

CHAPTER IV

EXPERIMENT

Preparation of the Silicoaluminophosphate of 34-type (SAPO-34)

The preparation procedure of SAPO-34 by the rapid crystallization method [92] is shown in Figure 4.1 and 4.2, while reagents used shown in Table 4.1(see Appendix A-1).

Table 4.1 reagents used preparation of SAPO-34

Reagents	Mole composition
Aluminum isopropoxide	2
Tetraethylammonium hydroxide	0.5, 1.0, 1.3, 1.5
Colloidal silica	0.6, 1.0, 1.5, 2.0
Phosphoric acid	1.5, 2.0, 2.5, 3.0
Water	52
Hydrofluoric acid	0.2, 0.3, 0.5, 1.0

1. Preparation of Gel Mixture

The synthesis of SAPO-34 was described in the patent literature [93]. Aluminum isopropoxide (Nacalai Tesque, Inc.), colloidal silica (Cataloid 30,

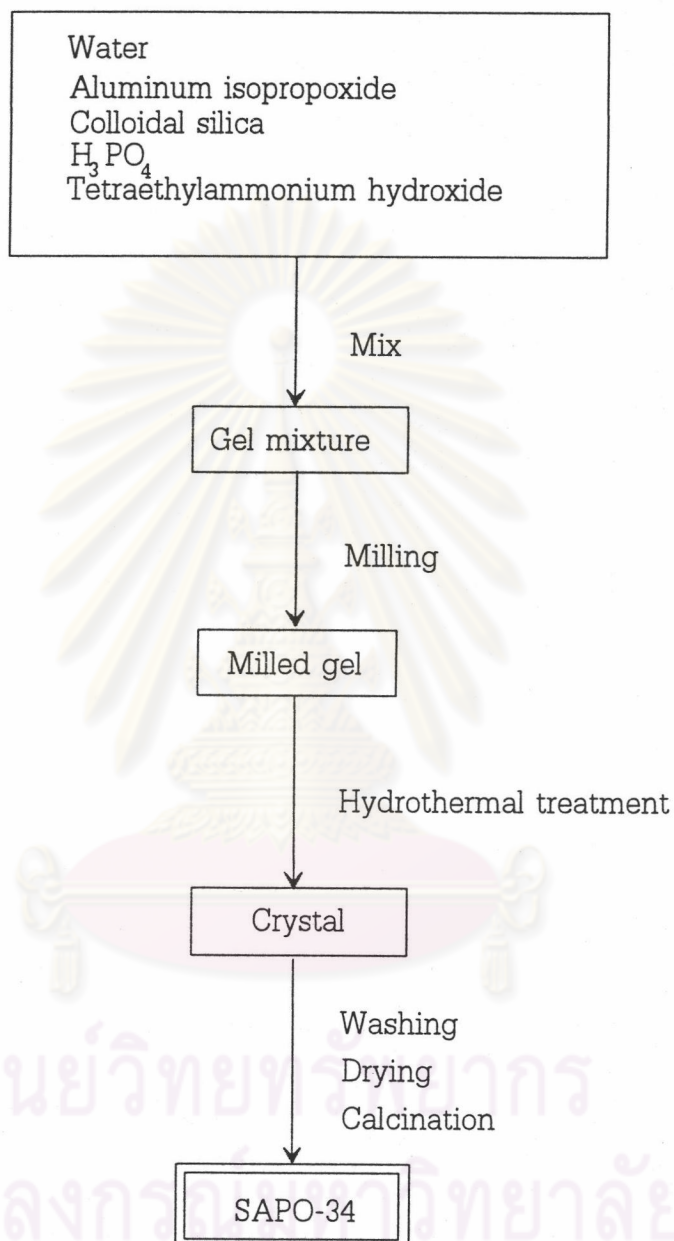


Figure 4.1 Procedure for the preparation of SAPO-34

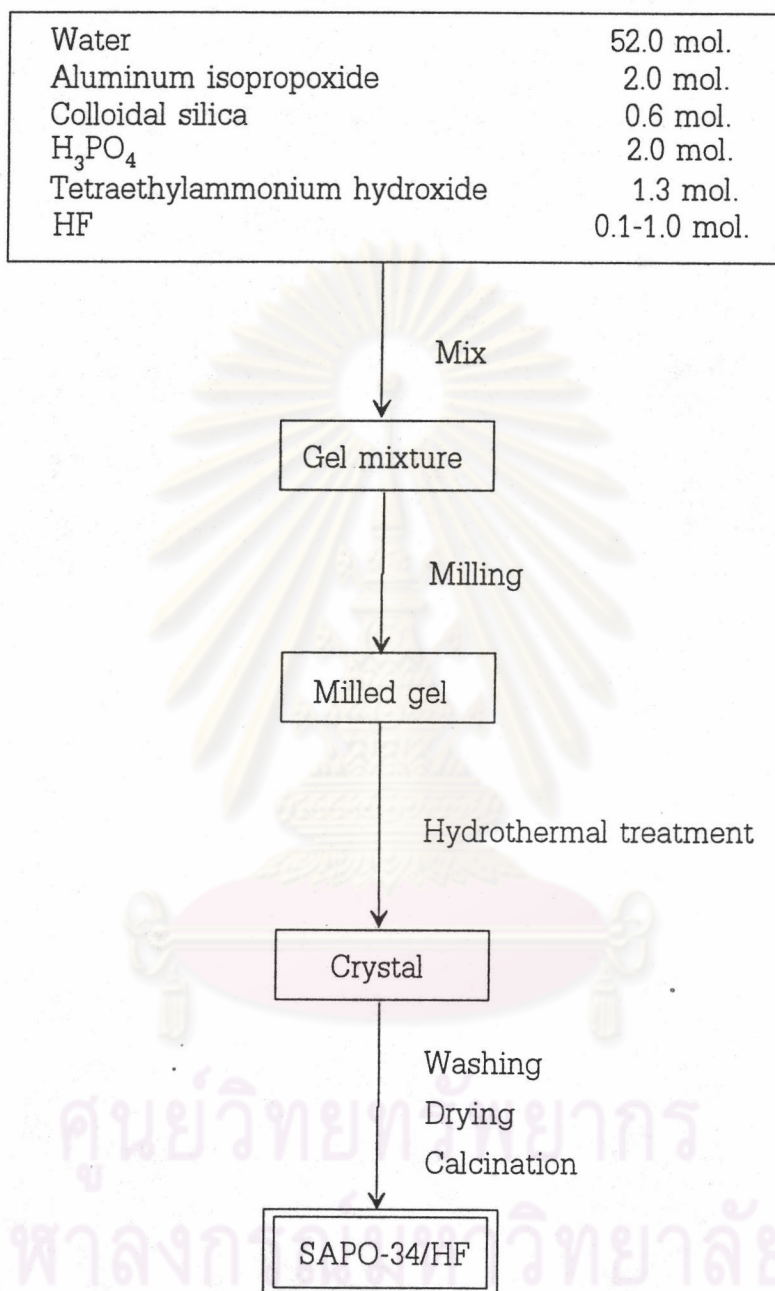


Figure 4.2 Procedure for the preparation of SAPO-34/HF

Shokubai Kasei Co.), phosphoric acid (MERCK) were used as sources of Al, Si and P, respectively. TEAOH (Tetraethylammonium Hydroxide), (Aldrich Chemical Company, Inc.), was used as an organic template.

The gel mixture was prepared by successively adding TEAOH, colloidal silica, phosphoric acid and water into aluminum isopropoxide with vigorous stirring. The obtained gel was milled for 1 h by motor-driven mortar and charged in a one liter stainless-steel autoclave.

The moles of TEAOH, Si, and P were varied while Al was fixed at 2 moles to find the optimum formula of the catalysts. Further application was made by adding to the gel mixture some HF whose amounts were varied between 0.2-1.0 mole. The catalyst thus obtained was designated as SAPO-34/HF.

2. Crystallization

The gel mixture was heated for crystallization in an autoclave from room temperature to 160 °C in 90 min and from 160 °C to 200 °C in 4.2 h under the N₂ atmosphere with a pressure of 3 kg/cm² (gauge). The temperature was then kept at 200 °C for 4 h. After the catalyst was left overnight to cool down to the ambient temperature, the product crystals were washed with distilled water by repeated cycles of centrifugation and decantation, and dried overnight at 110 °C.

