

CHAPTER IV

EXPERIMENTS

The catalyst study for aromatization of liquefied petroleum gas over metal containing MFI type zeolite catalysts was explained in the following section.

4.1 Catalyst Preparation

ZSM-5, Ga-silicate, Zn-silicate, Ga.Al-silicate, and Zn.Al-silicate catalyst having various metal contents were prepared. The AlCl_3 was replaced by $\text{Ga}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at the stage of gel formation in the rapid crystallization method for H-ZSM-5 synthesis [64]. The preparation procedures and the reagents used are shown in Figure 4.1 and Table 4.1, respectively. (For calculation see Appendix A-1).

4.1.1 Preparation of Decantation Solution and Gel Precipitation

Firstly, a decant solution was prepared by adding 60 ml. of S1-solution and 45 ml. aqueous solution of S2-solution to 104 ml. of S3-solution while stirring with a magnetic stirrer (Figure 4.2). S1-solution was added by a microfeeder with volumetric flow rate 12.0 cc/min and S2-solution was added from a 50 ml. burette by the manual control to keep the pH of the mixed solution in the range of 9-11. Upon the complete mixing the precipitating gel was then removed from the supernatant solution by a centrifuge and the supernatant solution was kept for mixing with gel precipitate. On the other hand, another gel mixture was prepared by adding 60 ml. of G1-solution and 45 ml. of G2-solution to 208 ml. of G3-solution. The method and condition of mixing were similar to the preparation of decantation solution. The precipitate from solution

