CHAPTER 4

EXPERIMENTAL METHODS

4.1 Preparation of Catalysts

The vanadosilicate catalysts were prepared by the improved method of Catalyst Engineering Laboratory, Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto university (9,17). TPABr (tetra-n-propyl ammonium bromide, $\left[(CH_3CH_2CH_2)_4N\right] Br$) was used as an organic template.

4.1.1 Preparation of Reagents

1) Decantation Solution

Al-solution : composed of

VCl_3	=	x	g
TPABr	=	7.53	"
H_2O	=	60.0	ml
(conc.)H_2SO_4	=	3.37	"

Bl-solution :

water glass	=	69.0	g
(9.3% Na_2O, 29% SiO_2)			
H_2O	=	45.0	ml

Cl-solution :

NaCl	=	26.27	g
H_2O	=	104.0	g

2) <u>Gel Solution</u> :

A2-solution :

VCl_3	=	x	g
TPABr	=	5.72	"
NaCl	=	11.95	"
H_2O	=	60.0	ml
(conc.)H_2SO_4	=	3.37	"

B2-solution :

water glass	=	69.0	g
H_2O	=	45	ml

C2-solution :

TPABr	=	2.16	g
NaCl	=	40.59	"
NaOH	=	2.39	"
H_2O	=	208.0	ml
(conc.)H_2SO_4	=	0.98	"

3) Stock solution of 1 M NH_4NO_3 1000 ml

4.1.2 <u>Preparation of Decantation Solution and Gel Precipitate</u>

<u>Formation</u> : Firstly, a decant solution was prepared by adding 60 ml of Al-solution and 45 ml aqueous solution of Bl-solution to 104 ml of Cl-solution, as shown in Figure 4.1, with vigorous stirring. From Figure 4.1, Al-solution was added by the microfeeder at a volumetric flow rate 12.0 cc/min and Bl-solution was added from a 50 ml. burette by the manual control to keep the pH of a mixed solution to constant at 9.8, since it is expected that this pH value is suitable for

1. pH meter
2. C-solution
3. B-solution
4. Homogenizer speed
   controller
5. Homogenizer
6. Adjustable base
7. A-solution contains
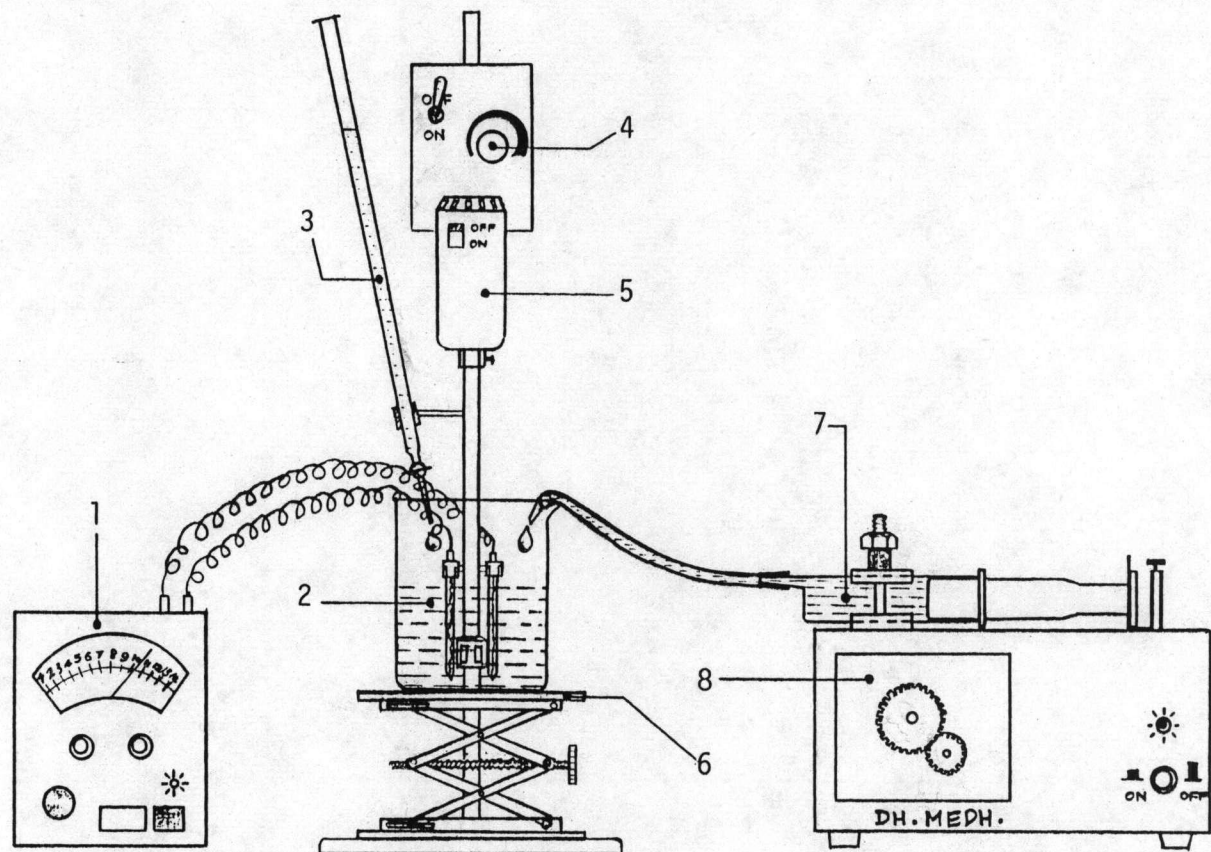   in syringe (100 ml)
8. Micro-feeder

