



CHAPTER IV

EXPERIMENTS

4.1 Preparation of H-ZSM-5 , H-Fe-Silicate and H-Cu-Silicate

The preparation procedure of H-ZSM-5, H-Fe-Silicate, and H-Cu-Silicate by the rapid crystallization method [77] developed by Prof. Tomoyuki Inui's laboratory are shown in figure 4.1, while reagents are shown in table 4.1, 4.2, and 4.3. As the source of metals, AlCl_3 for Al, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for Fe, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ for Cu were used, 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 / metal was set at 50.

4.1.1 Preparation of Decantation Solution and Gel Precipitation

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 with magnetic stirring (figure 4.2). 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. bullets by the manual control to keep the pH of the mixed solution in the range 9.5-10.5, since it is expected that is pH value is suitable for precipitation. After the mixing has ended, take the beaker C-solution out of the set. Let the magnetic bar out 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 were as the preparation of decantation solution, expecting that before mixing adjust the pH of solution between 9.5-10.5 with H_2SO_4 (conc.) or 1 M NaOH solution.

The sedimentation time of precipitate was measured and the precipitate from solution was separated 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.

4.1.2 Crystallization

The milling precipitate and the supernatant of decant solution was mixed 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 an oven at 110-120 ° C for at least 3 h.

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

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

room temperature 60 min. → 540 ° C, keeping constant at this temperature 3.5 h.