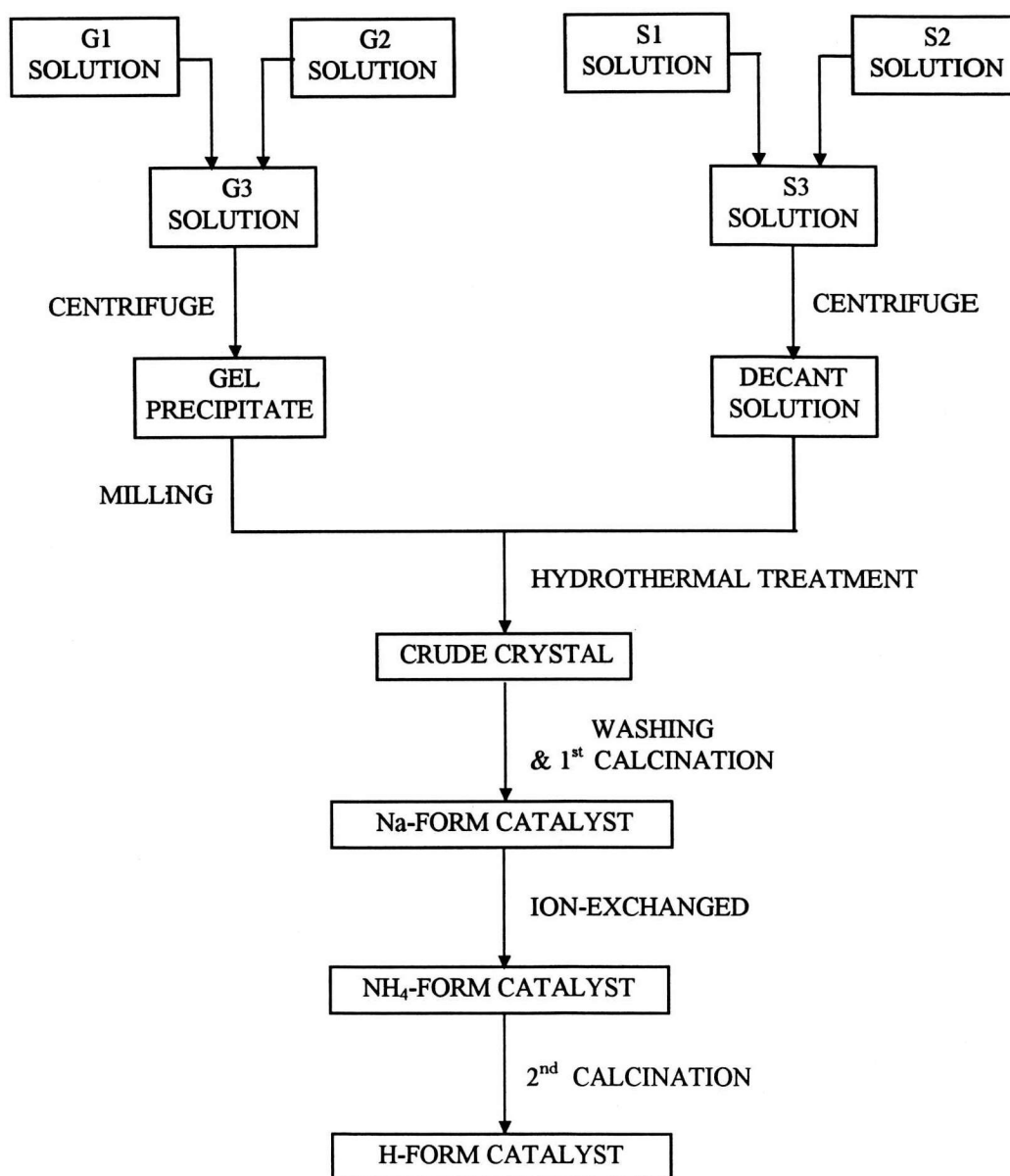


Figure 4.1 Preparation procedure of MFI catalysts by rapid crystallization

Table 4.1 Reagents used for the catalysts preparation

Reagents for the gel preparation		Reagents for decant-solution preparation	
<u>Solution G1</u>		<u>Solution S1</u>	
AlCl ₃ (g) and/or	x	AlCl ₃ (g) and/or	x
Ga ₂ (SO ₄) ₃ .nH ₂ O (g) and/or	y	Ga ₂ (SO ₄) ₃ .nH ₂ O (g) and/or	y
Zn(NO ₃) ₂ .6H ₂ O (g)	z	Zn(NO ₃) ₂ .6H ₂ O (g)	z
TPABr (g)	7.53	TPABr (g)	5.75
Distilled water (ml)	60	Distilled water (ml)	60
H ₂ SO ₄ (conc.) (g)	3.38	H ₂ SO ₄ (conc.) (g)	3.38
<u>Solution G2</u>		<u>Solution S2</u>	
Distilled water (ml)	45	Distilled water (ml)	45
Water glass (g)	69	Water glass (g)	69
<u>Solution G3</u>		<u>Solution S3</u>	
TPABr (g)	2.16	NaCl (g)	26.27
NaCl (g)	50.54	Distilled water (ml)	104
NaOH (g)	2.39		
Distilled water (ml)	208		
H ₂ SO ₄ (conc.)	1.55		

x, y, z; based on Si/Al, Si/Ga and Si/Zn charged ratio, respectively

was separated by centrifuge and then milled by powder miller (Yamato-Nitto, UT-22) as shown in Figure 4.3.

4.1.2 Crystallization

The milled gel and the supernatant solution were mixed together. The mixture was heated for crystallization in an autoclave from room temperature to 160 °C in 90 min and from 160 °C 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 centrifugal separator (about 15-20 min. for each time) and dry in an oven at 110-120 °C for at least 3 h.

4.1.3 Catalyst Calcination

A portion of 6-7 g. of dry crystals in a porcelain container was heated in a furnace under an air ambient from room temperature to 540 °C in 60 min and then kept at this temperature for 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 desiccator. After this step the so called “Na-form catalyst” was obtained.

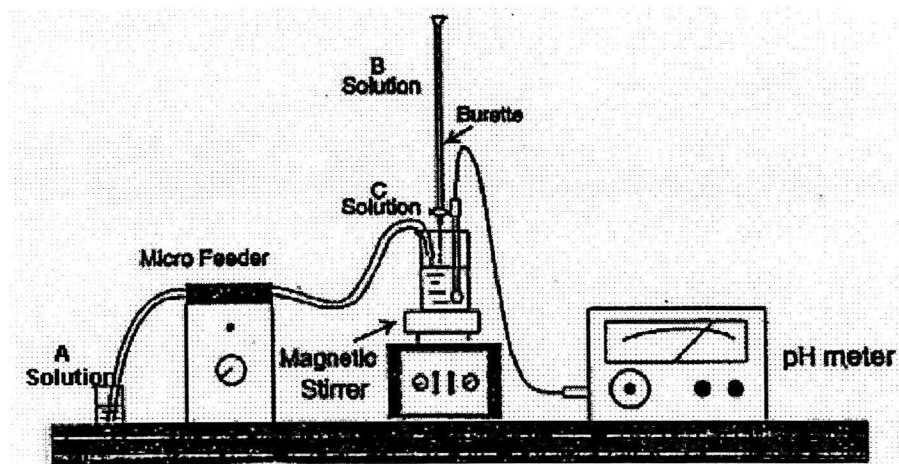


Figure 4.2 A set of apparatus used for preparation of supernatant solution and gel precipitation as providing for the rapid crystallization.