FIGURE 4.1 Preparation method for decant solution and gel precipitate formation

precipitation. After the mixing has ended, take the beaker C-solution out off the set. Let the precipitate settle down and measure the sedimentation time of the precipitate. The precipitating was removed form the supernatant solution by a centrifuge and the supernatant solution was kept for mixing with gel precipitate. Secondly, a gel mixtured 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 9.8-10 with H_2SO_4 (conc.) Measure the sedimentation time of precipitate and separate the precipitate from solution by centrifuge. The precipitated gel mixture was milled by powder miller (Yamato-Nitto, UT-21), Figure 4.2, as follows

milled 15 min. ⟶ centrifuged 15 min (for removed the water out) ⟶ milled 15 min. ⟶ centrifuged 15 min ⟶ milled 30 min.

4.1.3 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 $\xrightarrow{\text{90 min.}}$ 160° C $\xrightarrow{\text{4.2 h}}$ 210° C under a pressure of 3 kg/cm^2 (guage) of N_2 gas. Allowed the hot mixture to cool 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 seperator (about 15-20 min for each time) and dry in oven at 110-120°C for at least 3 h.

MOTOR RECEPTACLE
STAINLESS STEEL
MILLER ARMS
PORCELAIN ARMS
SCREW FIXER
PORCELAIN BOWL
RUBBER BASE
BOWL HOLDER
MOVING BASE

SPATULA HOLDER
SPATULA
MILLER ARMS
LIFT UP AND DOWN
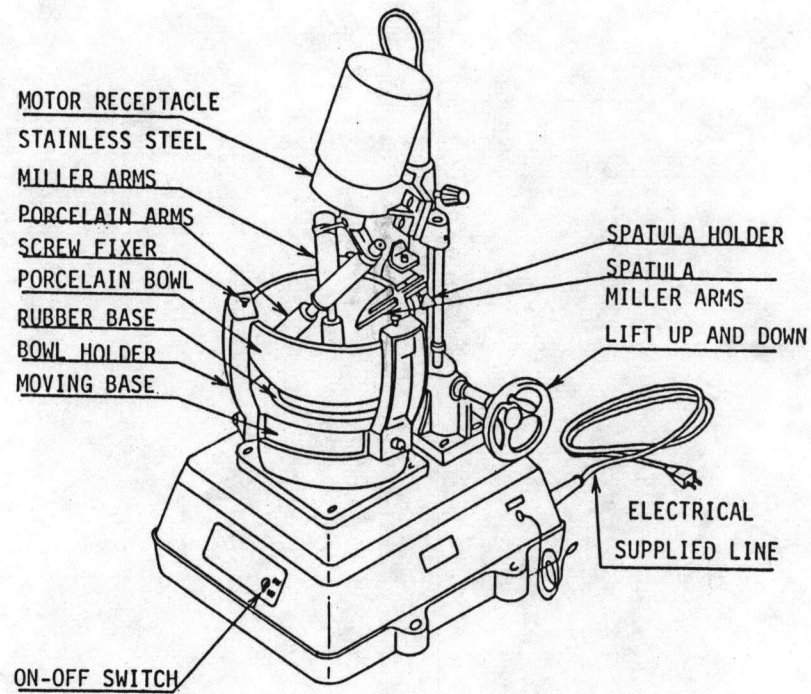
ELECTRICAL
SUPPLIED LINE

ON-OFF SWITCH

FIGURE 4.2 POWDER MILLER (YAMATO-NITTO, UT-21)

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

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

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

At this step TPABr was burned and created the cavities and channels occuring in the crystals. The calcined crystal was cooled to room temperature in a dessicator.