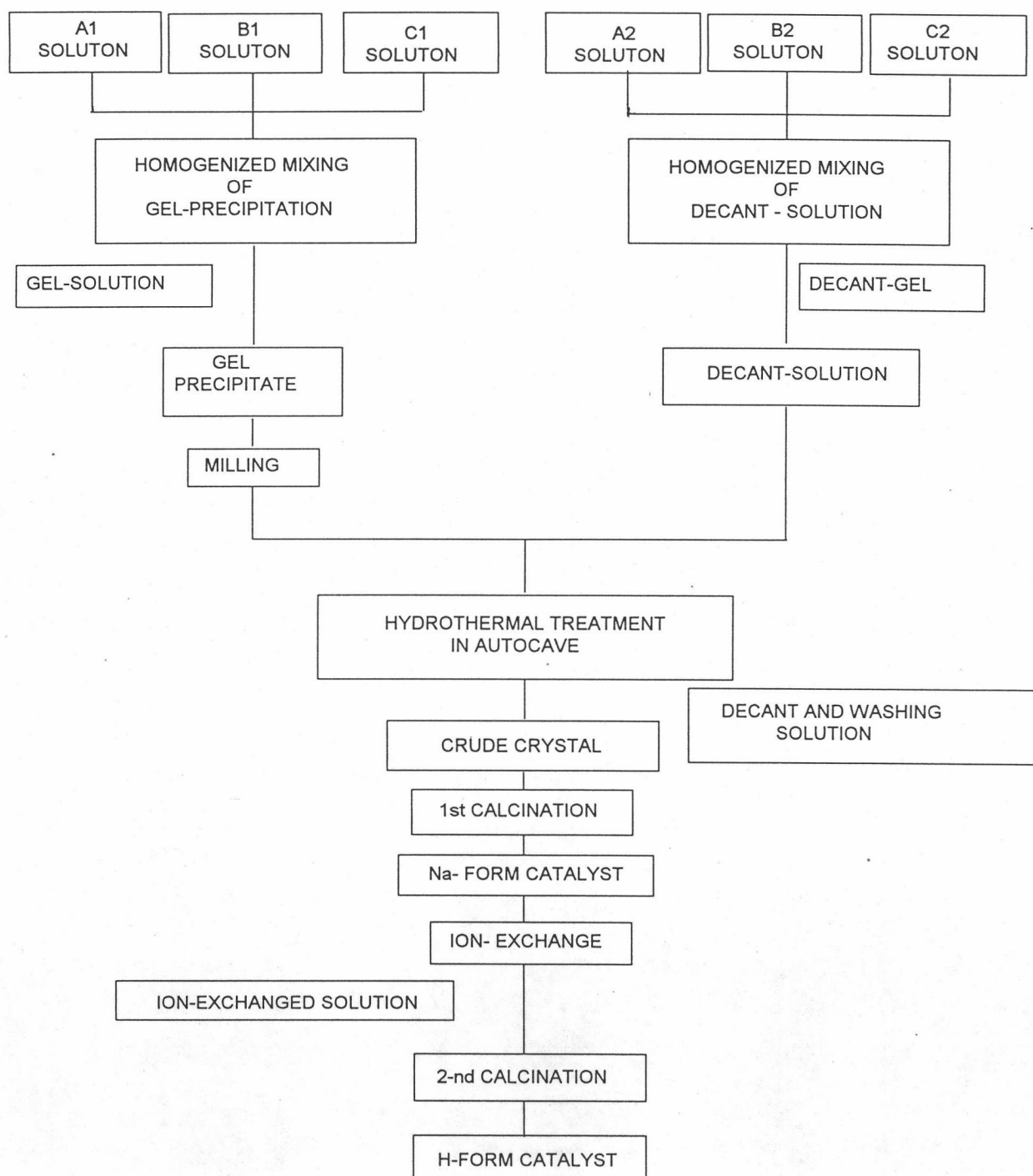


Figure 4.1 Preparation procedure of ZSM-5, Fe-silicate and Cu-silicate by rapid crystallization.

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

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

Table 4.2 Reagent used for the preparation of H-Fe-silicate (Si/Fe=50)

Solution for the gel preparation(wt.%)		Solution for decant-solution preparation(wt.%)	
<u>Solution A1</u>		<u>Solution A2</u>	
Fe(NO ₃) ₃ ·9H ₂ O	3.85	Fe(NO ₃) ₃ ·9H ₂ O	3.90
NaCl	1.43	Distilled water	87.09
Distilled water	85.85	H ₂ SO ₄ (conc.)	9.01
H ₂ SO ₄ (conc.)	8.87		
<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	2.90	TPABr	5.46
NaCl	18.90	NaCl	19.06
NaOH	0.88	Distilled water	75.48
Distilled water	76.28		
H ₂ SO ₄ (conc.)	1.04		

Table 4.3 Reagents used for the preparation of H-Cu-silicate (Si/Cu = 50).

Solution for the gel preparation(wt.%)		Solution for decant-solution preparation(wt.%)	
<u>Solution A1</u>		<u>Solution B1</u>	
Cu(NO ₃) ₂ ·3H ₂ O	2.34	Cu(NO ₃) ₂ ·3H ₂ O	2.37
NaCl	1.4	Distilled water	88.48
Distilled water	87.20	H ₂ SO ₄ (conc.)	9.14
H ₂ SO ₄ (conc.)	9.01		
<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	2.90	TPABr	5.46
NaCl	18.90	NaCl	19.06
NaOH	0.88	Distilled water	75.48
Distilled water	76.28		
H ₂ SO ₄ (conc.)	1.04		

