

CHAPTER IV

EXPERIMENT

4.1 Preparation of the H-ZSM-5

The preparation procedure of H-ZSM-5 by the rapid crystallization method [106] developed by Prof. Tomoyuki Inui's laboratory is shown in Figure 4.1, while reagents are shown in Table 4.1. TPABr (Tetra-n-Propyl Ammonium Bromide, $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]\text{Br}$) was used as an organic template. The atomic ratio of Si/Al was set at 50.

4.1.1 Preparation of Decantation Solution and Gel Precipitate

Formation : Firstly, a decant solution was prepared by adding 60 ml of A1-solution and 45 ml aqueous solution of B1-solution to 104 ml of C1-solution, as shown in Figure 4.2, with magnetic stirring. From Figure 4.2, A1-solution was added by the microfeeder at a volumetric flow rate 12.0 cc/min and B1-solution was added from a 50 ml burette by the manual control to keep the pH of a mixed solution in the range 9.5-10.5, since it is expected that this pH value is suitable for precipitation. After the mixing has ended, take the beaker C-solution out of the set. Let the magnetic

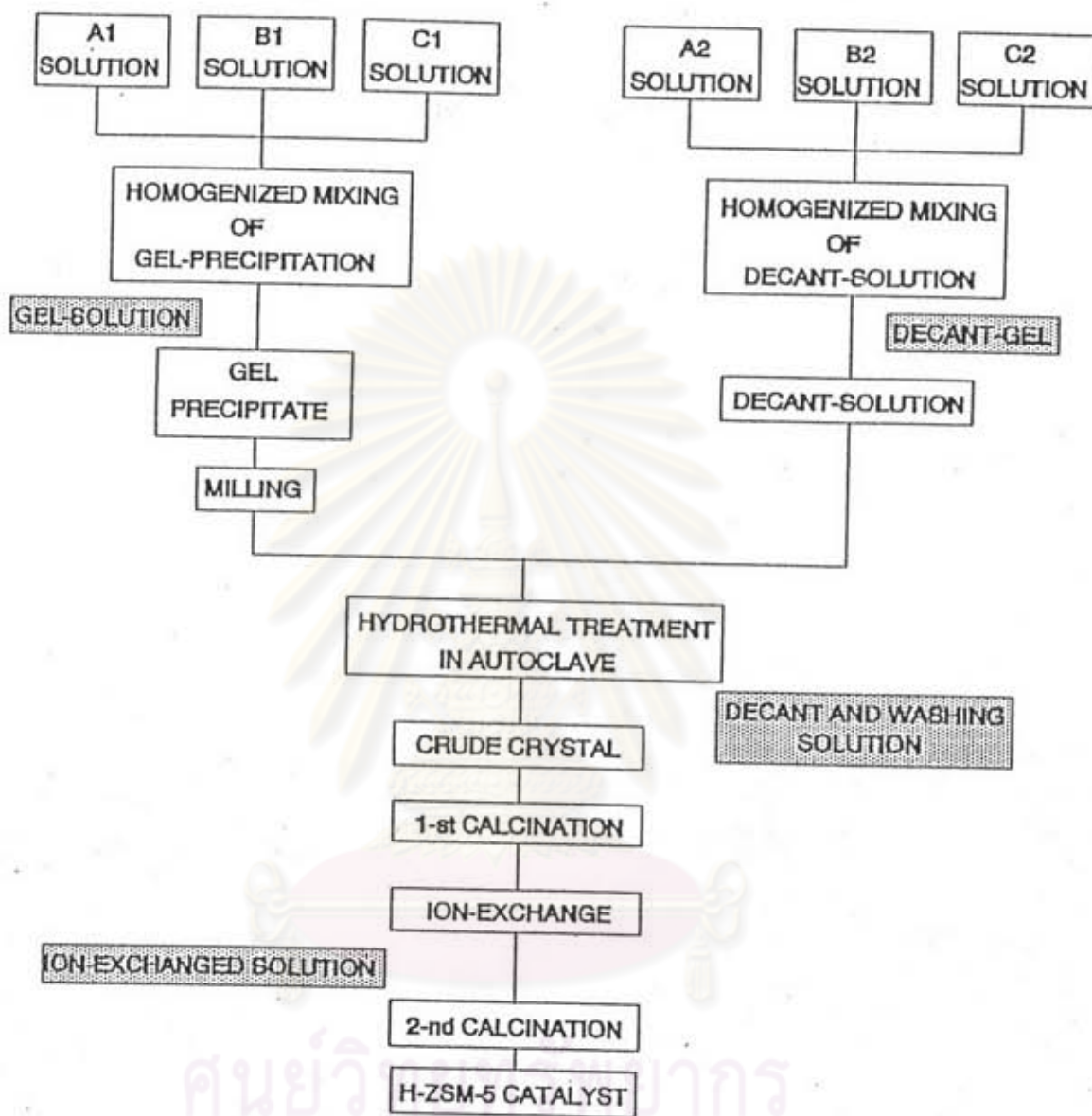


Figure 4.1 Preparation procedure of ZSM-5 by rapid crystallization method.

Table 4.1 Reagents used for the preparation of H-ZSM-5 (Si/Al=50).

Solution for the gel preparation (wt.%)	Solution for decant-solution preparation (wt.%)
<u>Solution A1</u>	<u>Solution A2</u>
AlCl ₃ 1.10	AlCl ₃ 1.25
TPABr 6.95	TPABr 10.45
NaCl 14.63	Distilled water 83.57
Distilled water 73.17	H ₂ SO ₄ (conc.) 4.73
H ₂ SO ₄ (conc.) 4.15	
<u>Solution B1</u>	<u>Solution B2</u>
Sodium silicate 60.53	Sodium silicate 60.53
Distilled water 39.47	Distilled water 39.47
<u>Solution C1</u>	<u>Solution C2</u>
TPABr 0.87	NaCl 20.18
NaCl 15.97	Distilled water 79.82
NaOH 0.94	
Distilled water 81.83	
H ₂ SO ₄ (conc.) 0.39	

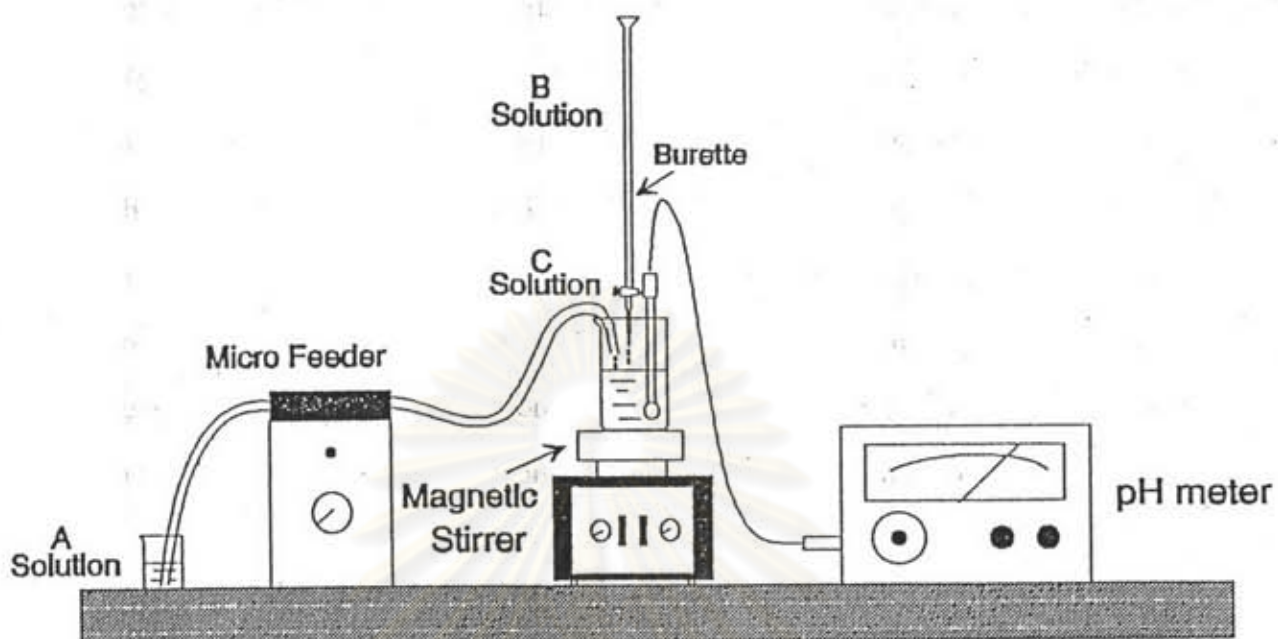


Figure 4.2 A set of apparatus used for preparation of supernatant solution and gel precipitate as provide for the rapid crystallization method.

