

## CHAPTER IV

### EXPERIMENTS

A aromatization of over metal containing MFI type zeolite catalysts are explained in the following section.

#### 4.1 Catalyst Preparation

ZSM-5, Fe-Silicate, Zn-Silicate, Fe.Al-Silicate, and Zn.Al-Silicate catalysts having various metal contents were prepared. The  $\text{AlCl}_3$  was replaced by  $\text{Fe}_2(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  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 G1-solution and 45 ml. aqueous solution of G2-solution to 104 ml. of G3-solution while stirring with a magnetic stirrer (Figure 4.2). G1-solution was added by a microfeeder at a volumetric flow rate 12.0 cc/min and G2-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 S1-solution and 45 ml. of S2-solution to 208 ml. of S3-solution. The method and condition of mixing were similar to the preparation of decantation solution. The precipitate from solution 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/cm<sup>2</sup> (gauge) of nitrogen gas. The hot mixture was allowed to cool down at room temperature in the autoclave over-night. The product crystals were washed with distilled water, to remove Cl<sup>-</sup> 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 was placed in a porcelain container then 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.

Puring this step, TPABr was burned out creating 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.

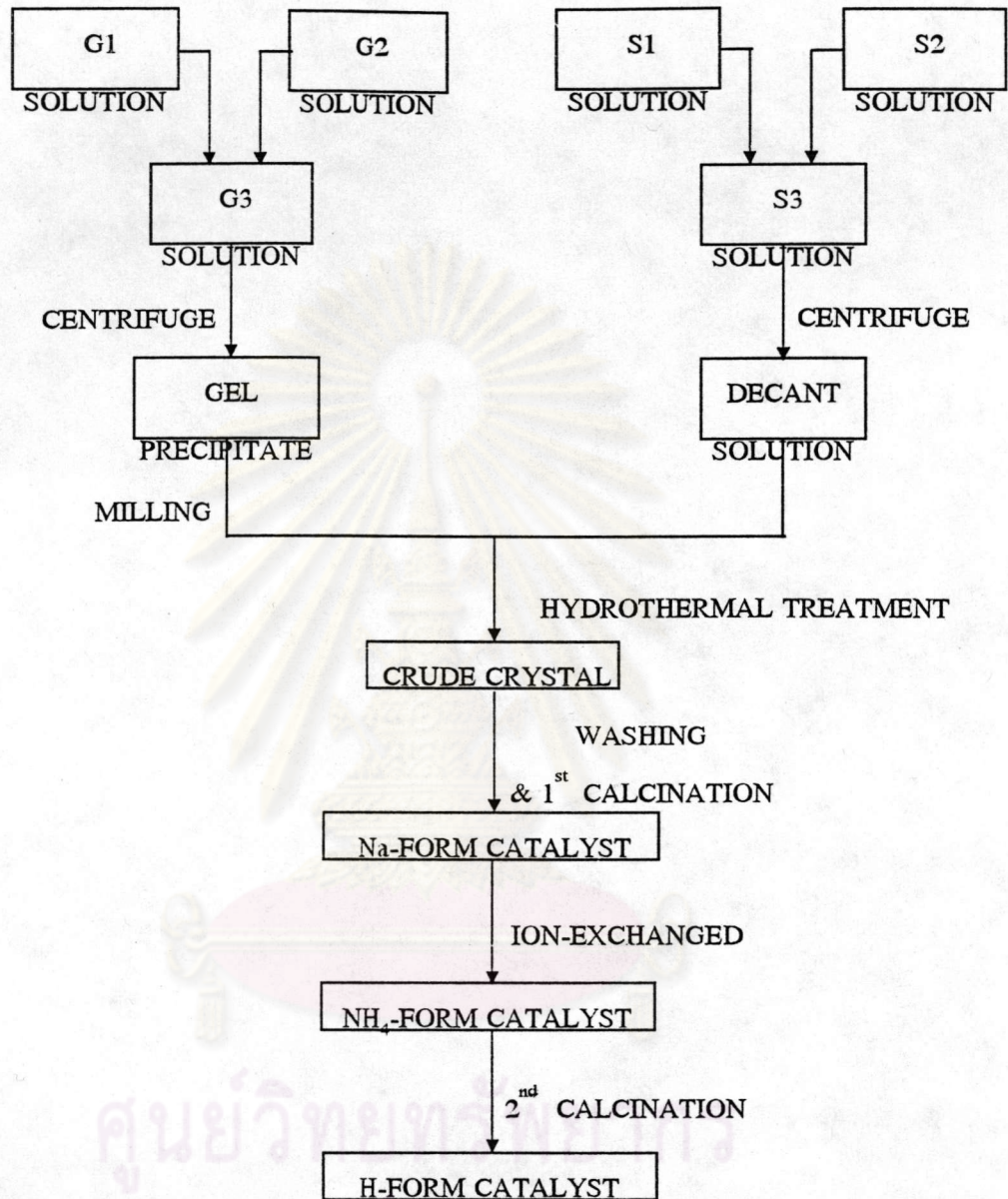


Figure 4.1 Preparation procedure of MFI catalysts by rapid crystallization



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 <sub>3</sub> (g) and/or	x	AlCl <sub>3</sub> (g) and/or	x
Fe(NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O (g) and/or	y	Fe(NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O (g) and/or	y
Zn(SO <sub>4</sub> ) <sub>2</sub> ·7H <sub>2</sub> O (g)	z	Zn(SO <sub>4</sub> ) <sub>2</sub> ·7H <sub>2</sub> O (g)	z
TPABr (g)	7.53	TPABr (g)	5.75
Distilled water (ml)	60	Distilled water (ml)	60
H <sub>2</sub> SO <sub>4</sub> (conc.) (g)	3.38	H <sub>2</sub> SO <sub>4</sub> (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 <sub>2</sub> SO <sub>4</sub> (conc.)	1.55		