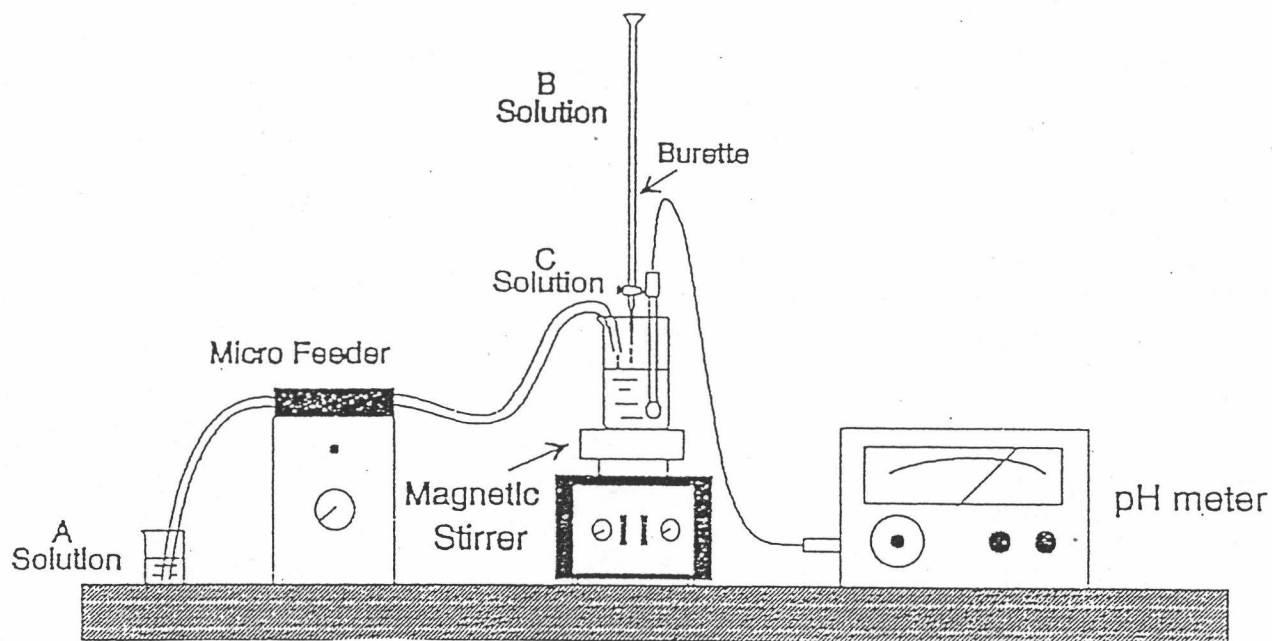


Figure 4.2 A set of apparatus used for preparation of supernatant solution and gel precipitation as providing for the rapid crystallinsation.

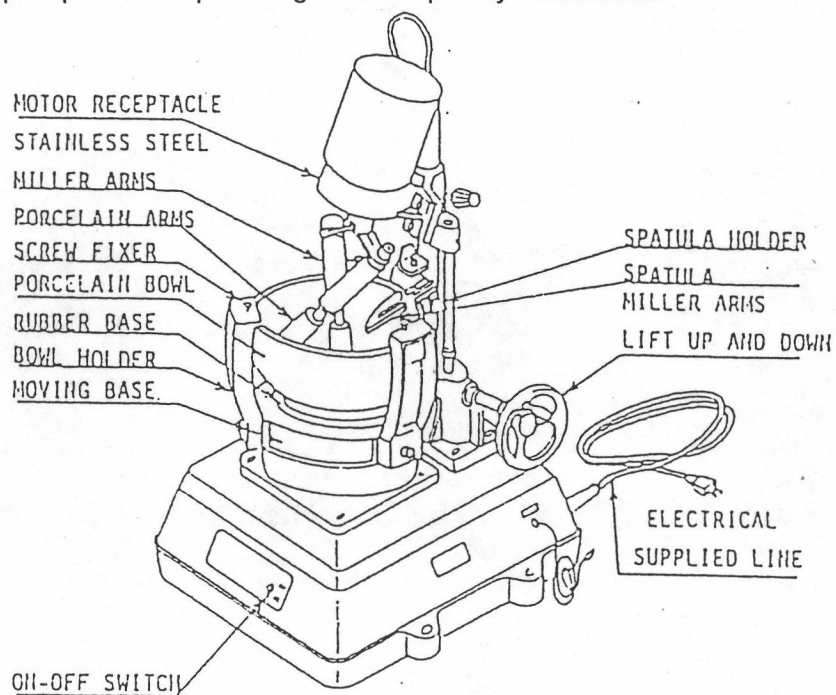


Figure 4.3 A powder miller (Yamato-Notto, UT-22).

At this step, TPABr was burned out and left the cavities and channel in the crystals. The calcined crystal was cooled to room temperature in a dessicator. After this step the catalyst forms called " Na-ZSM-5 ", " Na-Fe-silicate " and " Na-Cu-silicate " for ZSM-5, Fe-silicate and Cu-silicate, respectively, were obtained.

4.1.4 Ammonium ion - exchange

About 1.5 g. of the calcined crystal 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 were repeated. The ion-exchanged crystal was washed twice with deionized water by using centrifuge separator. Then, ion-exchange crystal was dried at 110-120 °C about 3 h. in oven. The dried crystals (" NH_4 -ZSM-5 " , " NH_4 -Fe-silicate " and " NH_4 -Cu-silicate" for ZSM-5, Fe-silicate and Cu-silicate) was obtained.

4.1.5 Second Calcination

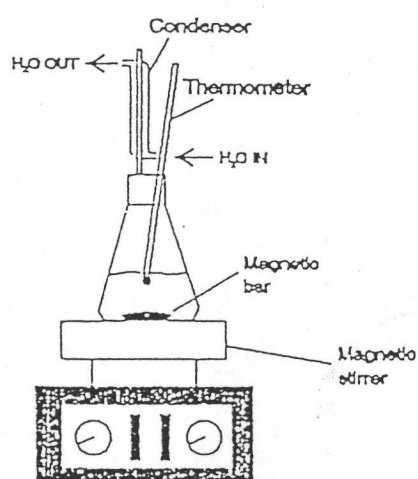
The removal species , i.e. NH_3 , NO_x , were decomposed by thermal treatment of the ion-exchanged crystal in a furnace at 540 °C, with the temperature operating line as the first calcination. After this step the catalyst forms called " H-ZSM-5 " or "H-Al-silicate" , " H-Fe-silicate",and " H-Cu-silicate " for ZSM-5 , Fe-silicate and Cu-silicate , respectively, were obtained.