bar out and measure the sedimentation time of the precipitate. The precipitating was removed from the supernatant solution by a centrifuge and the supernatant solution was kept for mixing with gel precipitate. Secondly, a gel mixture was prepared by adding 60 ml of A2-solution and 45 ml of B2-solution to 208 ml of C2-solution. The method of mixing and condition are the same as the preparation of decantation solution, except that before mixing adjust the pH of solution between 9.5–10.5 with H_2SO_4 (conc.) or 1 M NaOH solution. Measure the sedimentation time of precipitate and separate the precipitate from solution by centrifuge. The precipitated gel

mixture was milled by powder miller (Yamato-Notto, UT-22). Figure 4.3, as follows; milled 15 min → centrifuge 15 min (for removed the water out) → milled 15 min → centrifuge 15 min → milled 30 min.

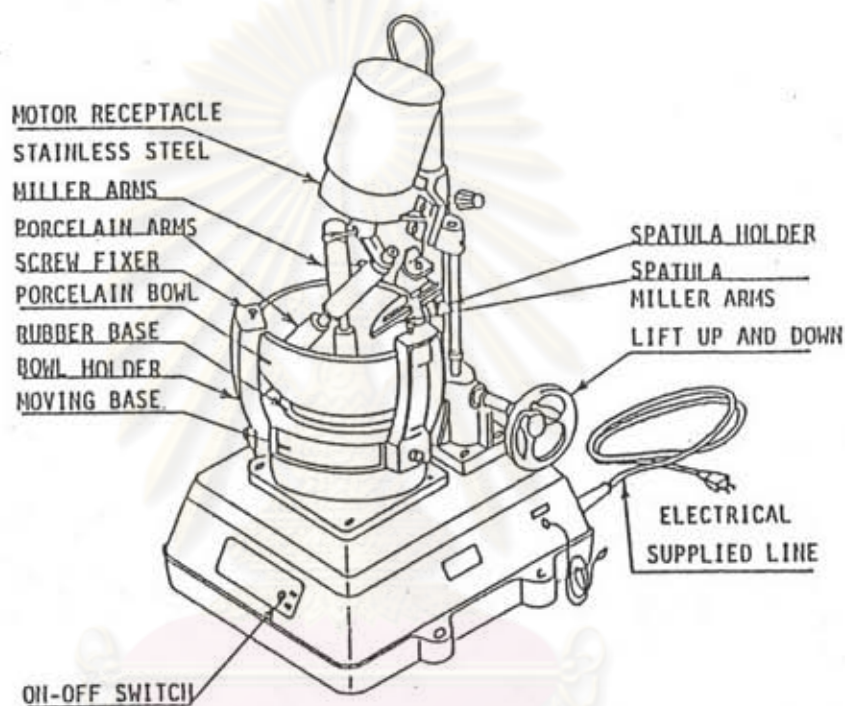


Figure 4.3 A powder miller (Yamato-Notto, UT-22).

4.1.2 Crystallization

The milling precipitate and the supernatant of decant solution would mix together. The mixture was heated for crystallization in an autoclave from room temperature to 160°C in 90 min and to 210°C in 4.2 h under a pressure of 3 kg/cm²(gauge)

of nitrogen gas. Allow the hot mixture to cool down at room temperature in an autoclave over-night. The product crystals were washed with distilled water, to remove Cl^- out of the crystals, about 8 times by using the centrifuge separator (about 15-20 min for each time) and dry in oven at 110-120 $^{\circ}\text{C}$ for at least 3 h.

4.1.3 First Calcination to Furnish the Pore Structure and Channel Dimensions in Crystals

Weighing 6-7 g of dry crystals in a porcelain container which have the shape like a boat, and heat in a furnace as follows;

room temperature $\xrightarrow{60 \text{ min}}$ 540 $^{\circ}\text{C}$, keep constant at this temperature 3.5 h.