4.1.5 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° C for 1 h. Washing the ion-exchange crystal with distilled water 2 times by using centrifugal seperator. Repeat ion-exchange step again 1 time, and then dry ion-exchange crystal in oven at 110°-120° C for at least 3 h.

4.1.6 Second Calcination

The removal species, i.e. NH_3, NO_x, were decomposed by thermal treatment the ion-exchange crystal in a furnace at 540° C, with the temperature operating line the same as above. The vanadosilicate just prepared were tableted to provide the MTG reaction. Charge ratios of Si/V were changed from 40 to infinity.

The summary of preparation steps of these catalysts are shown in Figure 4.3.

FIGURE 4.3 Flow chart diagram of catalyst preparation by the
improved method of Catalyst Engineering Laboratory,
Dept. of Hydrocarbon Chemistry, Kyoto University
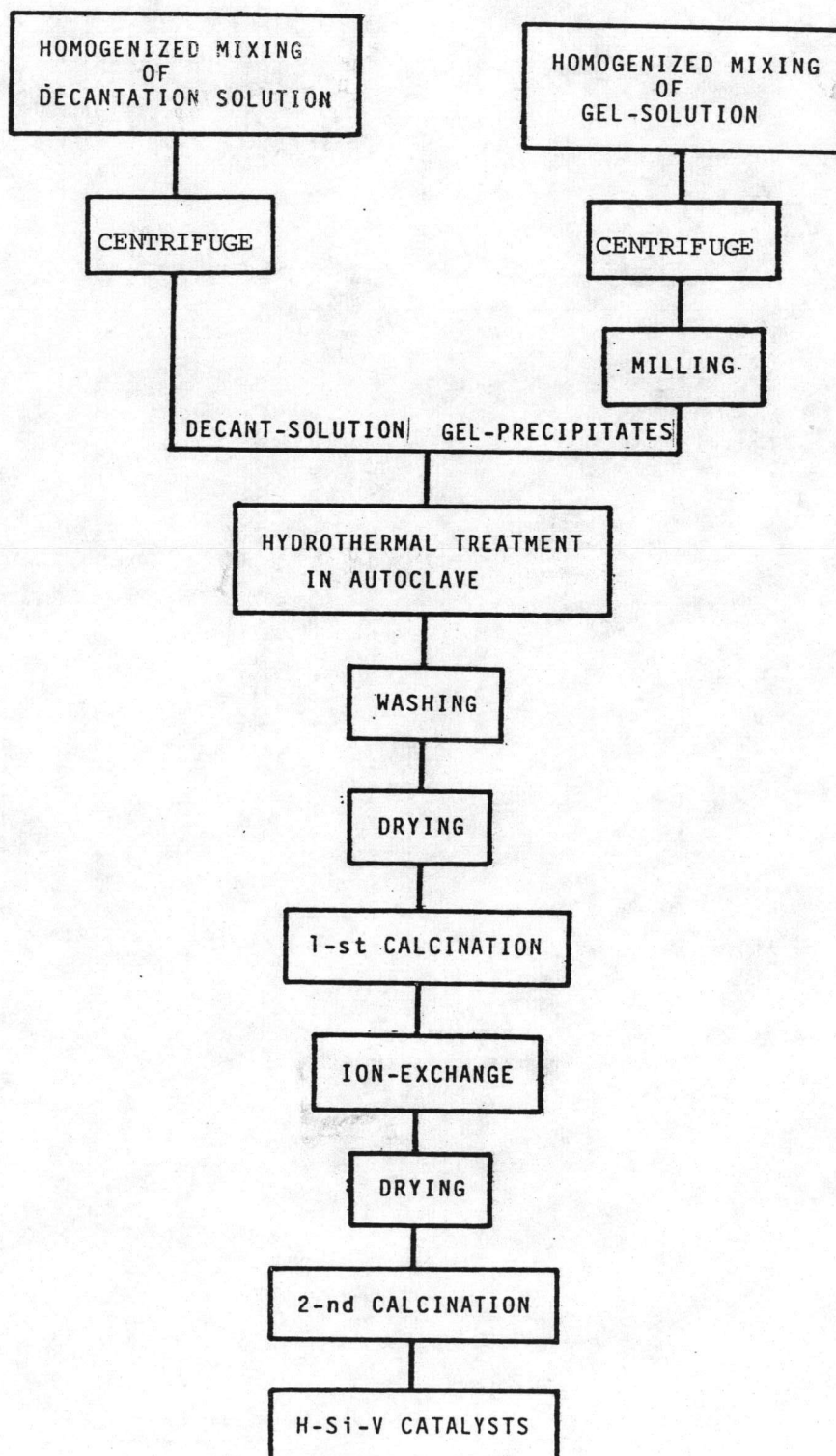
4.2 Reaction Engineering Test

4.2.1 Preparation of the Catalyst for the Reaction Test

A 120 mg of fine powder crystal of desired Si/V charged ratio catalyst was weighed to make 1 tablet catalyst, and to make 3 tablets for each Si/V charged ratio catalyst. Tablet sizes were then measured (appendix.C.). Tableted catalysts were crushed into 7-15 mesh in size and a 210 mg portion was packed into a quartz microtube fixed bed reactor of 6 mm i.d. The height of catalyst bed was then measured.