After the optimum formula of SAPO-34/HF was concluded, the time of crystallization was varied for 4 h., 24 h., and 72 hr.

3. Calcination of the Catalysts

The catalysts were calcined by heating in air from room temperature to 540 °C in 1 h and then kept at that temperature for 3.5 h to burn off the template molecule (TEAOH).

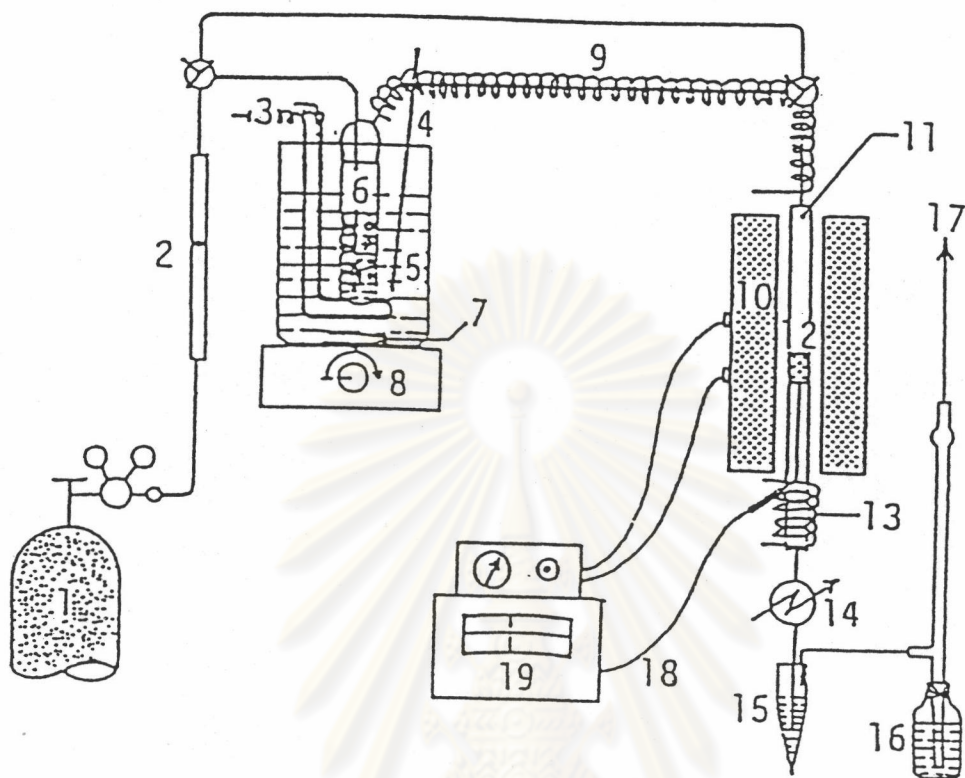
The catalysts were tableted by a tablet machine. They were crushed and sieved to the range of 8-16 mesh to provide and the reaction.

Apparatus and Reaction Method

The methanol conversion reaction was carried out by using a conventional flow apparatus shown in Figure 4.3. A 0.2 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 (see Appendix A-4). Methanol conversion reaction was carried out under the following conditions: total pressure, 1 atm; methanol composition 20% ; balance gas, nitrogen; GHSV, 2000 h⁻¹ ; reaction temperature, 450 °C.

The procedure used to operate this reactor was as follows;

- (1) Adjust the outlet pressure of N₂ gas to 1 kg/cm², and allow the gas to flow through a rotameter.
- (2) Adjust 2 three way valves to allow gas to pass through the upper line through the reactor and measure the outlet gas flow rate by using a bubble flowmeter.
- (3) Heat the reactor from room temperature to 450 °C with a heating rate of 20 °C/min and maintain at that temperature for 30 min. Then the reaction temperatures controlled by an on-off controller were set.
- (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 adjust the temperature of water-bath following the Antonic equation,



- | | | |
|-------------------------------------|------------------------|-----------------------------------|
| 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. stirred 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. | | |

Figure 4.3 Schematic diagram of the reaction apparatus for the methanol conversion.

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

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 also appendix B-1).

