

CHAPTER IV

EXPERIMENTS

The catalyst study for dehydrogenation of propane over metal containing MFI type zeolite catalysts was explained in the following section.

4.1 Preparation of Na-MFI and Zn-Al-silicate

Na-MFI, Zn,Al-silicate catalyst having various metal contents were prepared. The AlCl_3 was replaced by $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at the stage of gel formation in the rapid crystallization method for Na-Zn,Al-silicate synthesis [50]. The preparation procedures and the reagents used are shown in **Figure 4.1** and **Tables 4.1, 4.2**. (For calculation see Appendix A-1)

4.1.1 Preparation of Decantation Solution and Gel Solution

The source of metals for preparation of decantation and gel solutions were AlCl_3 for Al and $\text{Zn}((\text{NO})_3)_2 \cdot 3\text{H}_2\text{O}$ for Zn, respectively. TPABr (Tetra-n-Propyl Ammonium Bromide) $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]\text{Br}$ was used as organic template. The atomic ratio of Silicon/Aluminium was set at 40. The preparation of supernatant liquid was separated from that of gel, which was important to prepare the uniform crystals. The detailed procedures were as follows: Firstly, a gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise with

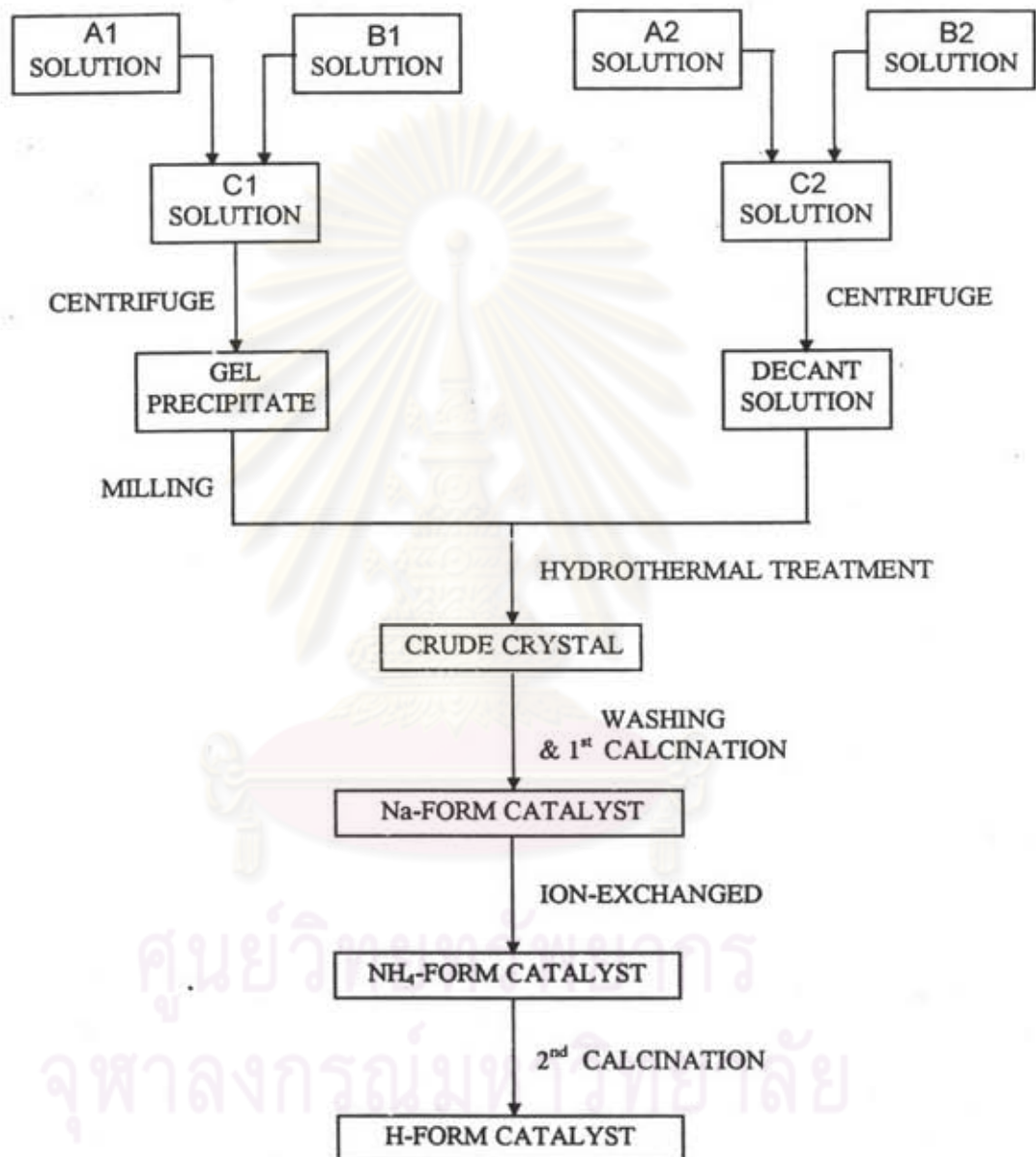


Figure 4.1 Preparation procedure of MFI type catalysts by rapid crystallization

Table 4.1 Reagents used for the preparation of Na-MFI

Solution for the gel preparation	Solution for decant-solution preparation
<u>Solution A1</u> AlCl ₃ 0.8998 g TPABr 5.72 g NaCl 1 g De-ionized water 60 ml H ₂ SO ₄ (conc.) 3.4 ml	<u>Solution A2</u> AlCl ₃ 0.8998 g TPABr 7.53 g De-ionized water 60 ml H ₂ SO ₄ (conc.) 3.4 ml
<u>Solution B1</u> Sodium silicate 69 g De-ionized water 45 ml	<u>Solution B2</u> Sodium silicate 69 g De-ionized water 45 ml