4.2 Loading Pt by Ion-exchange

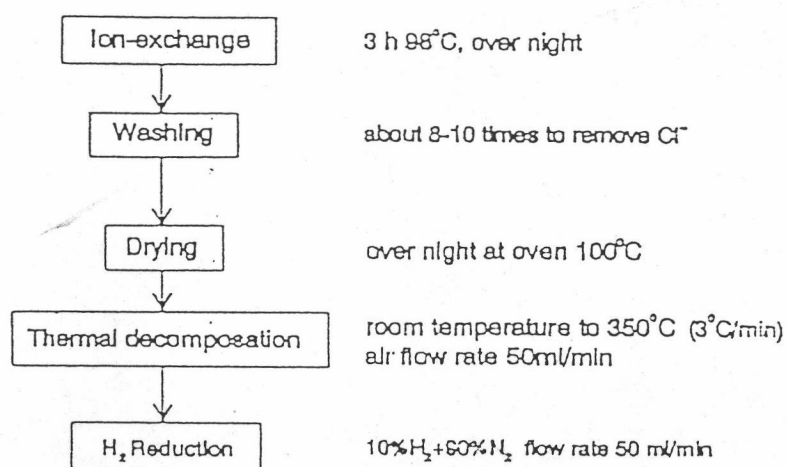
A part of protons in the H-form catalyst was replaced with Pt by ion-exchange method. The ion-exchange was conducted by treating the H-form catalyst with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution at 98 °C for 3 h. It was heated in air with a constant heating rate of 3 °C/min up to 350 °C and maintained for 10 min. The calcined H-form catalyst was treated with a stream of

20% H₂ - 80% N₂ and heated up from room temperature to 400 °C and kept on for 30 min (as show in figure 4.4). The percentage of Pt loading in the catalyst was 0.50 wt% [78] (The calculation see Appendix A-2)

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.



(a)



(b)

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) .

4.3 Loading Cu by Ion-exchange

A 1.5 g portion of mother catalyst was immersed in 40 ml of 0.003 M (3 mmol/l) copper salt aqueous solution (Cu/catalyst = 0.005) and stirred. It was washed with deionized water. Finally, the sample was dried over night at 110 °C, and dry crystal in container was heated in a furnace as follows; room temperature $\xrightarrow{60 \text{ min}}$ 540 °C, keeping constant at this temperature 3.5 h.

Table 4.4 Mother catalysts, chemical, ion-exchange time, and temperature used for the preparation of Cu ion-exchanged catalysts

Mother catalysts	Acidic-, and basic additives	Copper salt used	Ion-exchange time (h)	Ion-exchange temperature
H-Fe-silicate	NH ₄ OH, HCl	Cu(NO ₃) ₂ ·3H ₂ O	3, 6, 12,	30, 80,
H-Cu-silicate	HNO ₃ , KOH,	CuCl, CuCl ₂ ·2H ₂ O	18, and 24	150, and
H-ZSM-5	and NaOH	Cu(CH ₃ COO) ₂ ·H ₂ O,		200 °C
NH ₄ -ZSM-5		CuSO ₄ ·5H ₂ O		
Na-ZSM-5				

4.4 Nitric Oxide Reduction

4.4.1 Chemicals and Reagents

Nitric oxide (1%) in helium, Propane (3%) in helium, Oxygen of ultra high purity grade (99.999%) were provided by THAI INDUSTRIAL GASES LIMITED.

4.4.2 Instruments and Apparatus

4.4.2.1 Reactor: The NO reduction 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 atmosphere pressure. The effluent gas was sampled and analyzed by on-line gas chromatography.

4.4.2.2 Automation Temperature Controller: This consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller series REX-C900 connected to a thermocouple attached to the catalyst bed in reactor. A dial setting establishes a set pointed at any temperature within the range between 0 ° C to 1000 ° C.