At this step, TPABr was burned out and left the cavities and channels in the crystals. The calcined crystal was cooled to room temperature in a dessicator. After this step the catalyst was called "Na-ZSM-5".

4.1.4 Ion-exchange

About 1.5 g. of calcined crystal was mixed with 45 ml of 1 M NH_4NO_3 and heated on stirring hot plate at 80 $^{\circ}\text{C}$ for 1 h. Repeat ion-exchange step again 1 time. Washing the ion-exchanged crystal with deionized water 2 times by using centrifugal separator.

Then, ion-exchanged crystal was dried at 110–120 °C about 3 h in oven.

4.1.5 Second Calcination

The removal species, i.e. NH_3 , NO_x , were decomposed by thermal treatment the ion-exchanged crystal in a furnace at 540°C, with the temperature operating line the same as first calcination. After this step the catalyst was called "H-ZSM-5".

4.2 Loading Pt and/or Re by Ion-exchange

A part of protons in the H-ZSM-5 was replaced with Pt (or Re) by ion-exchange method. The ion-exchange was conducted by treating the H-ZSM-5 with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (or Re_2O_7) solution at 98°C for 3 h. It was heated in air with a constant heating rate of 3°C/min up to 350°C and maintained for 10 min. The calcined H-ZSM-5 was treated with a stream of 20% H_2 - 80% N_2 and heated up from room temperature to 400°C and keep on for 30 min (as shown in Figure 4.4). The percentage of Pt (or Re) in the catalyst varied as 0.25, 0.50, 0.75, and 1.00 wt% [108] (The calculation see Appendix A-2).

In case of loading Pt and Re into H-ZSM-5. Firstly, H-ZSM-5 was ion-exchanged with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ the same as above. The Pt content in the H-ZSM-5 was set at 0.5 wt%. Secondly, Pt/H-ZSM-5 was used to ion-exchange with Re_2O_7 by the same method as loading Pt. The percentage of Re content in the Pt/H-ZSM-5 varied as 0.01, 0.02, 0.05, and 0.10 wt%.

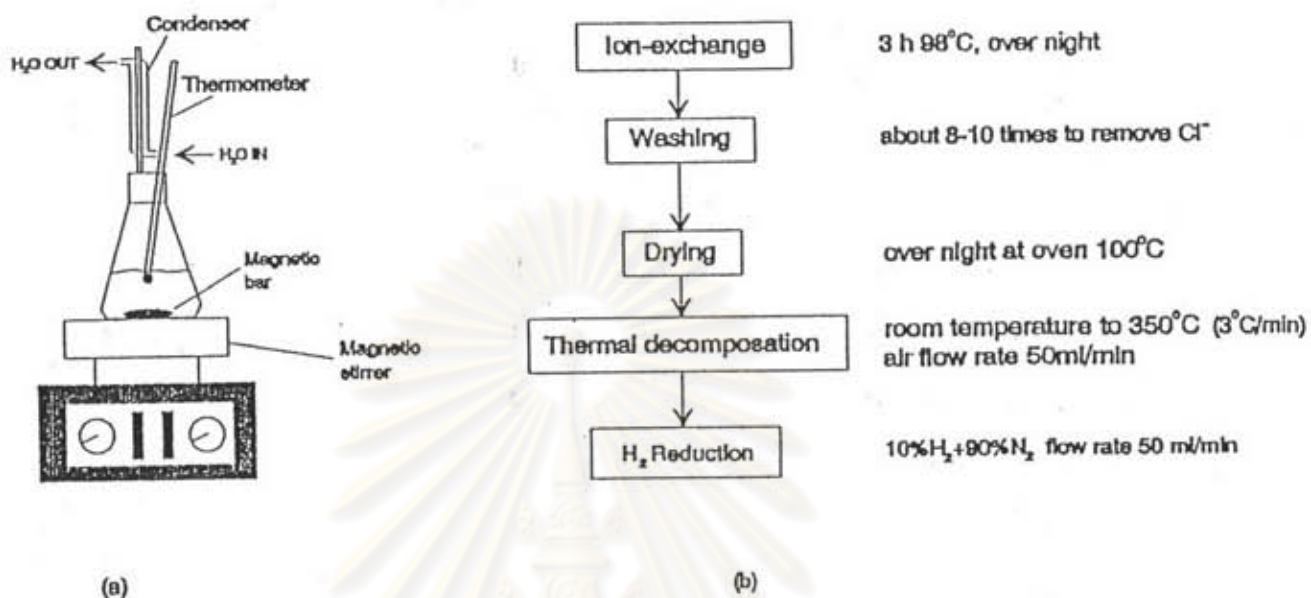


Figure 4.4 A set of apparatus used for preparation of metal ion-exchanged on catalysts (a). A diagram for metal ion-exchanged on catalysts (b).