4.2.2 Reaction Method

The reaction is carried out in the reactor as shown in Figure 4.4, The procedure used to operate this reactor is as follows;

(1) Adjust the outlet pressure of N_2 gas to 1 kg/cm^2, 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 up the reactor by raising the temperature as follow:

from room temperature $\xrightarrow{\text{20 C/min}}$ 450 $^\circ$C   (hold constant 30 min.)

adjust to

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

(4) At the same time switch on the heating line, magnetic

1. N_2 gas
2. Flow indicator
3. Electrical heater
4. Thermometer
5. Water bath
6. Tube contains MeOH
7. Magnetic bar
8. Magnetic stirror controller
9. Heating line
10. Reactor furnace
11. Reactor
12. Thermocouples
13. Position for take sample
14. Condenser
15. Receiver
16. Outlet gas flow meter
17. Vent line
18. On-off temperature controller
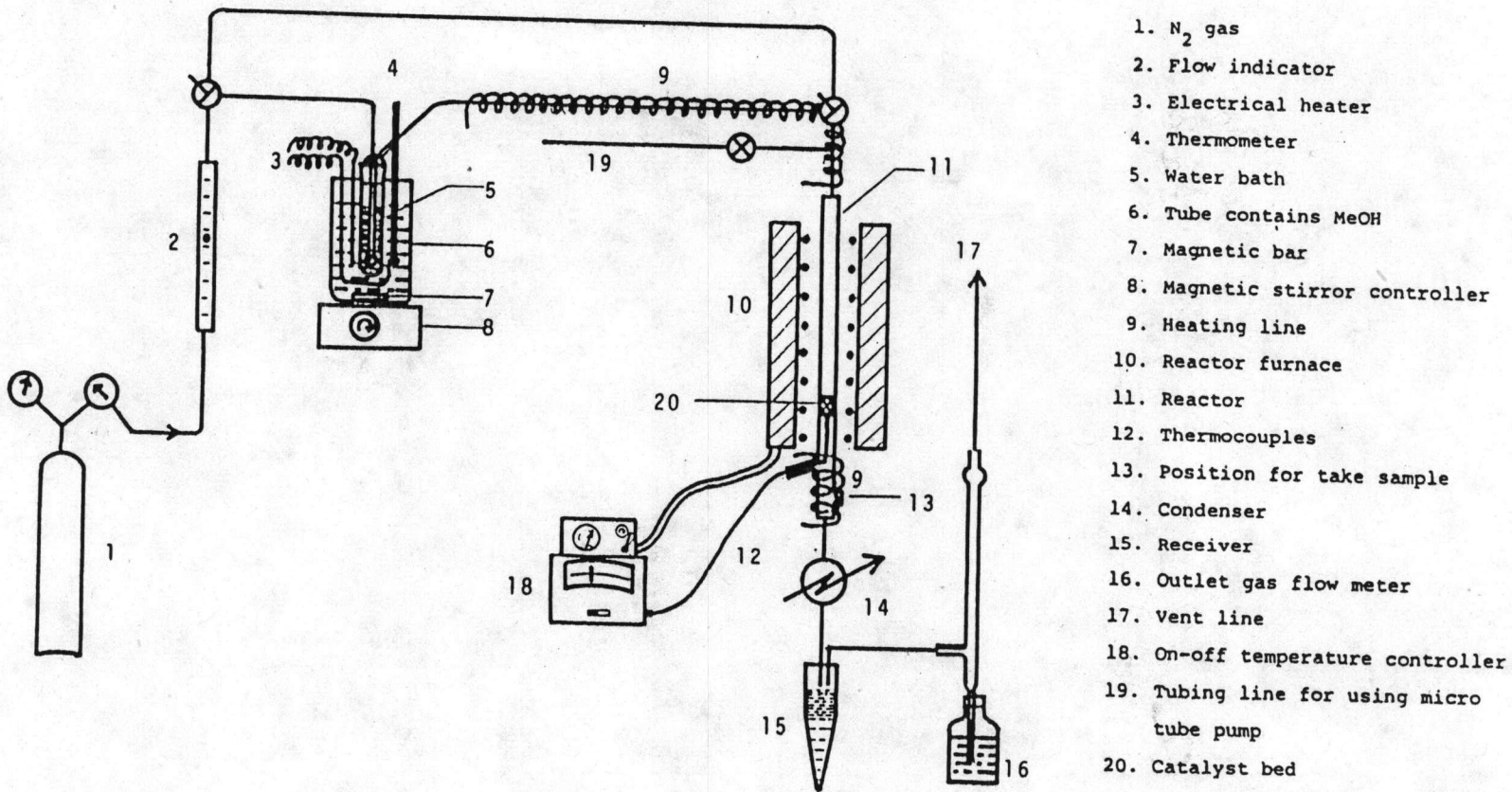19. Tubing line for using micro tube pump
20. Catalyst bed