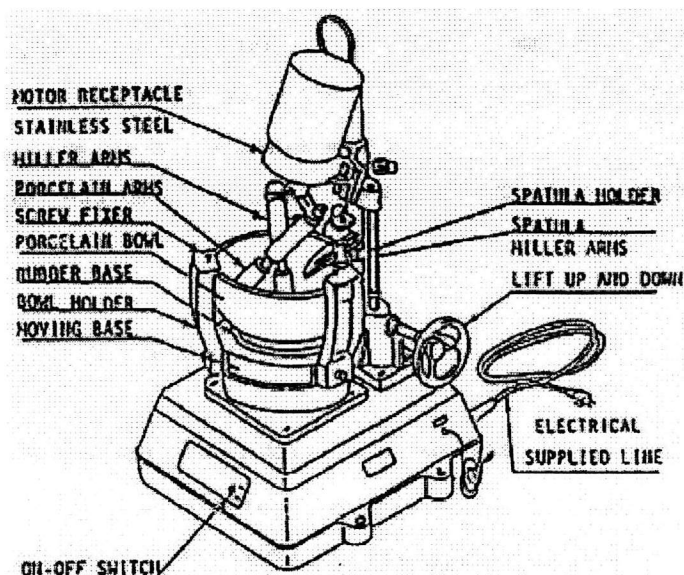


Figure 4.3 A powder miller (Yamato-Nitto, UT-22).

4.1.4 Ammonium Ion-exchange of Na-form Catalyst

About 1.5 g. of the Na-form catalyst was mixed with 45 ml. of 1 M NH_4NO_3 and heated on a stirring hot plate at 80 °C for 1 h. The ion-exchange step was repeated. The ion-exchanged crystal was washed twice with deionized water by using a centrifugal separator. Then, ion-exchanged crystal was dried at 110-120 °C for 3 h in an oven. The Na-form crystal was thus changed to “ NH_4 -form catalyst”.

4.1.5 Catalyst Calcination

The NH_4 -form catalyst was calcined in a furnace by heating from room temperature to 540 °C in 60 min and then kept at this temperature for 3.5h. After this step the catalyst thus obtained was called " H-form catalyst".

4.2 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 °C/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.% [65] (For calculation see Appendix A-2)

4.3 Metal Loading by Ion-exchange

A 2.0 g of catalyst was immersed in 40 ml of distilled water and treating catalyst with metal salt aqueous solution at 100 °C for 3 h. It was washed with deionized water. The sample was dried overnight at 110 °C. Finally, dry crystal was heated in air with constant heating rate of 10 °C/min up to 350 °C and maintained for 2 h.

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

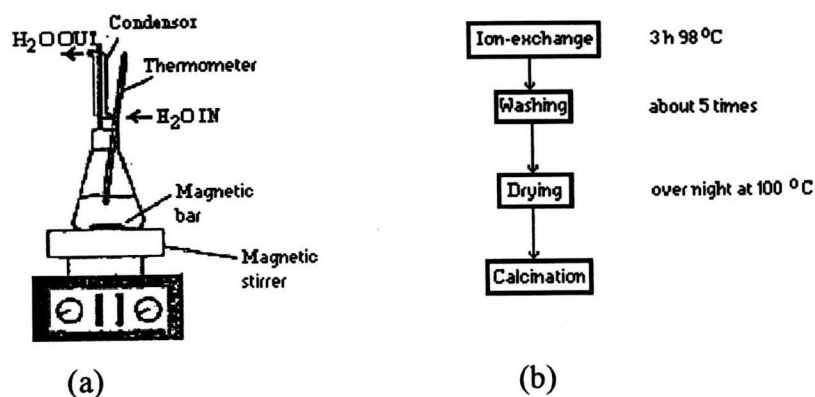


Figure 4.4 A Set of apparatus used for preparation of metal ion-exchanged on catalyst (a). A diagram for metal ion-exchanged on catalyst (b) .

4.4 Aromatization of Liquefied Petroleum Gas

4.4.1 Chemicals and Reagents

Propane (20%) in nitrogen and butane (20%) in nitrogen were 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 voltage.

4.4.2.4 Gas Controlling System: propane, butane 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 chromatographs, Shimadzu GC-14A and GC-GowMac were used to analyze feed and effluent gas. Operating conditions used are shown in Table 4.2.

