



CHAPTER IV

EXPERIMENTAL

This chapter described the experimental system and experimental procedures in this research. A description of catalyst preparation method is given in section 4.1 the preparation of silver cluster was described in section 4.2 and the characterization of catalysts are explained in section 4.3. The details of experimental procedures and materials are as follow.

4.1 Catalyst preparation

In this study, ZSM-5 catalysts with having different Si/Al ratios between 25-400 were used. Ag-ZSM-5 was prepared for studied of silver cluster formation. The preparations of Ag-ZSM-5 with different Si/Al ratio were described as follow.

4.1.1 Preparation of Na-ZSM-5

The preparation procedure of ZSM-5 by rapid crystallization method was shown in figure 4.1. The reagent used are shown in figure 4.1 and table 4.1. This method could advantageously and rapidly prepare the uniform and fine zeolite crystal. The detail preparation procedures of ZSM-5 were described below.

4.1.1.1 Preparation of Gel Precipitation and Decantation Solution

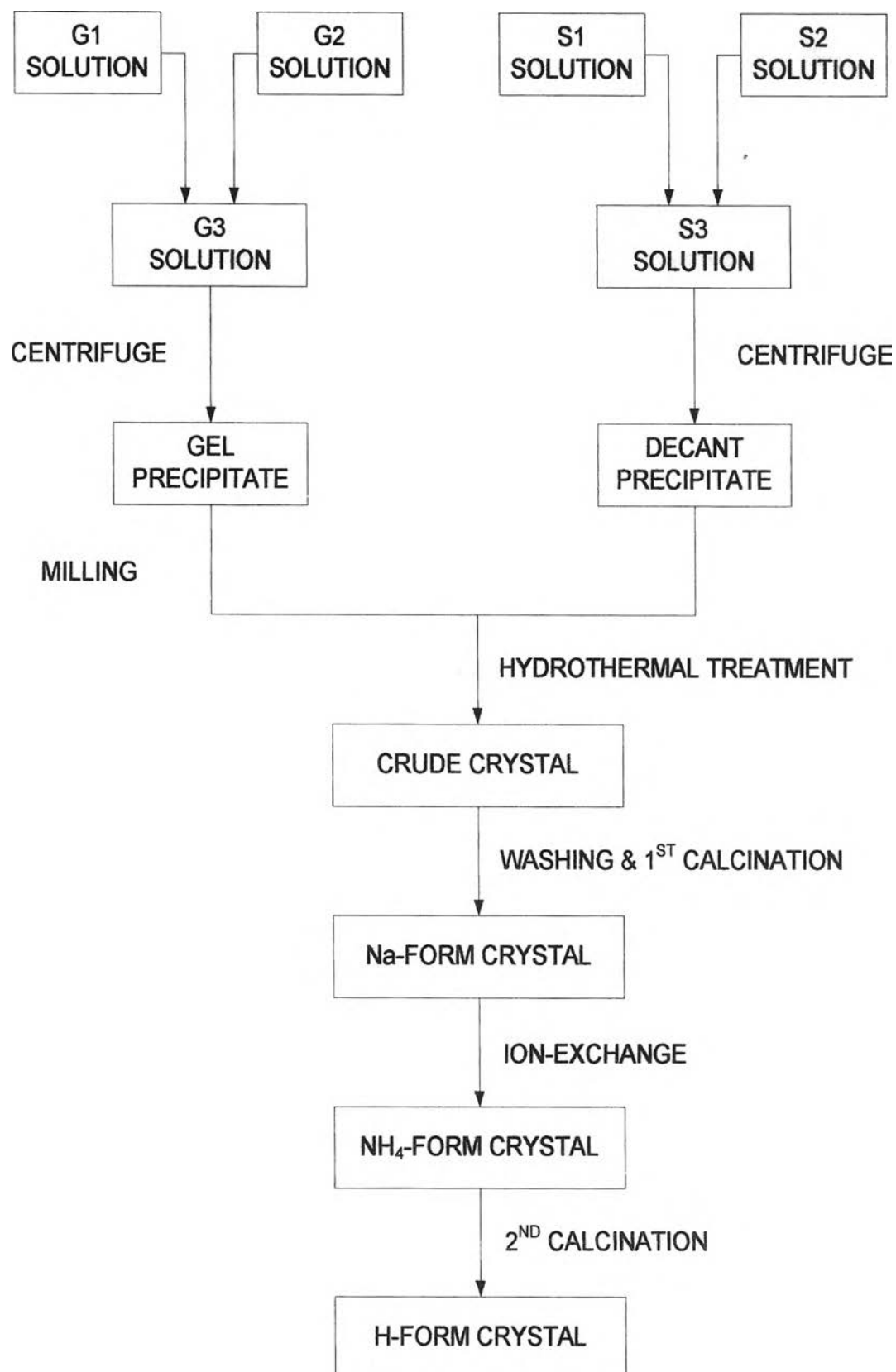
The preparation of supernatant liquid was separated from the gel, which is important for preparation the uniform crystals. A gel mixture was prepared by adding solution G1 and solution G2 into solution G3 while stirring with a magnetic stirrer at room temperature. G1 solution and G2 solution was added from burette by the manual control to keep the pH. The Ph of mixed solution was maintained within the range 9-11 because it was expected that this suitable for precipitation. The gel mixture was separated from the supernatant liquid by centrifuge. The precipitated gel mixture was milled for totally 1 hr by powder miller. The milling procedure was follows milled 20