<u>Solution C1</u> TPABr 2.16 g NaCl 51.54 g NaOH 2.39 g De-ionized water 208 ml H ₂ SO ₄ (conc.) 1.55 ml	<u>Solution C2</u> NaCl 26.27 g De-ionized water 104 ml

Table 4.2 Reagent used for the preparation of Zn, Al-silicate catalyst.

Solution for the gel preparation	Solution for decant-solution preparation
<u>Solution A1</u> AlCl ₃ 0.8998 g Zn(SO ₄).4H ₂ O X g TPABr 5.72 g NaCl 1 g De-ionized water 60 ml H ₂ SO ₄ (conc.) 3.4 ml	<u>Solution A2</u> AlCl ₃ 0.8998 g Zn(SO ₄).4H ₂ O X g TPABr 7.53 g De-ionized water 60 ml H ₂ SO ₄ (conc.) 3.4 ml
<u>Solution B1</u> Sodium silicate 69 g De-ionized water 45 ml	<u>Solution B2</u> Sodium silicate 69 g De-ionized water 45 ml
<u>Solution C1</u> TPABr 2.16 g NaCl 51.54 g NaOH 2.39 g De-ionized water 208 ml H ₂ SO ₄ (conc.) 1.55 ml	<u>Solution C2</u> NaCl 26.27 g De-ionized water 104 ml

vigorous stirring using a magnetic stirrer at room temperature . The pH of the mixed solution was maintained within 9-11, since it was expected that this pH value was suitable for precipitation. The gel mixture was separated from the supernatant liquid by centrifugation. The precipitation gel mixture was milled for totally 1 hr . The milling was done for 15 min and then the supernatant solution was removed by centrifugal separation. The milling process was repeated twice with the milling time of 15 and 30 min, respectively. Milling the gel mixture before the hydrothermal treatment was essential to obtain the uniform and fine crystals. Secondly, a decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2 with the same method of the preparation of gel mixture. The supernatant liquids from A-2, B-2 and C-2 were mixed together with the milled gel mixture. However, before mixing, the pH of solution was adjusted to be between 9-11 with H_2SO_4 (conc.) or 1 M NaOH solution.