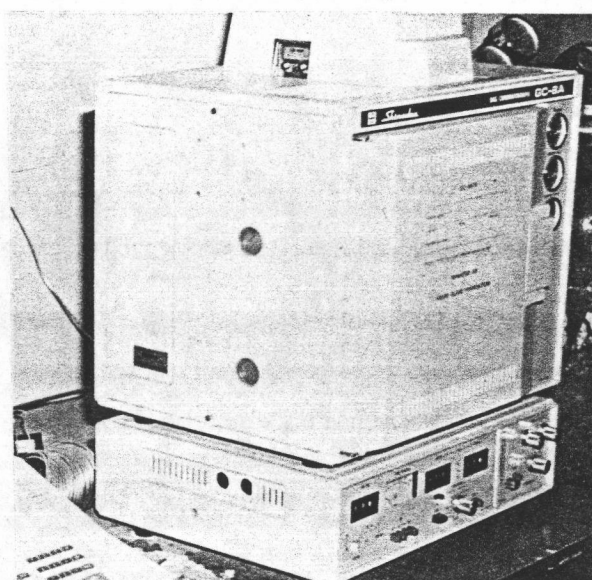
4.4.2.3 Electrical furnace: This supplies the required heating to the reactor for NO reduction reaction. The reactor can be operated from room temperature up to 700 °C at maximum voltage of 200 voltage.

4.4.2.4 Gas Controlling System: Nitric Oxide, propane, oxygen and helium 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. Sampling valve was used to take effluent gas.

4.4.2.5 Gas Chromatography: thermal conductivity detector gas chromatography, SHIMADZU GC-8APT and SHIMADZU GC-8AIT were used to analyze feed and effluent gas. Operating condition used are shown in Table 4.5.

Table 4.5 Operating conditions for gas chromatograph

Gas chromatography	SHIMADZU GC- 8APT	SHIMADZU GC - AIT
Detector	T.C.D.	T.C.D.
Packed column	MS-5A	PORAPAK - Q
Carrier gas	He(99.999%)	He(99.99%)
Flow rate of carrier gas	30 cc/min	60 cc/min
Column temperature	90 °C	90 °C
Detector temperature	100 °C	100°C
Injector temperature	100 °C	100 °C
Analyzed gas	O ₂ , N ₂ , CO	C ₃ H ₈ , CO ₂