Table 4.2 Operating conditions for gas chromatograph

Gas chromatographs	Shimadzu GC- 14A	GC - GowMac
Detector	FID	FID
Column	Silicon OV-1 ϕ 0.25 x 50 m.	VZ-10 ϕ 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

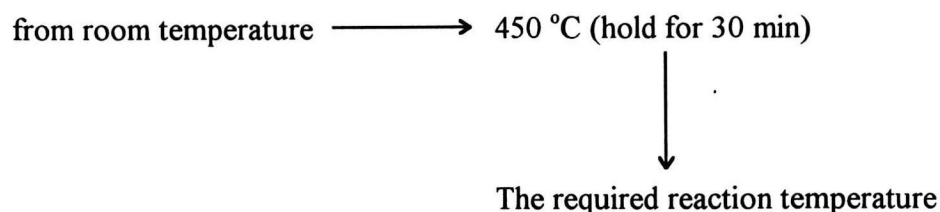
4.4.3 Reaction Method

The aromatization of liquefied petroleum gas reaction 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), 2000-8000 h⁻¹; reaction temperature, 450-600 °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.

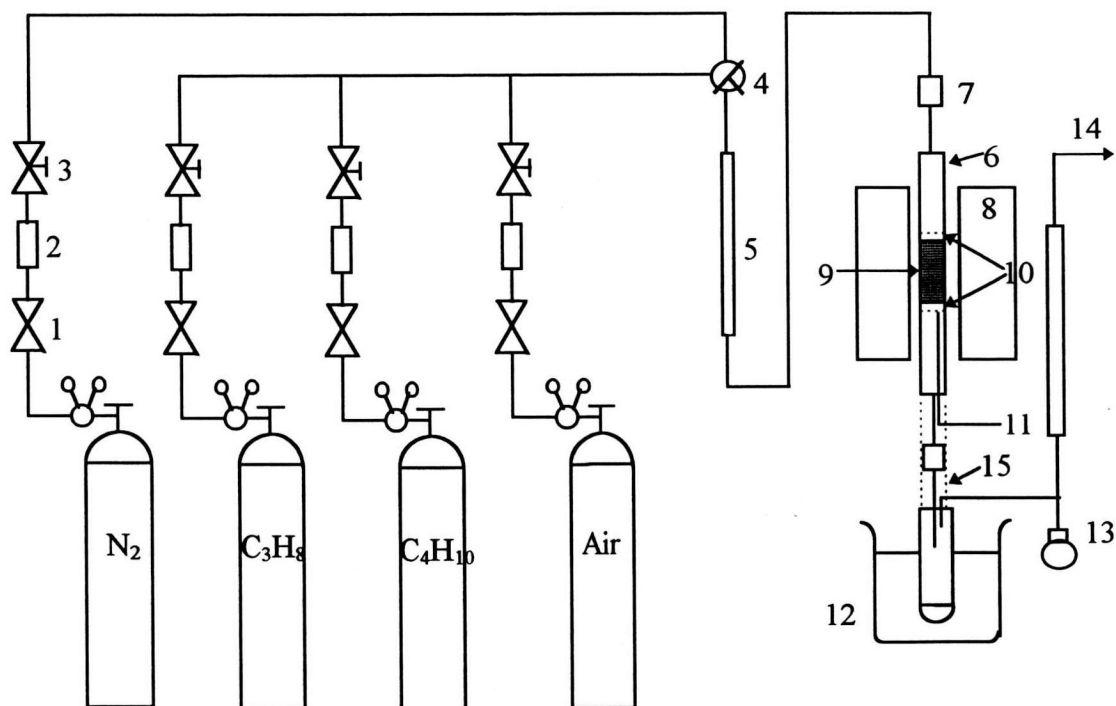
(2) Heat up the reactor (N₂ flow) by raising the temperature as follows:



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 the aromatization of LPG.

4.5 Characterization of the Catalysts

4.5.1 BET Surface Area Measurement

This method was a physical adsorption of nitrogen gas on the surface of catalyst to find the total surface area. BET surface areas of these catalyst were measured by Micromeritics ASAP 2000 of Chemical Laboratory of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

4.5.2 X-ray Diffraction Patterns

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

4.5.3 Morphology

The size and shape of the catalysts was observed by using JEOL JSM-35CF at the Scientific and Technological Research Equipment Centre, Chulalongkorn University(STREC).