4.1.2 Crystallization

The milling precipitate and the supernatant of decant solution were mixed together in a glass vessel in an autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm² gauge. Then, the autoclave was heated from room temperature to 160 °C in 90 min. and then up to 210 °C with a constant heating rate of 12 °C/h, followed by cooling down the hot mixture to room temperature overnight. The temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization. The produced crystals were washed with de-ionized water about 8 times by using the centrifugal separator for each 15-20 min to remove chloride out of the crystals, and dried in an oven at 110 °C for at least 3 h.

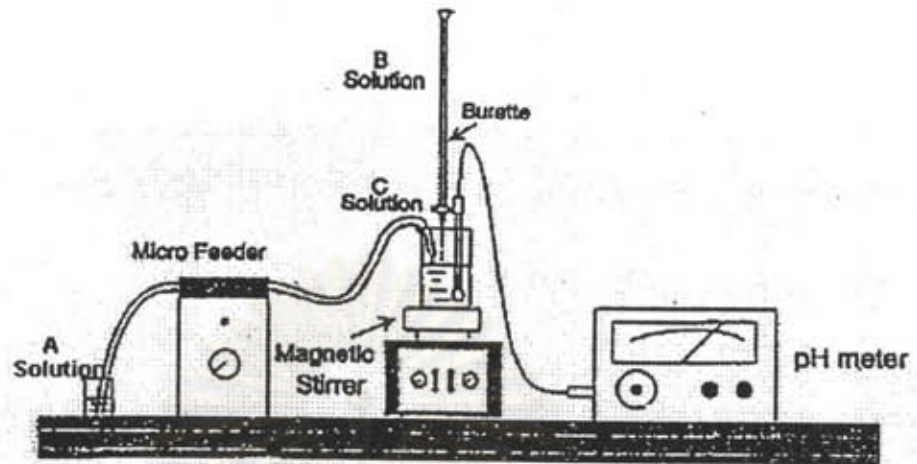


Figure 4.2 A set of apparatus used for preparation of supernatant solution gel precipitation as providing for the rapid crystallization.

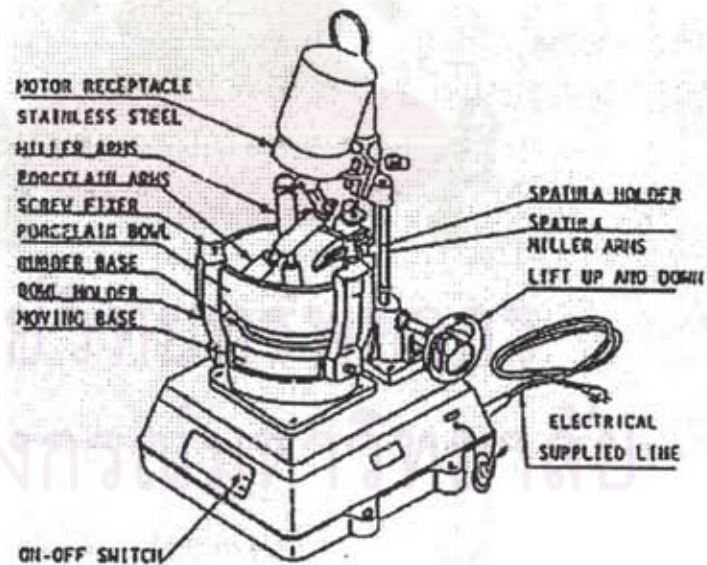


Figure 4.3 A powder miller (Yamato-Nitto, UT-22).

4.1.3 First Calcination

The dry crystals were calcined in an air stream at 540 °C for 3.5 h by heating them from room temperature to 540 °C in 60 min. This step was to burn off the organic template and to leave the cavities and channels in the crystals. Then, the calcined crystals were cooled to room temperature in a dessicator. After this step the catalysts formed were called Na-MFI and Na-Zn,Al-silicate, respectively.