a) G.C. 8APT

Figure 4.5 Gas Chromatographic System. a) G.C. 8APT b) G.C. 8AIT



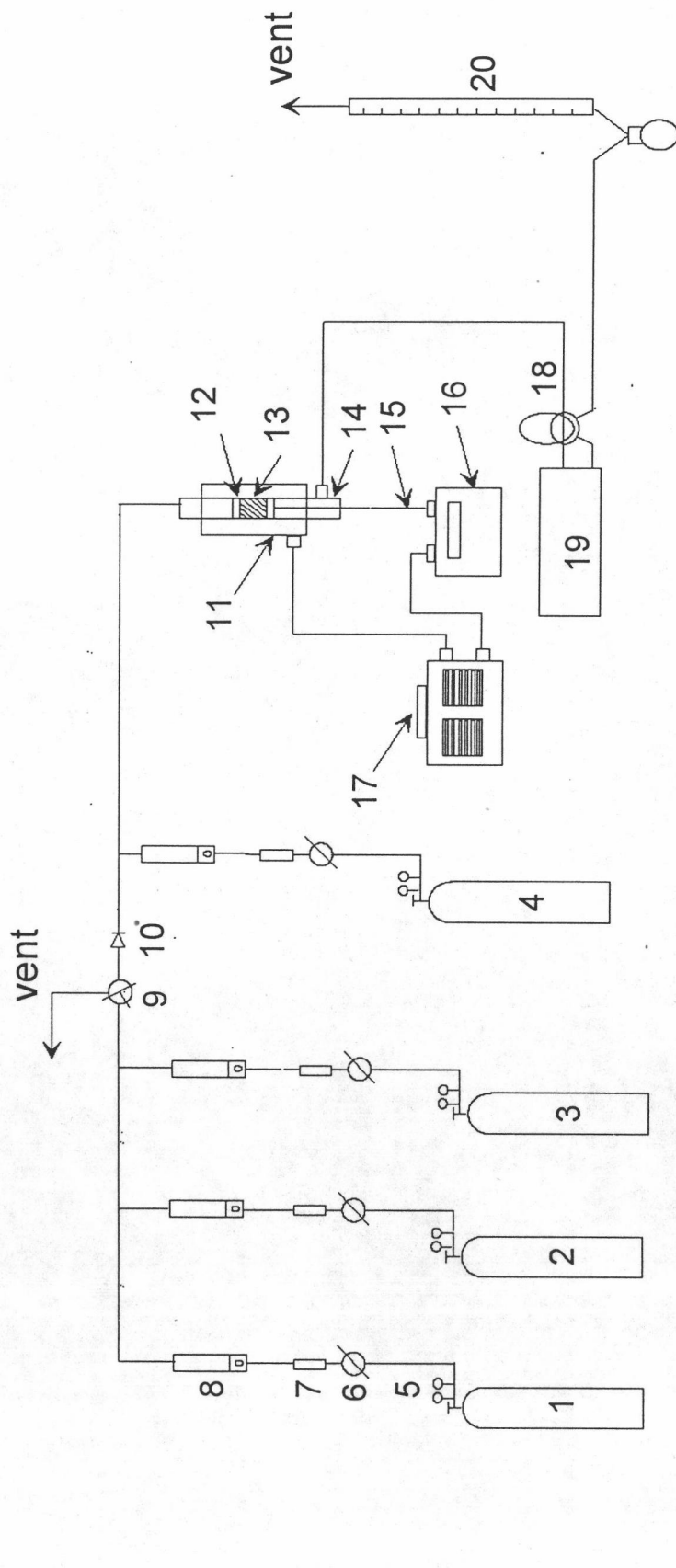
b) G.C. 8AIT

Figure 4.5 continued.

The photograph of gas chromatography and the chromatograms obtained from gas analysis are shown in figure 4.5 and Appendix B , respectively.

4.4.3 Procedure

Catalyst was heated at room temperature to 500 °C for 1 h under a He stream (35 cc/min), held at this temperature for 1 h and then cooled down to room temperature. The catalytic reaction was then started. A gas mixture containing NO(1000 ppm), C₃H₈(3000 ppm), O₂(10 volume%), and He (balance) was fed at a flow rate of 50 cc/min (GHSV ~ 4,000 h⁻¹). The reaction temperature was increased stepwise from 150 to 600 °C. The catalysts were heated up every 20 min (50 °C per time interval). At each of the reaction temperatures, the gas composition was analyzed by gas chromatography using Porapak - Q (CO₂ and C₃H₈) and Molecular Sieve - 5A (O₂, N₂, and CO) columns. The concentration of C₃H₈ at the inlet and outlet stream was therefore analyzed for C₃H₈ combustion. The catalytic activity for NO removal was evaluated by extent of conversion into N₂. The flow diagram of nitric oxide reduction system was shown in figure 4.6.



- | | | |
|-----------------------|---------------------|----------------------------------|
| 1. NO tank | 11. Reactor furnace | 16. Temperature controller |
| 2. C3H8 tank | 12. Quartz wool | 17. Variable voltage transformer |
| 3. O2 tank | 13. Catalyst bed | 18. Sampler |
| 4. He tank | 14. Reactor | 19. G.C. |
| 5. Pressure regulator | 15. Thermocouple | 20. Soap film flow meter |

Figure 4.6 Flow diagram of the nitric oxide reduction system.

4.5 Characterization of the Catalysts

4.5.1 BET Surface Area Measurement

Specific surface area of the catalyst was measured by a BET Surface Area Analyzer. This method employed a physical adsorption of N_2 on the surface of catalyst.

BET surface area was measured by a surface area analyzer as shown in figure 4.8. The gas mixture of He and N_2 was flown through the system at N_2 partial pressure of 0.3. The gas detector used was of thermal conductivity type (T.C.D.) and operated at detector temperature of 80 °C and filament current of 80 mA.

The sample was placed in a sample cell and connected to the surface analyzer. The sample was then heated up to 120 °C, held at this temperature for 1 h and cooled down to room temperature. There were three steps in this surface area measurement: adsorption, desorption, and calibration.

- Adsorption step: The sample cell was dipped into liquid nitrogen. The N_2 in gas mixture would be desorbed onto the surface of the catalyst sample, shown as a peak on the recorder, when the equilibrium was reached, a straight line was shown on the recorder.

- Desorption step: The sample cell was taken out of liquid nitrogen and then dipped into water. The adsorbed N_2 was desorbed from the surface of the catalyst sample until the equilibrium was reached, shown as a peak in the opposite direction to adsorption.