The catalysts were tableted by a tablet machine. They were crushed and sieved in the range of 8-16 mesh to provide the same diffusion rate and the reaction.

4.3 Apparatus and Reaction Method

The methanol to gasoline conversion reaction was carried out by using a conventional flow apparatus shown in Figure 4.5. A 214 mg portion of the catalyst (ca. 0.3 ml) was packed in a quartz tubular reactor of 6 mm inner diameter. Nitrogen gas was supplied from a

cylinder to control methanol partial pressure and flow rate of the system. Methanol conversion reaction was carried out under the following conditions: total pressure, 1 atm; partial pressure of methanol, 0.2 atm; balance gas, nitrogen; GHSV (Gas Hourly Space Velocity), 2000-4000 h⁻¹; reaction temperature, 350-450 °C.

The procedure used to operate this reactor is as follows;

(1) Adjust the outlet pressure of N₂ gas to 1 kg/cm², and allow the gas to flow through a rotameter (See Appendix A-3).

(2) Adjust 2 three way valves to allow gas to pass through the upper line of the reactor and measure the outlet gas flow rate by using a bubble flowmeter.

(3) Heat up the reactor by raising the temperature as follows:

from room temperature $\xrightarrow{20^{\circ}\text{C}/\text{min}}$ 450°C (hold for 30 min)
 \downarrow adjust to
 The required reaction temperature

and wait until the required reaction temperature becomes constant (the reactor's temperature was controlled by an on-off controller).

(4) At the same time switch on the heating line, magnetic stirrer and water-bath.

(5) Set the partial vapour pressure of methanol to the requirement by adjusting the temperature of water-bath followed the Antonic equation,

$$\log p = A - B/(t+C) \quad (4.1)$$

where p = vapour pressure of methanol, mmHg

t = temperature, °C

A,B,C = constants

For methanol, at range -14°C to 65°C,

$A = 7.89750$, $B = 1474.08$ and $C = 229.13$. (See Appendix B)

(6) Start to run the reaction by adjust 2 three way valves to allow nitrogen gas to pass through the line to the saturator setting in the water-bath used to carry methanol vapour to the reactor, and at that time the reaction time is taken as zero.

(7) Take sample to analyze at 1 and 3 h time on stream. The reaction products were analyzed by two FID-type gas chromatographs and two TCD-type ones. Column used were silicon-OV-1 (0.25 ϕ x 50 m, FID) for gasoline range hydrocarbons, VZ-10 (3 ϕ x 3 m, FID) for gaseous hydrocarbons, Porapak Q (6 ϕ x 3 m, TCD) for CO₂, MeOH, and MeOMe, and MS-5A (6 ϕ x 2 m, TCD) for CO.

4.4 Characterization of the Catalysts

4.4.1 Specific surface area

BET surface areas of these catalysts were measured by N₂ adsorption with the continuous flow method using the gas chromatograph at liquid N₂ temperature. Helium was used as the