4.1.4 Ammonium ion-exchange

The ion-exchange step was carried out by mixing 3 g of the calcined crystal with 90 ml of 1 M NH_4NO_3 and heated on a stirring hot plate at 80 °C for 1 h. Then, the mixture was cooled down to room temperature. Then, the ion exchange step was repeated again. After that, the ion-exchanged crystal was washed twice with deionized water by using centrifugal separator. Then, ion-exchanged crystal was dried at 110-120 °C for at least 3 h in oven. The dried crystals ("NH₄-MFI" and "NH₄-Zn,Al-silicate") were then obtained.

4.1.5 Second Calcination

The removed species, i.e. NH_3 , NO_x , were decomposed by thermal treatment of the ion-exchanged crystal in a furnace at 540 °C, with the same temperature as the first calcination. The catalyst formed in this step were called "H-MFI" and "H-Zn,Al-silicate" for MFI type catalyst and Zn,Al-silicate, respectively.

4.2 Loading Zn by Ion-exchange

About 2 g of MFI type zeolite was stirred with 60 ml of 0.04 M NaNO_3 for two times then added with 53 ml aqueous zinc sulfate solution of an adequate concentration and adjust pH to 8. This was stirred for 12 hr. The wet cake was obtained by separation from the solution and washed with de-ionized water and dried at 110°C overnight.

4.3 Platinum Loading by Ion-exchange

The ion-exchange was conducted by treating the catalyst with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution at 98°C for 3 h. Dry crystals was heated in air with a constant heating rate of $3^\circ\text{C}/\text{min}$. up to 350°C and maintained for 10 min. The calcined catalyst was treated with a stream of 20 % H_2 , 80 % N_2 and heated up from room temperature to 400°C and kept at 400°C for 30 min. (as shown in Figure 4.4). The amount of Pt loading in the catalyst was 0.50 wt.% (For calculation see Appendix A-2)

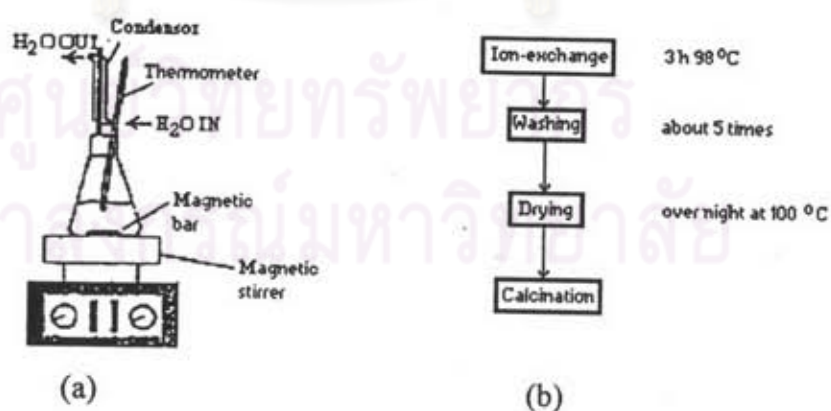


Figure 4.4 A set of apparatus used for preparation of metal ion-exchanged on catalyst (a). A diagram for metal ion-exchanged on catalyst (b).

4.4 Dehydrogenation of Propane

4.4.1 Chemicals and Reagents

Propane (20 %) balanced with nitrogen was provided by Thai Industrial Gases Limited (TIG).

4.4.2 Instruments and Apparatus

4.4.2.1 Reactor : The reactor is a conventional microreactor made from quartz tube with 0.6 mm. inside diameter, so it can be operated at high temperature. The reaction was carried out under ordinary gas flow and atmospheric pressure.

4.4.2.2 Automation Temperature Controller : This consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller connected to a thermocouple attached to the catalyst bed in reactor. A dial setting establishes a set point at any temperature within the range between 0 °C to 600 °C.

4.4.2.3 Electrical furnace : This supplies the required heat to the reactor for reaction. The reactor can be operated from room temperature up to 700 °C at maximum voltage of 200 volt.