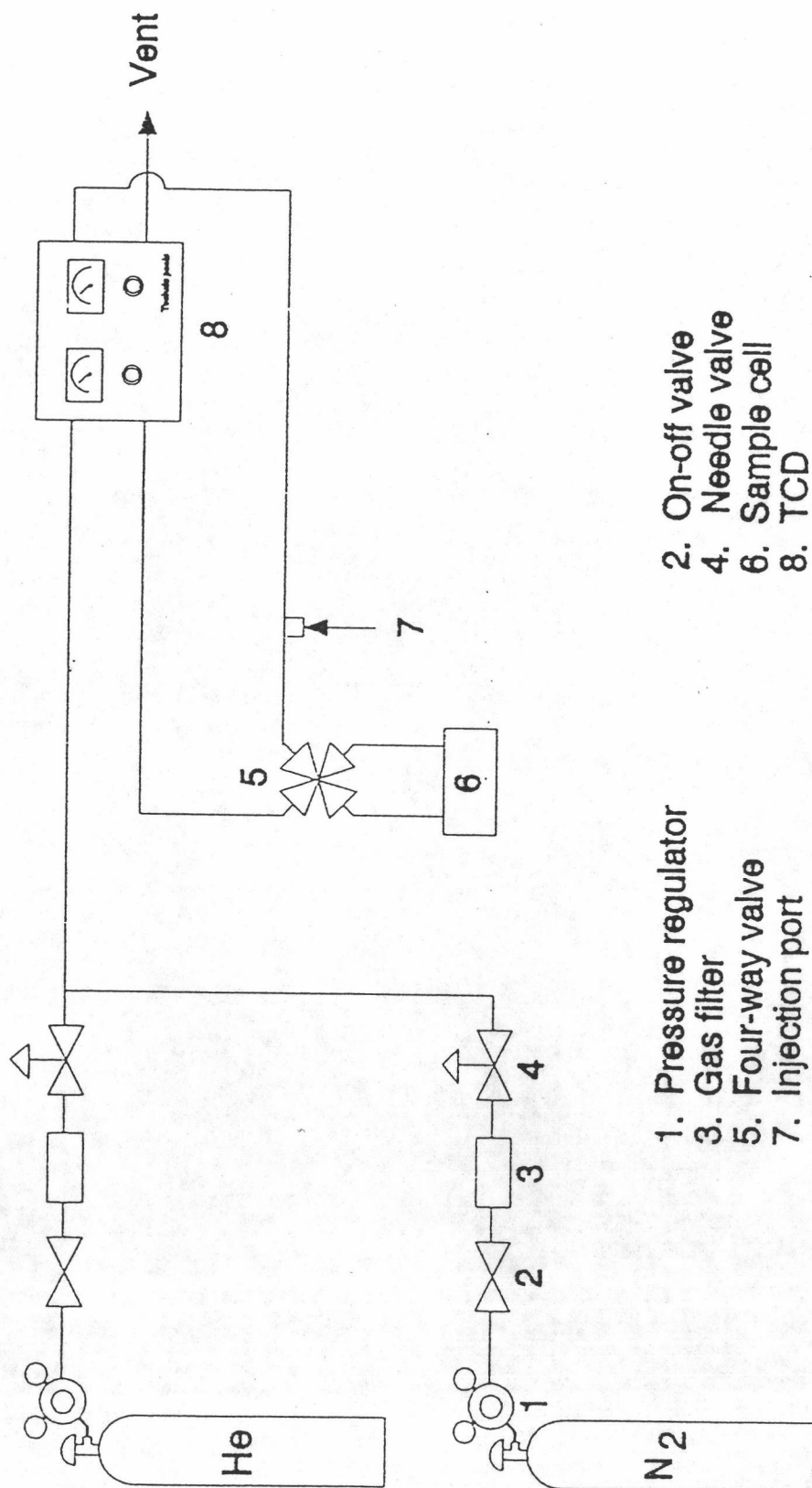


Figure 4.7 Flow diagram of the BET surface area analyzer.

- Calibration step: Nitrogen gas of 1 cc. at atmosphere pressure was injected at the sampling point. The standard nitrogen peak appeared at the same site of desorption.

4.5.2 X-ray Diffraction Patterns

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

4.5.3 Morphology

The size of the catalysts was determined 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(AA) and inductive coupled plasma spectrometry method (ICPS). 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 color 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 cleared. The volume of the solution was made up to 50 ml. using de-ionized water.

The prepared solution was analyzed for copper by atomic absorption(AA) and for platinum by inductive coupled plasma spectrometry(ICPS). The ICPS measurements were performed at the Scientific and Technological Research Equipment Centre, Chulalongkorn University.