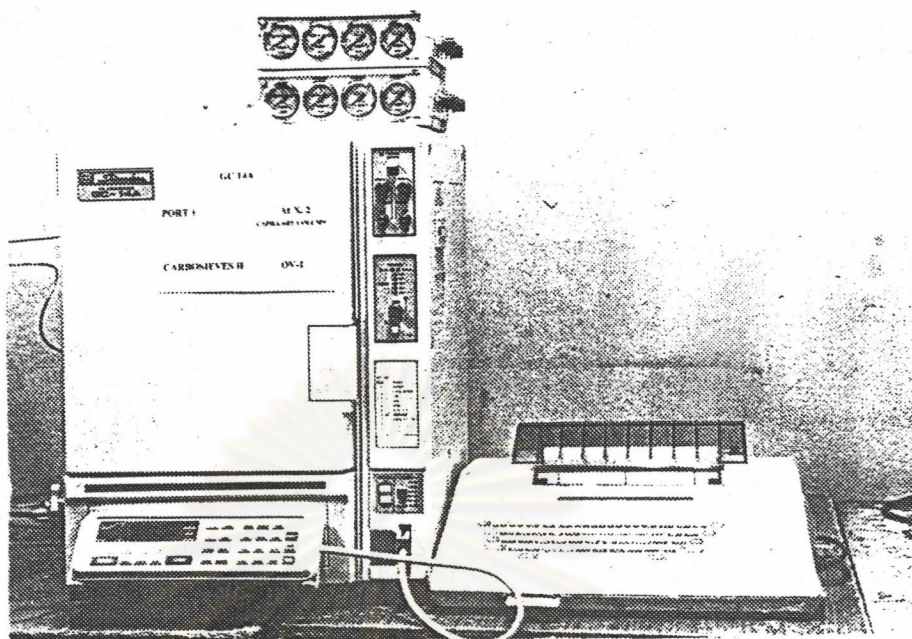
(6) Start to run the reaction by adjust 2 three way valves to allow nitrogen gas to pass through methanol inside the saturator set in the water-bath. The partial pressure of methanol was controlled by the water-bath temperature.

(7) Take sample for analysis at 1 h on stream (see Appendix A-5). The reaction products were analyzed by two FID-type gas chromatographs and two TCD-type ones as shown in Figure 4.4 and 4.5. Column used were silicon-OV-1 (0.25 Φ x 50 m ,FID) for gasoline range hydrocarbons, VZ-10 (3 Φ x 3,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 (see Appendix A-6).

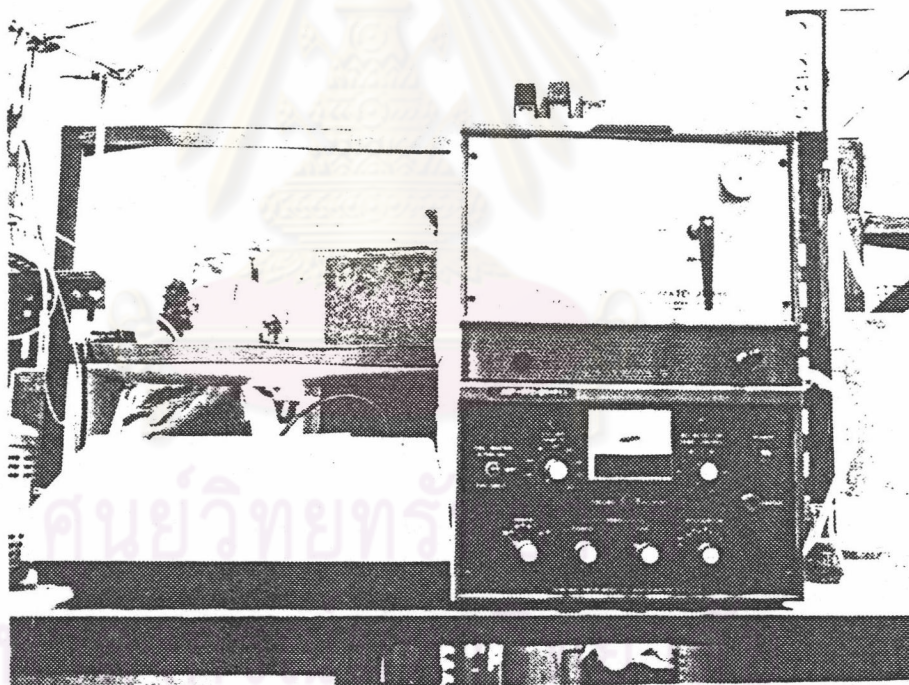
(8) The conditions were varied as follows :

GHSV	2,000-10,000 h ⁻¹
Temperature	250-600 °C
Methanol composition	15-30 % balanced with N ₂
Time on stream	

(9) The effect of the presence of water in methanol feed on product selectivity was observed by conducting the reaction at the same conditions as mentioned above (see Appendix B-2).