4.4.2.4 Gas Controlling System : propane and nitrogen cylinders are equipped with a pressure regulator (0-120 psig), an on-off valve and needle valve were used to adjust flow rate of gas.

4.4.2.5 Gas Chromatographs : flame ionization detector-type gas chromatograph, Shimadzu GC-14A and GC-GowMac were used to analyze feed and effluent gas. Operating conditions used are shown in **Table 4.3**.

Table 4.3 Operating conditions for gas chromatograph

Gas chromatographs	Shimadzu GC-14A	GC-GowMac
Detector	FID	FID
Column	Silicon OV-1 0.25 x 50 m	VZ-10 3 x 3 m
Carrier gas	N ₂ (99.99 %)	N ₂ (99.99 %)
Flow rate of carrier gas	25 cc/min.	25 cc/min.
Column temperature		50 °C
- Initial	30 °C	
- Final	140 °C	
Detector temperature	150 °C	80 °C
Injector temperature	40 °C	80 °C
Analyzed gas	gasoline range hydrocarbon	gaseous hydrocarbon

4.4.3 Reaction Method

The propane dehydrogenation was carried out by using a conventional flow apparatus shown in Figure 4.5. A 0.5 g portion of the catalyst was packed in a quartz tubular reactor. Aromatization of LPG reaction was carried out under the following conditions : atmospheric pressure, gas hourly space velocity (GHSV), 2000-10000 h⁻¹, reaction temperature, 550-600 °C.

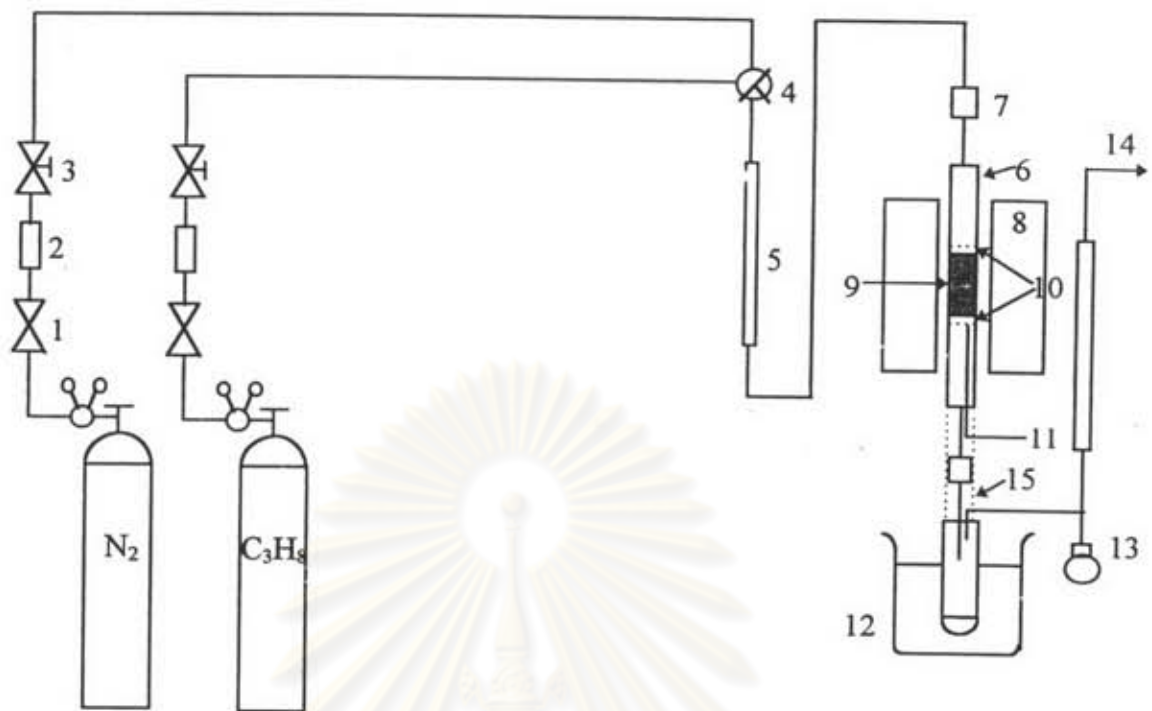
The procedure used to operate this reactor is as follows :

(1) Adjust the outlet pressure of nitrogen and LPG to 1 kg/cm², and allow the gas to flow through a rotameter (See Appendix A-4), measure the outlet gas flow rate by using a bubble flowmeter.