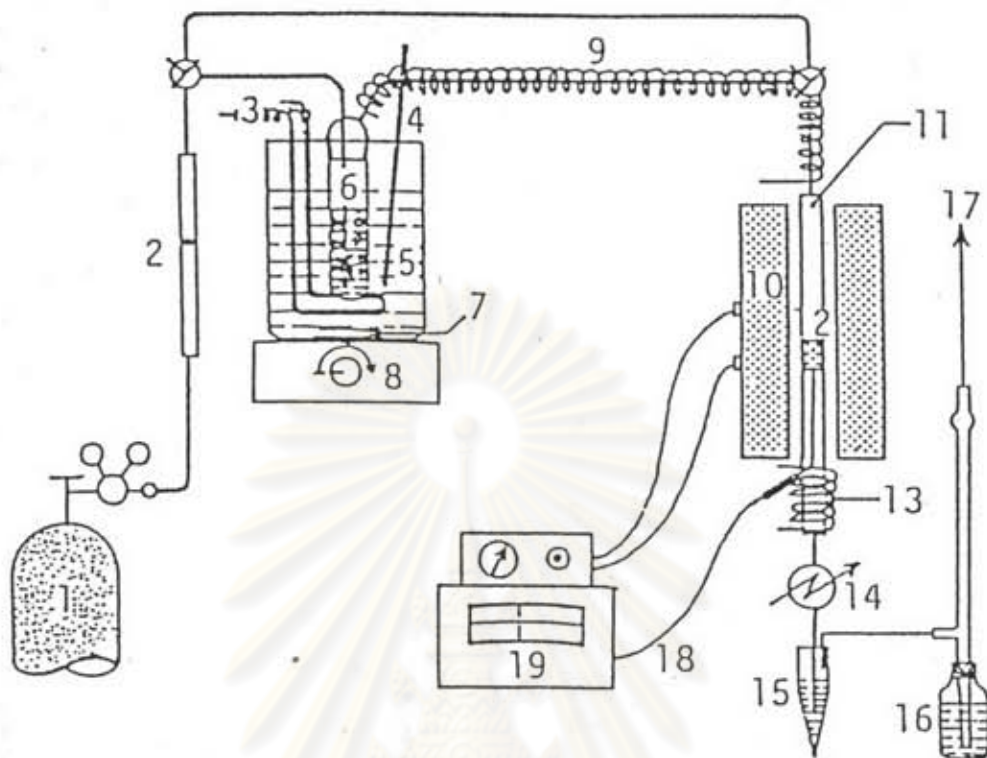


Figure 4.5 Schematic diagram of the reaction apparatus for the methanol conversion.

1. N_2 gas cylinder, 2. flow indicator, 3. water bath heater
4. thermometer, 5. water bath,
6. saturator set containing MeOH, 7. magnetic bar,
8. stirrer controller, 9. heating line,
10. furnace, 11. quartz reactor, 12. catalyst-bed,
13. sampling port, 14. condenser, 15. product receiver,
16. outlet gas flow meter, 17. vent out line,
18. thermocouple control reactor,
19. reactor temperature controller.

carrier gas. The flow rate of helium was set at ca. 28 ml/min. The oven temperature of detector was set at 80°C, and the current was set at 80 mA. Nitrogen gas was introduced to the line of helium flowing and the partial pressure of nitrogen was set at 0.3. The sample was heated from room temperature to 150°C and kept at that temperature for 1 h, then cooled down to room temperature. The sample was further cooled down to the temperature of liquid nitrogen and the amount of nitrogen adsorption was measured. The BET surface area of the catalyst can be calculated by the One Point Method (see Appendix A-5).

4.4.2 X-ray Diffraction Patterns

X-ray diffraction patterns (XRD) of the catalysts were performed by Scientific And Technological Research Equipment Center Chulalongkorn University (STREC).

4.4.3 Morphology

The shape and size of the crystals were determined by Scientific And Technological Research Equipment Center Chulalongkorn University (STREC).

4.4.4 Acidity

The acidity of catalysts was measured as follows by using the technique of temperature-programmed desorption (TPD) of

NH₃ with a Rigaku thermal analyzer DSC.

The program of temperature for TPD measurement and the change in the catalyst weight in the measurement were shown in Figure 4.6.

0.150 g of catalyst was heated from room temperature to 450°C with a constant heating rate of 20°C/min with N₂ gas flowing (50 ml/min). The temperature was kept at 450°C for 5 min. After the catalyst was dried, the temperature was downed to 50°C on N₂ gas stream. Thus N₂ gas was stopped and 5% NH₃ (95% N₂) gas was flowed. When the amount of a desorbed-NH₃ attained to its maximum, the NH₃/N₂ gas was stopped and N₂ gas was again fed. The catalyst was heated to 80°C and kept at that temperature until physically-adsorbed NH₃ was removed. The temperature was risen from 80°C to 600°C (10°C/min). Chemically adsorbed NH₃ was removed in this stage (The Calculation See Appendix A-6).