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

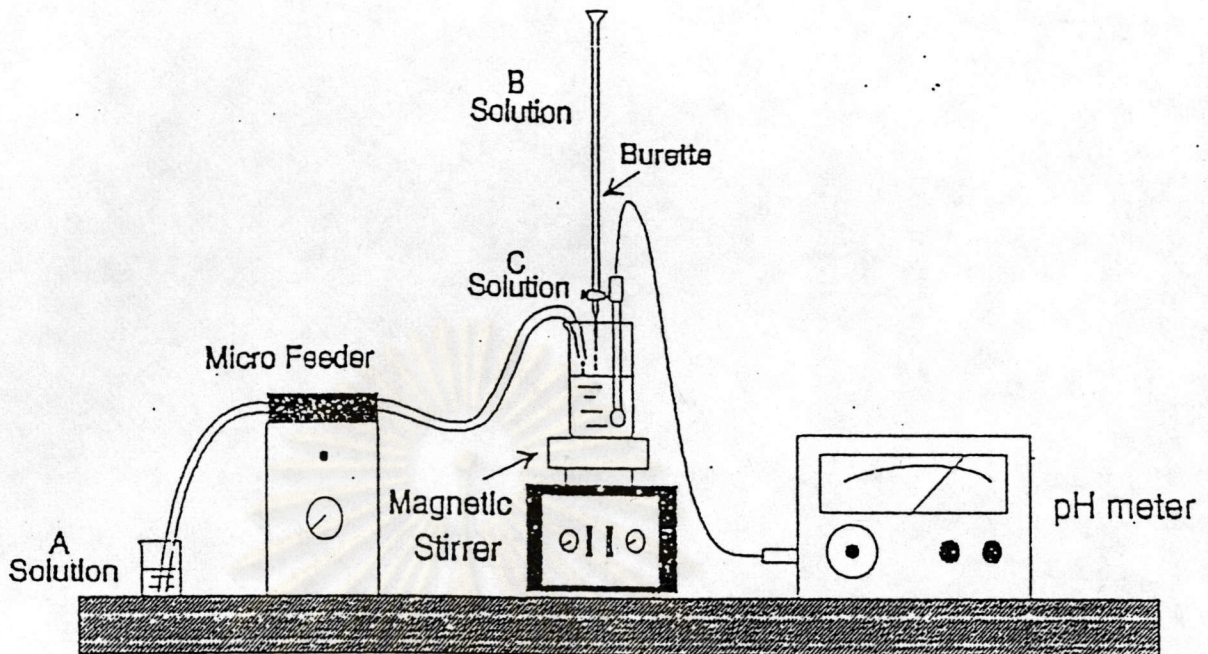


Figure 4.2 A set of apparatus used for preparation of supernatant solution and gel precipitation as providing for the rapid crystallization.

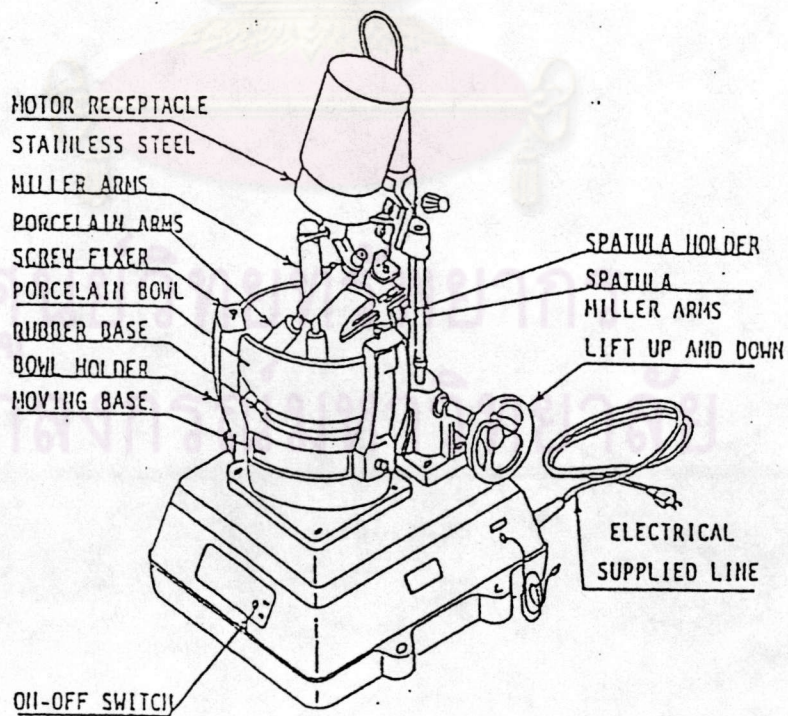


Figure 4.3 A powder miller (Yamato-Nitto, UT-22).

#### 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  $\text{NH}_4\text{NO}_3$  and heated on a stirring hot plate at  $80\text{ }^\circ\text{C}$  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  $110\text{-}120\text{ }^\circ\text{C}$  for 3 h in an oven. The Na-form crystal was thus changed to "NH<sub>4</sub>-form catalyst".

#### 4.1.5 Catalyst Calcination

The NH<sub>4</sub>-form catalyst was calcined in a furnace by heating from room temperature to  $540\text{ }^\circ\text{C}$  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  $98\text{ }^\circ\text{C}$  for 3 h. Dry crystals was heated in air with a constant heating rate of  $3\text{ }^\circ\text{C}/\text{min}$  up to  $350\text{ }^\circ\text{C}$  and maintained for 10 min. The calcined catalyst was treated with a stream of 20%  $\text{H}_2$  - 80%  $\text{N}_2$  and heated up from room temperature to  $400\text{ }^\circ\text{C}$  and kept at  $400\text{ }^\circ\text{C}$  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. followed by washing 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 at this temperature for 2 h.