(2) Heat up the reactor (under N₂ flow) by raising the temperature from room temperature to 450 °C in 30 min and then hold at that temperature for 30 min. Then the temperature was raised from 450 °C to the required temperature and wait until the required reaction temperature becomes constant.

(3) Start to run the reaction by replace nitrogen gas with LPG to flow through the reactor, and at that time the reaction time is taken as zero.

(4) Take sample to analyze at 1 h on stream. The reaction products were analyzed by gas chromatographs (For calculation see Appendix A-5).



1. On-off valve ; 2. Gas filter ; 3. Needle valve ; 4. Three-way stop-cock ;
 5. Flow meter ; 6. Tubular reactor ; 7. Sampling port ; 8. Electric furnace
 9. Catalyst ; 10. Quartz wool ; 11. Thermocouple ; 12. Trap ;
 13. Soap-film flowmeter ; 14. Purge ; 15. Ribbon heater

Figure 4.5 Schematic diagram of the reaction apparatus for propane dehydrogenation.

4.5 Characterization of the Catalysts

4.5.1 X-ray Diffraction Patterns

X-ray diffraction (XRD) patterns of the catalysts were performed at Sedimentology laboratory of Department of Geology, Faculty of Science, Chulalongkorn University.

4.5.2 Specific Surface Area and Pore Size Distribution Measurement

Surface areas and pore size distribution of the catalysts were measured by the BET method, with nitrogen as the adsorbate using a micromeritics model ASAP 2000 at liquid-nitrogen boiling point temperature at the Analysis Centre of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

4.5.3 Morphology

The shape and the distribution of the size of the crystals were observed by JEOL Scanning Electron Microscope (SEM) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC).

4.5.4 Chemical Analysis

Percentage of metals loading was analyzed by atomic absorption spectrometry (AAS) method. The catalyst was dissolved by the following procedure:

A certain amount of catalyst (about 100 mg) was digested by digesting solution containing solution of 20 ml of conc. HCl, 10 ml of conc. HNO₃, and 10 ml of H₂O. The mixture was heated up until the color of the support changed into white. During heating step, H₂O had to be added into the mixture to maintain the volume of mixture. Then, 5 drops of HF were added into the mixture in order to digest the support. Heating step was repeated until

the solution became clear. Then volume of the solution was made up to 50 ml by adding de-ionized water.

The zinc content of the prepared solution was analyzed by atomic absorption spectrometry (AAS) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University.

4.5.5 Acidity Measurement

The acidity measurement was assessed by using the technique of temperature-programmed desorption (TPD) of NH_3 with a Shimadzu thermal analyzer TA-51 at Petrochemical Engineering Research Laboratory, Chulalongkorn University.

The temperature program for the NH_3 -TPD measurement is shown in Figure 4.6. Catalyst (15 mg) was heated from room temperature to $450\text{ }^\circ\text{C}$ with a constant heating rate of $20\text{ }^\circ\text{C}/\text{min}$. with N_2 gas flowing at $50\text{ ml}/\text{min}$. The temperature was kept at $450\text{ }^\circ\text{C}$ for 5 min. After the catalyst was dried, the temperature was lowered to $50\text{ }^\circ\text{C}$ in N_2 gas stream. N_2 gas was then replaced with 5 % NH_3 (95 % N_2). When the amount of adsorbed -NH_3 attained its maximum, NH_3/N_2 gas was replaced with N_2 gas again. The catalyst was heated to $80\text{ }^\circ\text{C}$ and kept at that temperature until physically adsorbed NH_3 was desorbed. The temperature was then raised from $80\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C}/\text{min}$.) to desorb the chemically adsorbed NH_3 (For calculation see Appendix A-3).