FIGURE 4.4 DIAGRAM OF MTG REACTION EXPERIMENT FOR MICRO TUBE REACTOR.

stirrer and water bath.

(5) Set the partial vapour pressure of MeOH to the requirement by adjust the temperature of waterbath followed the Antonic equation (18),

$$\log p \quad = \quad A - \frac{B}{t+C} \qquad (4.1)$$

where   p   =   vapour pressure of MeOH in mm Hg.

t   =   temperature, $^{\circ}$C

A,B,C   are constants

For MeOH, at range -14°C to 65 $^{\circ}$C,

A = 7.89750, B= 1474.08, C = 229.13   (See also appendix A-4)

(6) Start to run the reaction by adjust 2 three way valves to allow N_2 gas to pass through the line to the saturator setting in the water-bath use to carry MeOH vapour to the reactor, and at that time the reaction time is taken as zero.

(7) Take samples to analysis at 1 and 3 hours time on stream, products are analysed by three gas chromatographs where

7.1) CO and MeOH were analysed using MS-5A column 3.5 mm ϕ x 2 m and Porapak-T column 3.5 mm ϕ x 2 m respectively, and the gas chromatograph uses for this analysis was a Shimadzu model GC-8A,.

Setting condition of G.C. are;

Injection/detector temperature	:	130° C
Column temperature	:	100° C
Current	:	60 mA
Attenuation	:	2
Carrier gas	:	Ar
Detector	:	TCD

Regulator Pressure : 6 kg/cm^2

MS-5A Column Pressure : 1.6-1.7 kg/cm^2

Porapak-T column Pressure : 0.75-0.8 kg/cm^2

Recorder Shimadzu Model R-111

Chart Speed : 5 mm/min

The recorder was connected to a digital integrator TAKEDA-RIKEN MODEL TR-2213

7.2) C_1-C_4 hydrocarbons were analysed by using VZ-10 column(3 mm ϕ x 6 m) and gas chromatograph YANACO MODEL G-1800;

Setting condition of G.C. are;

Injection Temperature : 100° C

Column Temperature : 80° C

Sensitivity : 1 x 10^{-3}

Attenuation : ½

Air : 4

Carrier gas : He

Regulator pressure of He : 6 kg/cm^2

Regulator pressure of H$_2$: 2.5 kg/cm^2

Column pressure : 2 kg/cm^2

Detector : FID

H$_2$ pressure for detector : 0.5 kg/cm^2

The Recorder connect to a digital integrator TAKEDA-RIKEN MODEL TR-2213.

7.3) C_5-C_{11} hydrocarbons (gasoline fraction) were analysed using a silicone-OV-101 (0.25 mm. ϕ x 30 m) column and a gas chromatograph Shimadzu MODEL GC.-4C PTF.

Setting condition of G.C. are;

Injection Temperature	:	$150^{\circ}C$
Detector Temperature	:	$150^{\circ}C$
Initial Temperature	:	$40^{\circ}C$
Final Temperature	:	$120^{\circ}C$
Program temperature rate	:	$3^{\circ}C$ / min
Sensitivity	:	10^{2} MΩ
range	:	0.01 V
Detector	:	FID-4C
MODE	:	DIFF. 1
Column pressure	:	0.2 kg/cm^{2}
Regulator pressure of He	:	6 kg/cm^{2}
Regulator pressure of H_2	:	2.5 kg/cm^{2}
H_2 pressure for detector	:	0.5 kg/cm^{2}
Air pressure for detector	:	1 kg/cm^{2}

(Air supply by air compressor through the pack bed of silica gel for adsorbed the moisture.)