4.5.5 Acidity

The acidity measurement were performed at Professor Inui's Laboratory in Kyoto University. The acidity of catalysts was measured as follows using the technique of temperature -programmed desorption (TPD) of NH_3 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, Catalyst(0.150 g) was heated from room temperature to 450 °C with a constant heating rate 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 downed to 50 °C on N_2 gas stream. N_2 gas was stopped and 5% NH_3 (95% N_2) gas was started to flowed. When the amount of a desorbed -NH_3 attained to its maximum, NH_3/N_2 gas was stop and N_2 gas was again fed. The catalyst was heated to 80 °C and kept at that temperature until physically-adsorbed NH_3 was removed. The temperature was risen from 80 °C to 600 °C (10 °C/min). Chemically adsorbed NH_3 was removed in this stage (The Calculation See Appendix A-5.).

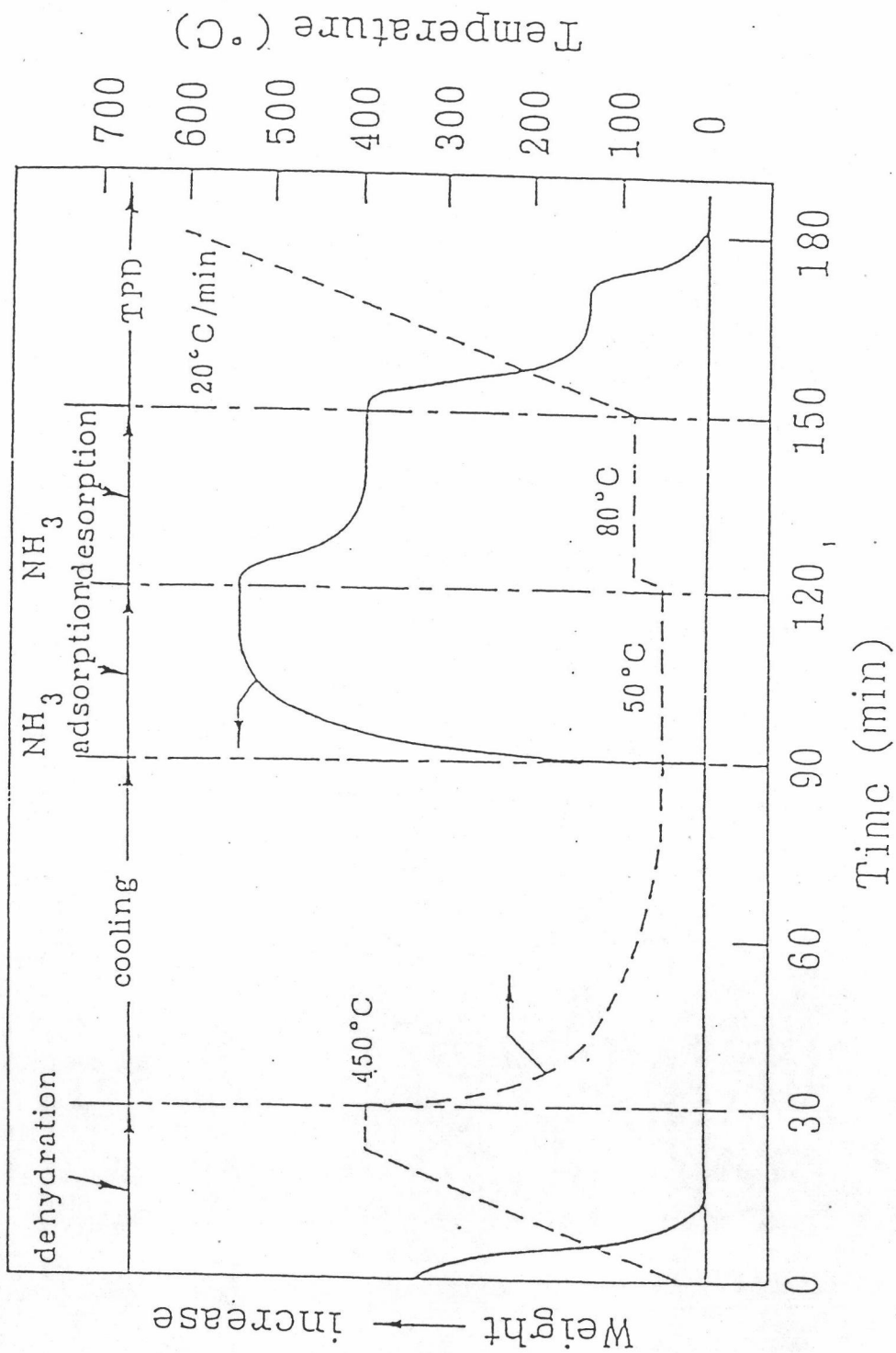


Figure 4.8 Temperature program for the NH₃-TPD measurement.