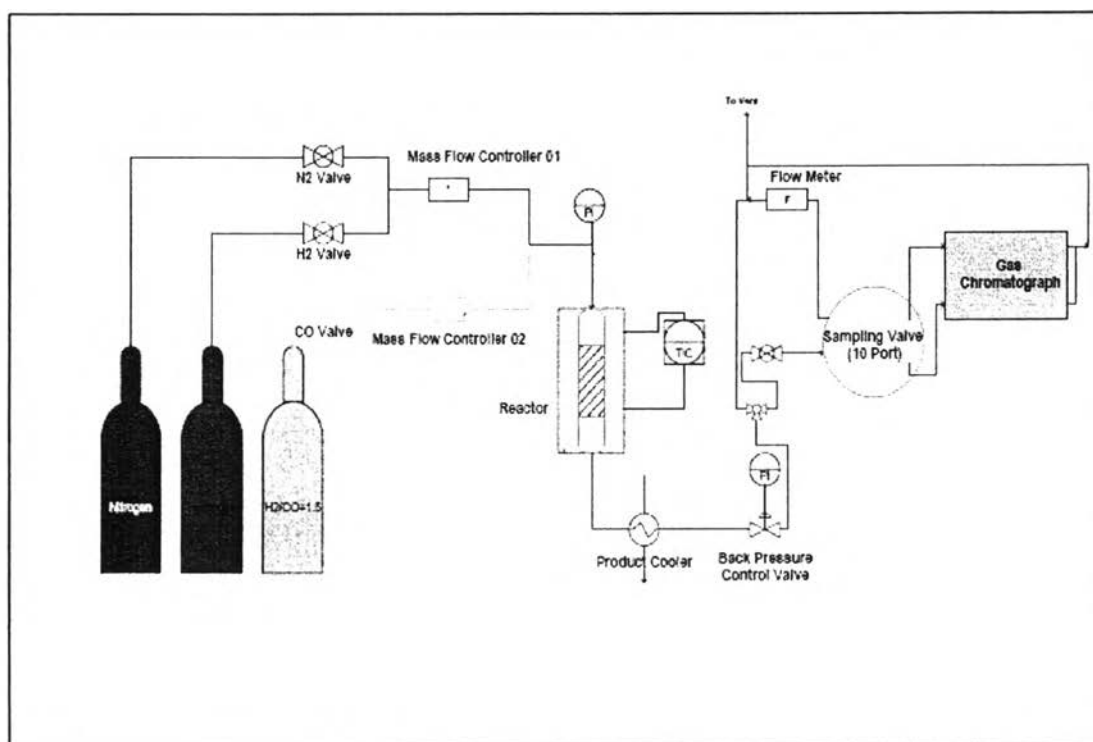


Figure 3.2 Flow schematic for the catalyst testing.

Each catalyst was reduced in-situ with H<sub>2</sub> (100 cm<sup>3</sup>/g.min) for 3 h before the reaction. The reducing temperature determined by TPR and literature was used for each catalyst.

After reduction, temperature was brought to the reaction temperature decided and the reactant mixture was introduced to the reactor with relevant flow rate to maintain the required GHSV. The flow rate of the gas was measured and controlled by a mass flow controller as shown in the Figure 3.2. The product flow rate was measured by the wet test gas flow meter which is installed at the end of the process line.

The reaction products were analyzed by an online Agilent 6890N network gas chromatograph equipped with a HP-Plot Al<sub>2</sub>O<sub>3</sub> capillary column connected to FID for hydrocarbon analysis and a Hayesep T packed column for permanent gases with TCD. Activity of the catalyst was determined over the time of reaction to observe the deactivation and selectivity changes by analyzing product samples hourly (in some cases it was one sample every 60 or 90 min).

The catalyst testing experiments were conducted as in the following sequence for different forms of catalysts.

#### 3.2.3.1 *Activity of Fe/KL zeolite and FeCoK catalysts*

Before conducting the aromatization of syngas, the activity and product selectivity of Fe impregnated on KL zeolite was conducted to establish a suitable temperature for obtaining better range of paraffin to be converted to aromatics in the aromatization catalysts.

#### 3.2.3.2 *Syngas aromatization with co-impregnated FePt/KL and physically mixed catalysts*

Catalysts prepared by co-impregnation of Fe and Pt and physically mixed catalysts (Fe/KL and Pt/KL) were tested for syngas aromatization with conditions obtained from previous experiments. Further, FeCoK physically mixed with Pt/KL was also studied.



3.2.3.3 *Syngas aromatization with physically mixed hybrid catalysts of FeCoK and HZSM5 (with different proportions)*

FeCoK and HZSM5 hybrid catalysts were tested for syngas aromatization by varying the HZSM5 portion in the catalyst to observe the influence on activity and selectivity.

Hybrid catalysts containing FeCoK and HZSM5 were denoted by following notation with HZSM5 weight percentage in the catalyst. Any catalyst is noted as  $yZ\text{FeCoK}$  where  $y$  indicates the percentage of HZSM5 in the catalyst and  $Z$  is for HZSM5. As an example, hybrid catalyst which contains 75 wt. % of HZSM5 in the catalyst by weight is noted as  $75Z\text{FeCoK}$ .