A recorder connected to a Shimadzu C-R1-A chromatopac, where the program condition of the recorder were

CAL PM	1
WIDTH	5
SLOPE	70
DRIFT	10
MIN AR	3
T-DBL	15
LOCK	0

STP TM	70
ATTEN	0
SPEED	7
METHOD	41
SPL WT	100
IS WT	1

4.2.3 Study of Optimum Operating Condition

4.2.3.1 Influence of Vanadium Element on the Activity and Selectivity. To study this effect, the vanadosilicate catalysts charged ratio 40, 90, 200, 400, 1600, 3200 and ∞ were prepared. The reaction conditions for this purpose were SV(space velocity) = 2,000 h^{-1}, reaction temperature 300 and 360° C, and MeOH concentration = 20 % , N_2 gas = 80 %, reaction time 1 and 3 h. time on stream.

4.2.3.2 Effect of Space Velocity The vanadosilicate catalysts charged ratio 200, 400 and ∞ were chosen for this study. The reaction conditions were reaction temperature 300° C, MeOH concentration = 20 % , N_2 gas = 80 % reaction time 1 and 3 h time on stream, and the space velocity varied at 500, 1000, 2000, 4000 and 8000 h^{-1}.

4.2.3.3 Effect of Reaction Temperature To study this effects Si/V charged ratio 1600 and 90 catalysts were used, where the reaction were SV = 2000 h^{-1}, MeOH concentration = 20 % , N_2 gas = 80 %, and the reaction temperature varied at 260, 280, 300, 330, 360° C for Si/V charged ratio 1600 catalyst and for Si/V charged ratio 90 catalyst, the reaction temperature varied at 300, 330, 360, 390 and 420° C.

4.2.3.4 <u>Effect of MeOH Concentration</u> For this purpose, the vanadosilicate charged ratio 1600 catalyst was chosen. To study this effect, the reaction conditions were at SV = 2000 h^{-1}, reaction temperature 300° C, and the MeOH concentration varied at 5, 10, 20, 40 and 100 %. For MeOH concentration 100 %, it was fed to the reactor by using a microtube pump. At GHSV = 2000 h^{-1} change to WHSV as shown in appendix A-2.

4.3 <u>Physical Properties Measurement</u>

For study the physical properties of vanadosilicate catalyst, the following properties are measured;

4.3.1 <u>BET surface area</u> : BET surface area of catalysts were measured by N_2 adsorption with continuous flow at liquid nitrogen temperature range by using He as a diluted gas. Figure 4.5. The procedure for BET measurement of Figure 4.5 are as follows;

1. adjust outlet pressure of He gas regulator to 7 kg/cm^2 and adjust He pressure in column to 2.6 kg/cm^2

2. line on

3. set oven temperature at 50°C and detector supply on and wait for steady about 30 min.

4. measure flow rate of He and record room temperature

5. Open and adjust N_2 pressure regulator at 3.5 kg/cm^2 and adjust to 3 kg/cm^2 for column

6. mix N_2 and He gas for get the N_2 mole fraction = 0.3 by calculating as follows:

$$\text{mole fraction of } N_2 = \frac{\text{Flow rate of } (N_2 + He) - \text{flow rate of He}}{\text{Flow rate of } (N_2 + He)}$$

7. weigh about 40 mg of sample and put into sample U-tube bottle (Figure 4.5)

8. adjust TANK knob from close to open for about 3-4 sec and then close

9. adjust TUBE knob from close to open about 3-4 sec and close

10. repeat steps 8 and 9 again twice

11. cooling mixed gas tube using liquid N_2 to trap the moisture in mixed gas

12. place sample U-tube bottle at sample position

13. adjust COCK 1 knob from SHORT to EVAP.

14. adjust COCK 2 knob from CAL to SAMP

15. heat sample by adjusting AC line on and set temperature at $300^{o}C$ for 30 min

16. cooling sample to room temperature and set recorder at the condition :

chart speed   20   mm/min

mV range   256   mV

injection temperature   1

record at   POS

17. cool sample with liquid N_2 and run recorder

18. measure N_2 desorption by take liquid N_2 out and heat sample by water (at room temperature) run speed chart at 40 mm/min and adjust mV range to suitable range, record to NEG.