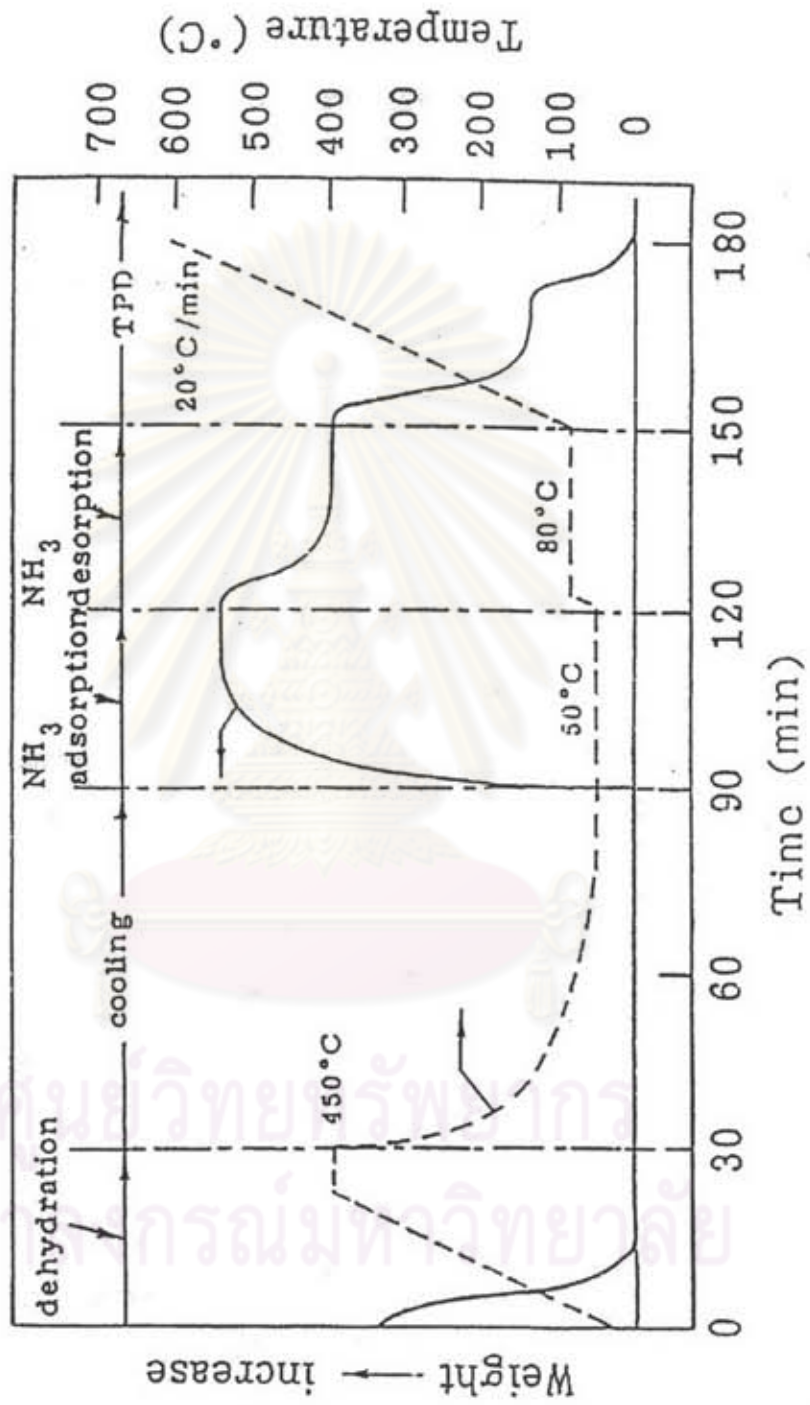


Figure 4.6 Temperature program for the NH₃-TPD measurement [19]