4.5.4 Chemical Analysis

The amount of metals actually observed in the catalyst was analyzed by atomic absorption (AA). Catalyst was prepared in solution as 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. A mixture was heated up until the colour of support was changed into white. During heating step, H₂O must 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 was made clear. The volume of the solution was made up to 50 ml. using de-ionized water.

The prepared solution was analyzed by atomic absorption (AA) 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 °C with a constant heating rate of 20 °C/min with N_2 gas flowing at 50 ml/min. The temperature was kept at 450 °C for 5 min. After the catalyst was dried, the temperature was lowered to 50 °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 °C and kept at that temperature until physically-adsorbed NH_3 was desorbed. The temperature was then raised from 80 °C to 600 °C (10 °C/min) to desorb the chemically adsorbed NH_3 (For calculation see Appendix A-3.).

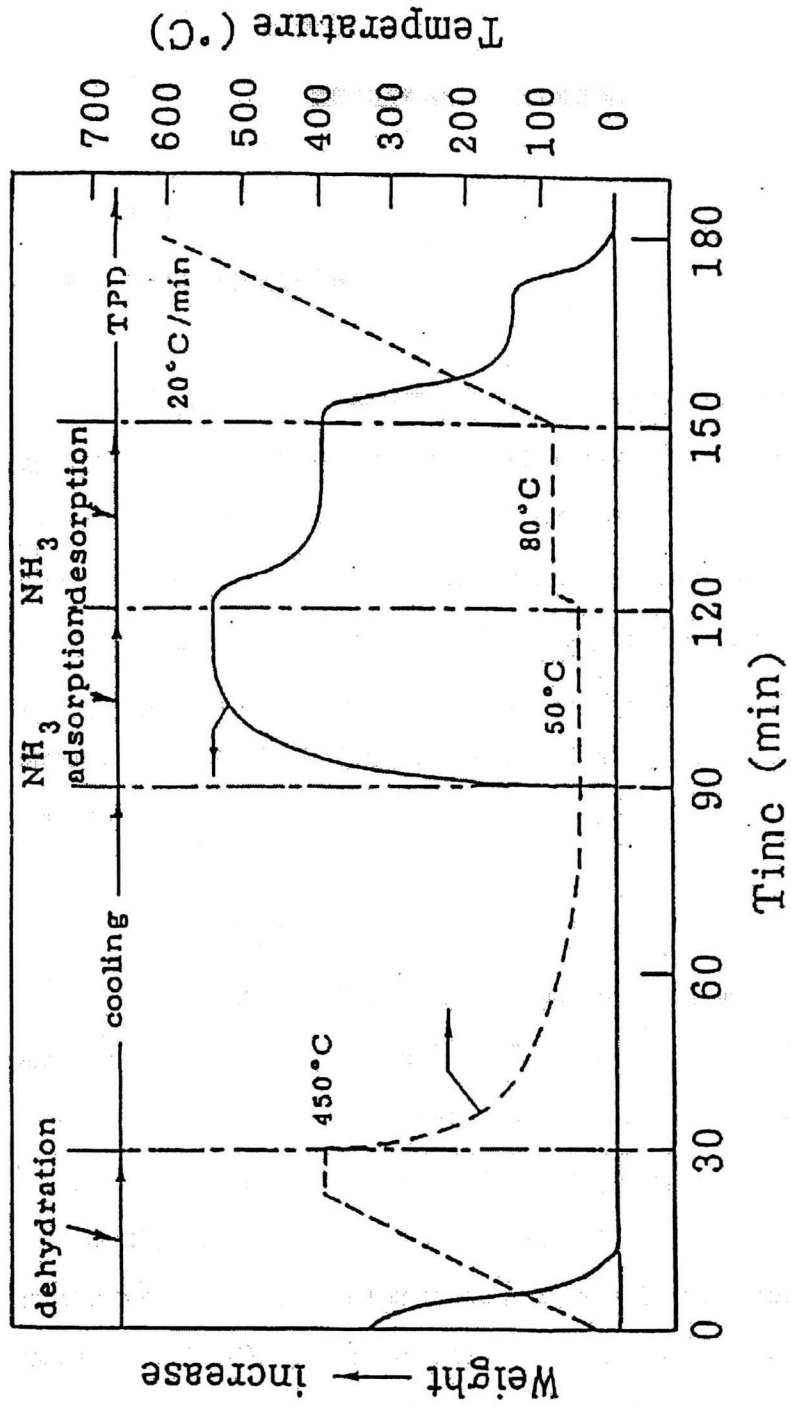


Figure 4.6 Temperature program for the NH_3 -TPD measurement