19. adjust TUBE knob from close to open about 10 sec and then close

20. wait for about 10 min then adjust COCK 2 knob from SAMP to CA 2 and recorder conditions being the same as N_2 desorption measurement (calculation of BET surface area, see appendix A-5)
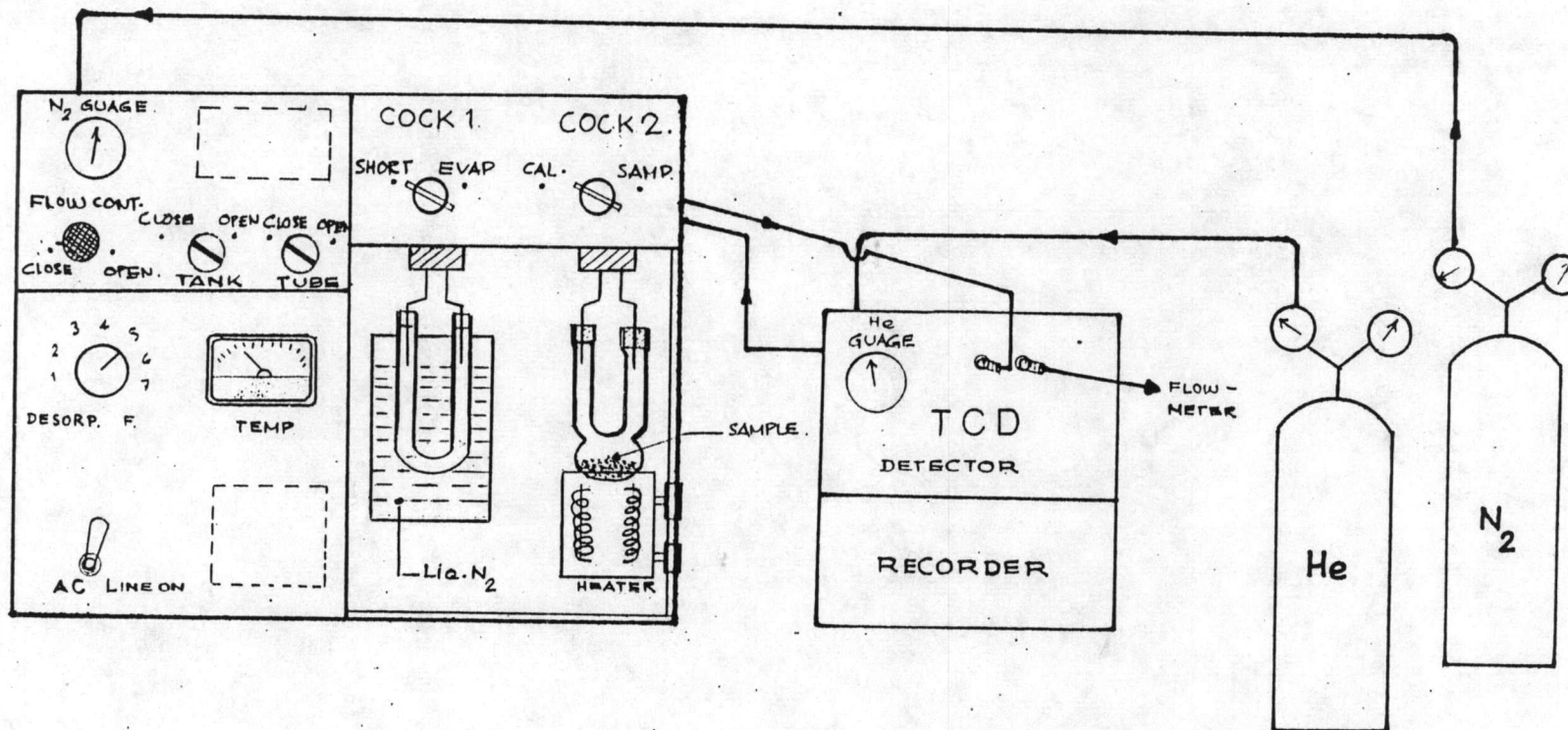
Figure 4.5   Diagram of BET surface area measurement system

4.3.2 <u>X-ray diffraction</u> : The catalysts Si/V charged ratio
range from ∞ to 40 were prepared for XRD, and measured by Mr. T.
Miyake. The method for preparing sample for XRD is shown in
appendix B-1.

4.3.3 <u>Acidity of catalysts</u> For study the acidity of catalysts,
measured by using the technique of temperature program desorption of
NH_3. The catalysts Si/V changed ratio from ∞ to 40 were measured;
where about 150 mg of sample was put into sample disc and N_2 gas was
flown through the sample set at 50 ml/min. A dry sample was taken for
finding the dry weight and heated at a temperature programe of $20\,^{\circ}C$/min
to the final temperature of $430\,^{\circ}C$, during which weight loss and
temperature lins were measured by a recorder at chart speed 5 mm/min
and 10 mg per chart full scale was setted. Then, cooling sample to
$60\,^{\circ}C$, and seted 5 mg per chart full scale. Flow rate of NH_3 was
adjusted at 50 ml/min, the recorded weight increased up to a constant
value. Finally, NH_3 desorption was measured by heating the sample at
a temperature program rate of $10\,^{\circ}C$/min to the final temperature of $600\,^{\circ}C$

4.3.4 <u>Chemical Composition Analysis</u>

To study the actual Si/V charge ratio of prepared catalysts,
the samples, Si/V charged ratio from ∞ to 40 were made into solutions
for atomic absorption measurement. The method used for preparing the
sample solution and the standard solution is explained in appendix
B-2. These samples were measured by Mr.K.Fukuda.