(a)



(b)

Figure 4.4 FID-type gas Chromatograph systems

(a) GC 14A for silicon OV-1

(b) GOW-MAC for VZ-10

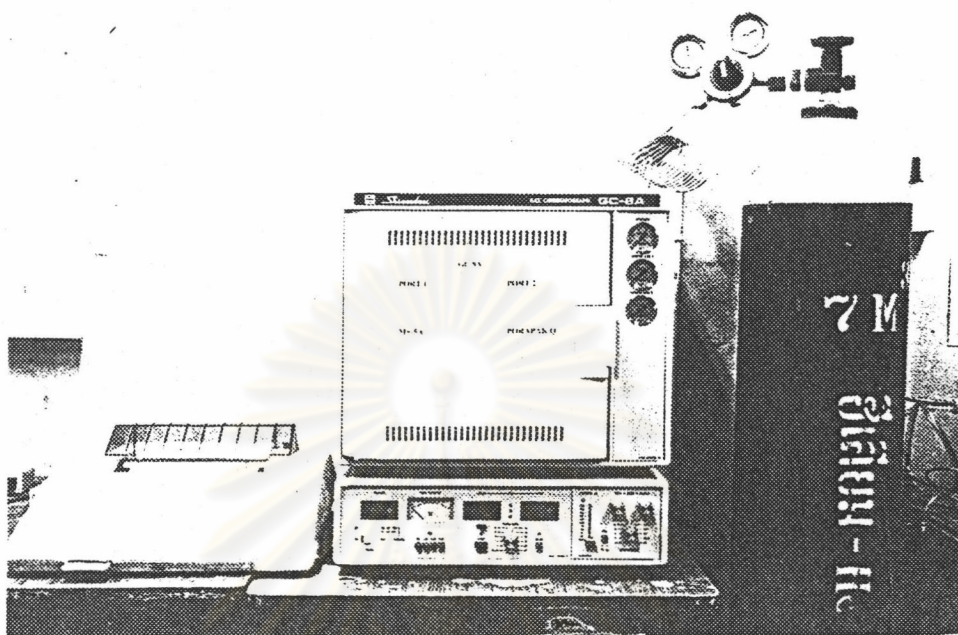


Figure 4.5 TCD-type Gas chromatograph system.

Characterization of the Catalysts

1. BET surface area

BET surface areas of these catalysts were measured by N_2 adsorption with the continuous flow method using the gas chromatograph at liquid N_2 temperature. Helium was used as the carrier gas. The flow rate of helium was set at ca. 28 ml/min. The oven temperature of detector was set at $80\text{ }^\circ\text{C}$, and the current was set at 80 mA. Nitrogen gas was introduced to the line of flowing helium and the partial pressure of nitrogen was set at 0.3. The sample was heated from room temperature to $150\text{ }^\circ\text{C}$ 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-2).

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).

3. Morphology

The shape and size of the crystals were determined by Chemical Laboratory of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

4. Acidity

The acidity of catalysts was measured as follows by using the technique of temperature-programmed desorption (TPD) of NH_3 with a Rigaku thermal analyzer DSC.