4.4.5 Mole Ratio Si/Al of H-ZSM-5 Catalyst

Mole ratio Si/Al of H-ZSM-5 catalyst was analysed by SIE Instrumentation Laboratory Model IL 551 AA/AE Spectrophotometer of Chemical Laboratory of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

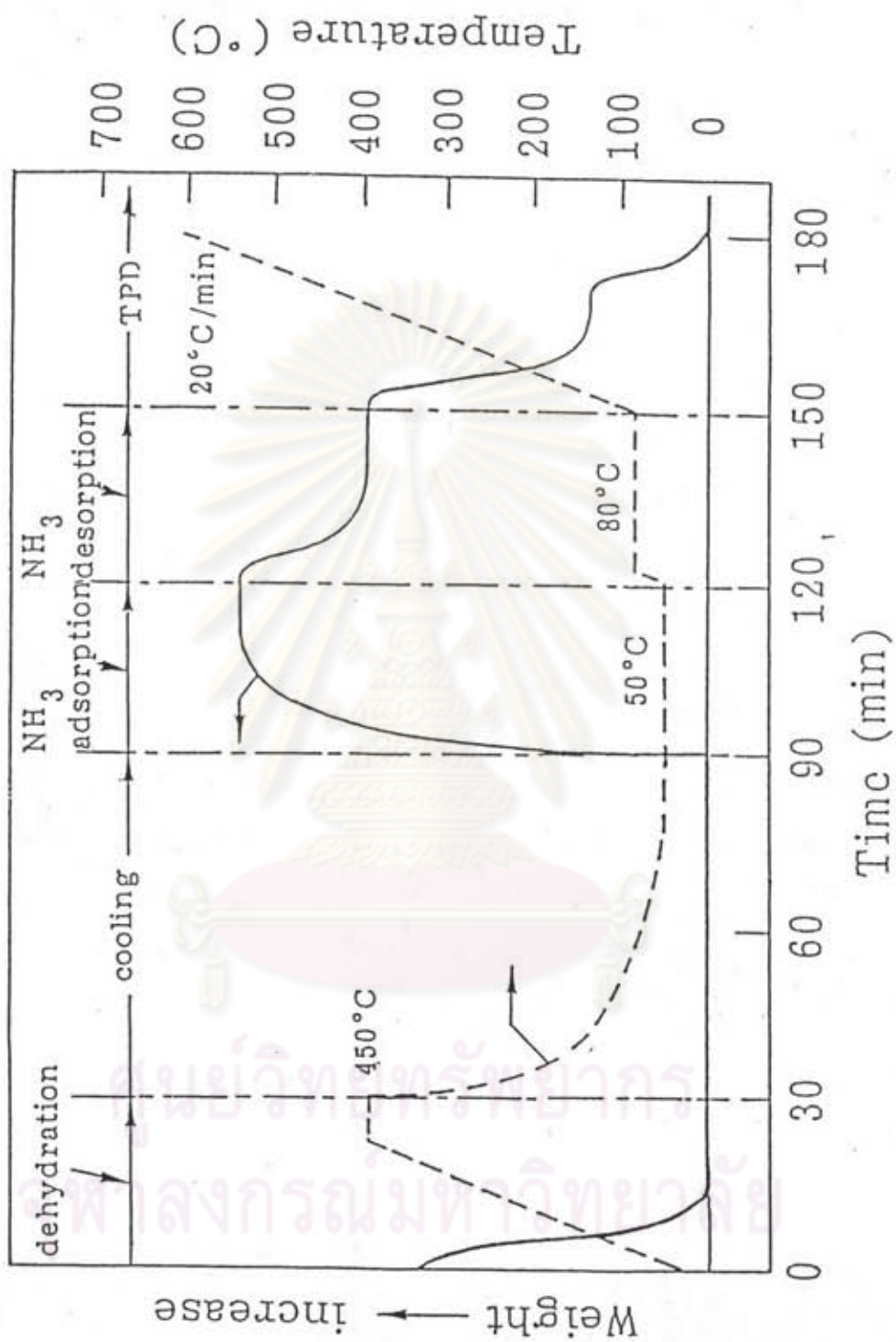


Figure 4.6 Temperature program for the NH_3 -TPD measurement.