4.3.5 <u>Scanning Electron Microscope</u> (SEM)

To study the outside structure of vanadosilicate catalysts,
Si/V charged ratio ∞ , 90, and 40 were chosen for this purpose by
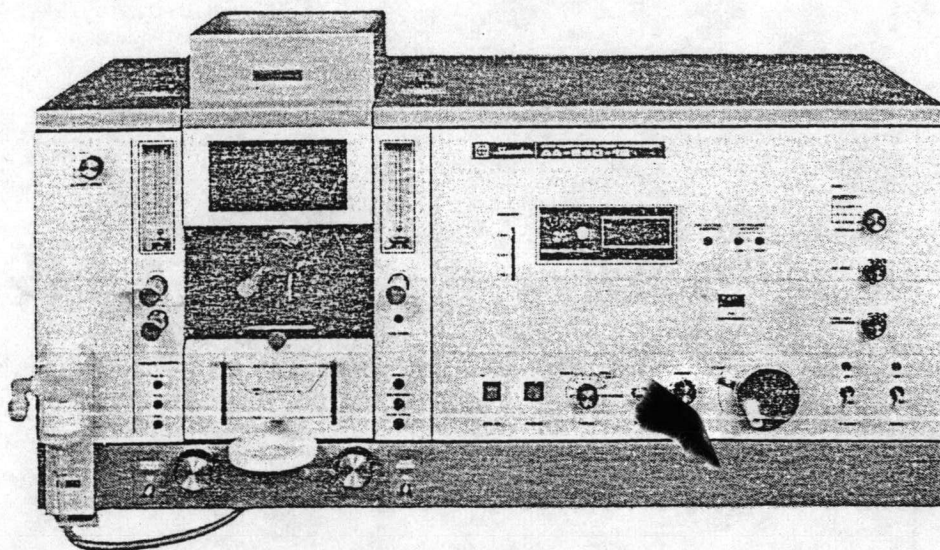
Figure 4.6 Atomic Absorption Equipment

using the scanning electron microscope as detector. These catalysts were measured by Mr. Sakamoto and Miss T. Ukawa.
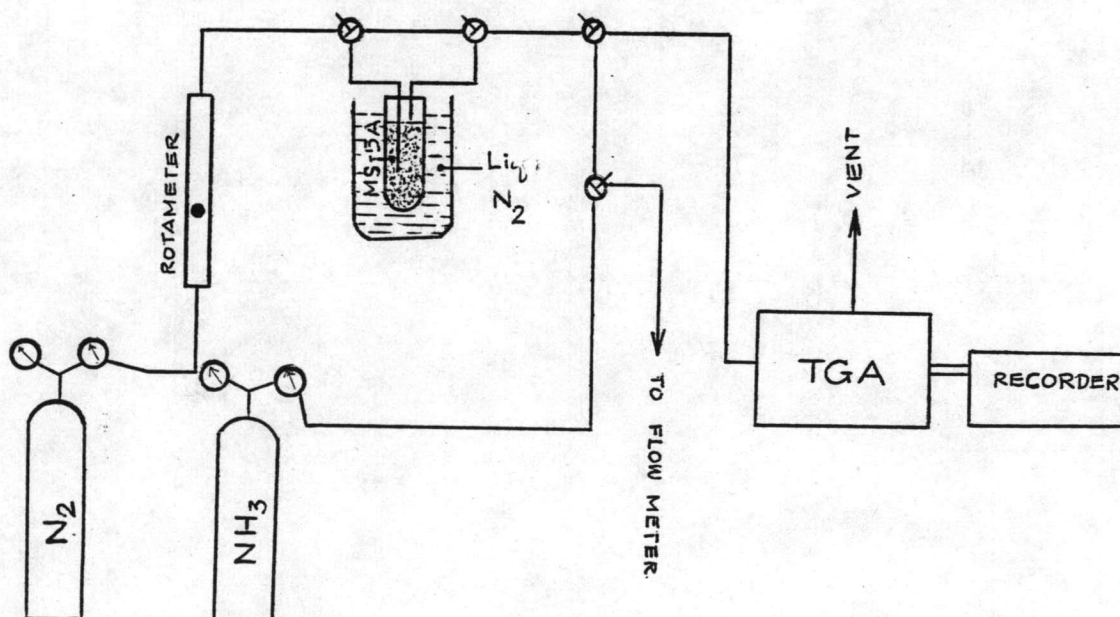

Figure 4.7 Flow chart of TPD(NH_3) measurement system