The temperature program 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 $450\text{ }^\circ\text{C}$ with a constant heating rate of $20\text{ }^\circ\text{C}/\text{min}$ with N_2 gas flow rate of $50\text{ ml}/\text{min}$. 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. Then N_2 gas was replaced with 5% NH_3 (95% N_2). When the amount of a desorbed- NH_3 attained to its maximum, the NH_3/N_2 gas was stopped and N_2 gas was again fed. The catalyst was heated to $80\text{ }^\circ\text{C}$ and kept at that temperature until physically-adsorbed NH_3 was removed. The temperature was raised from $80\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C}/\text{min}$). Chemically adsorbed NH_3 was removed at this stage (see Appendix A-3 for Calculation)

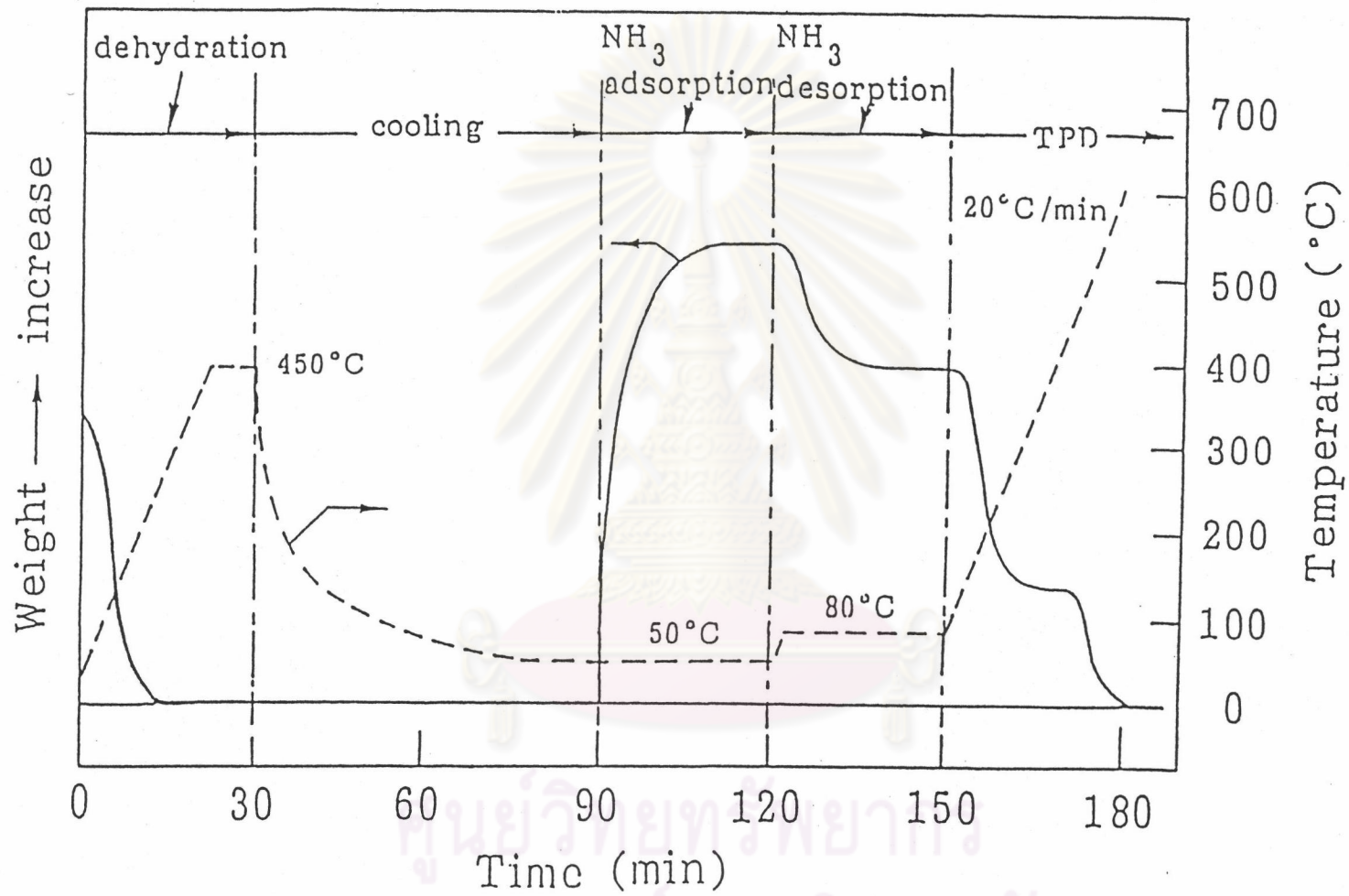


Figure 4.6 Temperature program for the NH₃-TPD measurement