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

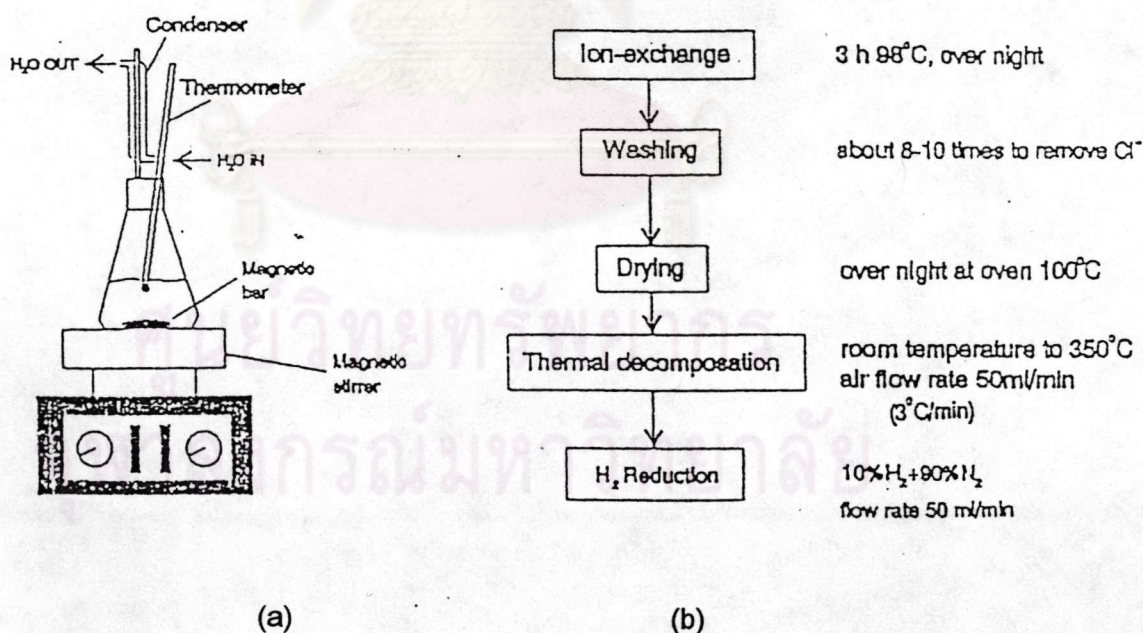


Figure 4.4 A Set of apparatus used for preparation of metal ion-exchanged on catalyst (a). A diagram for metal ion-exchanged on catalyst(b).

#### 4.4 Apparatus and Reaction Method

The methanol conversion reaction was carried out by using a conventional flow apparatus shown in Figures 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,  $2000 \text{ h}^{-1}$  ; reaction temperature,  $450 \text{ }^{\circ}\text{C}$ .

The procedure used to operate this reactor was as follows;

- (1) Adjust the outlet pressure of  $\text{N}_2$  gas to  $1 \text{ kg/cm}^2$ , 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 the reactor from room temperature to  $450 \text{ }^{\circ}\text{C}$  with a heating rate of  $20 \text{ }^{\circ}\text{C} / \text{min}$  and maintain at that temperature for 30 min. Then the reaction temperature controlled by an on-off controller is 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,

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



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 adjusting 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. The operating conditions for each GC are shown in Table 4.2  
Column used were silicon-OV-1 (0.25  $\Phi$  x 2m, TCD) for CO (see Appendix A-6)

(8) The conditions were varied as follows:

GHSV	2,000-10,000 h <sup>-1</sup>
Temperature	250-600 °C
Methanol composition	15-30 % balance with N <sub>2</sub>

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.2 Operating conditions for gas chromatograph

Gas chromatographs	Shimadzu GC- 14A	GC - GowMac	GC - 8A	GC - 8A
Detector	FID	FID	TCD	TCD
Column	Silicon OV-1 φ 0.25 x 50 m.	VZ-10 φ 3 x 3 m	Porapak-Q φ6 x 3m	MS-5A φ6 x 2m
Carrier gas	N <sub>2</sub> (99.99%)	N <sub>2</sub> (99.99%)	N <sub>2</sub> (99.999%)	N <sub>2</sub> (99.999%)
Column temperature				
-Initial	30° C	50° C	90° C	90° C
-Final	140° C	50° C	90° C	90° C
Detector temperature	150° C	80° C	100° C	100° C
Injector temperature	40° C	80° C	100° C	100° C
Analyzed gas	gasoline range hydrocarbon	gaseous hydrocarbon	CO <sub>2</sub> , CH <sub>3</sub> OH, MeOMe	CO

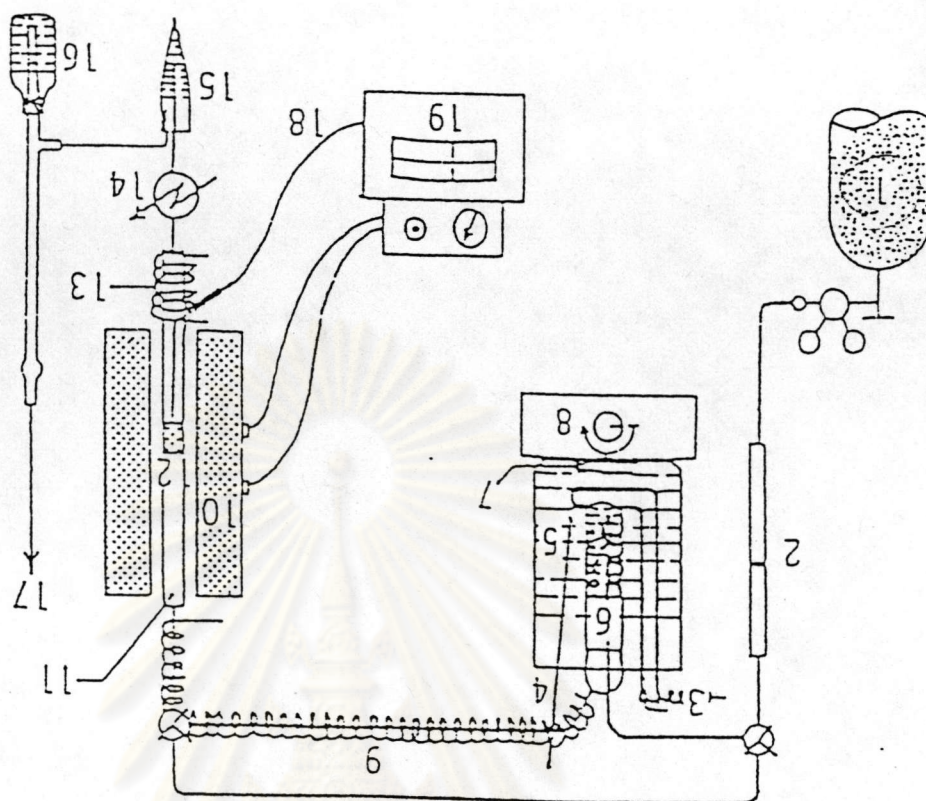


Figure 4.5 Schematic diagram of the reaction apparatus for the methanol conversion.

- |                                     |                    |                       |
|-------------------------------------|--------------------|-----------------------|
| 1. N <sub>2</sub> gas cylinder,     | 2. flow indicator, | 3. water batch heater |
| 4. thermometer                      | 5. water bath,     |                       |
| 6. saturator set containing MeOH,   | 7. magnetic bar,   |                       |
| 8. stirrer controller               | 9. heating line,   |                       |
| 10. funace,                         | 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. |                    |                       |

## 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 a catalyst to find the total surface area. BET surface areas of these catalysts 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).