min and centrifuge (to remove the liquid out) about three times. Milling the gel mixture before the hydrothermal treatment was essential to obtain the uniform and fine crystal the gel precipitate was keep for mixing with supernatant solution. On the other hand, another decantation solution was prepared by adding S1 solution and S2 solution into S3 solution. The method and condition of mixing were similar to preparation of gel mixture. Upon the complete mixing the precipitating gel was then removed from supernatant solution by the centrifuge and the supernatant solution was mixed with the milled gel, expecting that before mixing adjust the pH of solution between 9-11 with H_2SO_4 (conc.) or 1 M NaOH solution.

Table4.1 Reagent used for the preparation of Na-ZSM-5: Si/Al 50

Reagents for the gel Preparation		Reagents for decant solution Preparation	
Solution G1		Solution G1	
AlCl_3 (g)	2.2496	AlCl_3 (g)	2.2496
AgNO_3	X	AgNO_3	X
TPABr (g)	5.72	TPABr (g)	5.72
NaCl (g)	11.95	-	-
Distilled Water (ml)	60	Distilled Water (ml)	60
H_2SO_4 (conc.) (g)	3.40	H_2SO_4 (conc.) (g)	3.40
Solution G2		Solution G2	
Distilled Water (ml)	45	Distilled Water (ml)	45
Water glass (g)	69	Water glass (g)	69
Solution G3		Solution G3	
TPABr (g)	2.61	-	-
NaCl (g)	40.59	NaCl (g)	26.27
NaOH	2.39	-	-
Distilled Water (ml)	208	Distilled Water (ml)	104
H_2SO_4 (conc.) (g)	1.55	-	-

Figure 4.1 The preparation procedure of H-ZSM-5 by rapid crystallization method.



4.1.1.2 Crystallization

The mixture of milling precipitate and the supernatant of decant solution was charged in liter stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm² gauge. Then the mixture in the autoclave was heated from room temperature to 160 °c in 90 min. and then up to 210 °c in 4.2 hr while being stirred at 60 rpm, followed by cooling down the hot mixture to room temperature in the autoclave overnight. The temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization. The produced crystals were washed with deionized water, to remove C1 out of the crystals, about 8 times by using the centrifugal separator (about 10 min. for each time) and dried in an oven at 110 °c for at least 3hr.

4.1.1.3 First Calcination

The dry catalysts in a porcelain 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 hr.

At this step, the organic template (TPABr) was burned out and left the cavities and channels in the crystals were cooled to room temperature in a desiccator. After this step the crystals formed were called “Na-form catalyst”.

4.1.1.4 Ammonium Ion-Exchange of Na-form Crystal

The ion-exchange step was carried out by mixing 3 g of Na-form catalyst with 90 ml of 1 M NH₄NO₃ and heated on a stirring hot plate at 80 °c by Reflux for about 40 min. After that the heating mixture was cooled down to room temperature and washed with deionized water about 3 times by using the centrifugal separator (about 10 min. for each time). The ion-exchange step was repeated about 3 times. Then the ion-exchange crystal was dried at 110 °c for at least 3 hr. in an oven. The Na-form crystal was thus changed to “NH₄-form catalyst”.

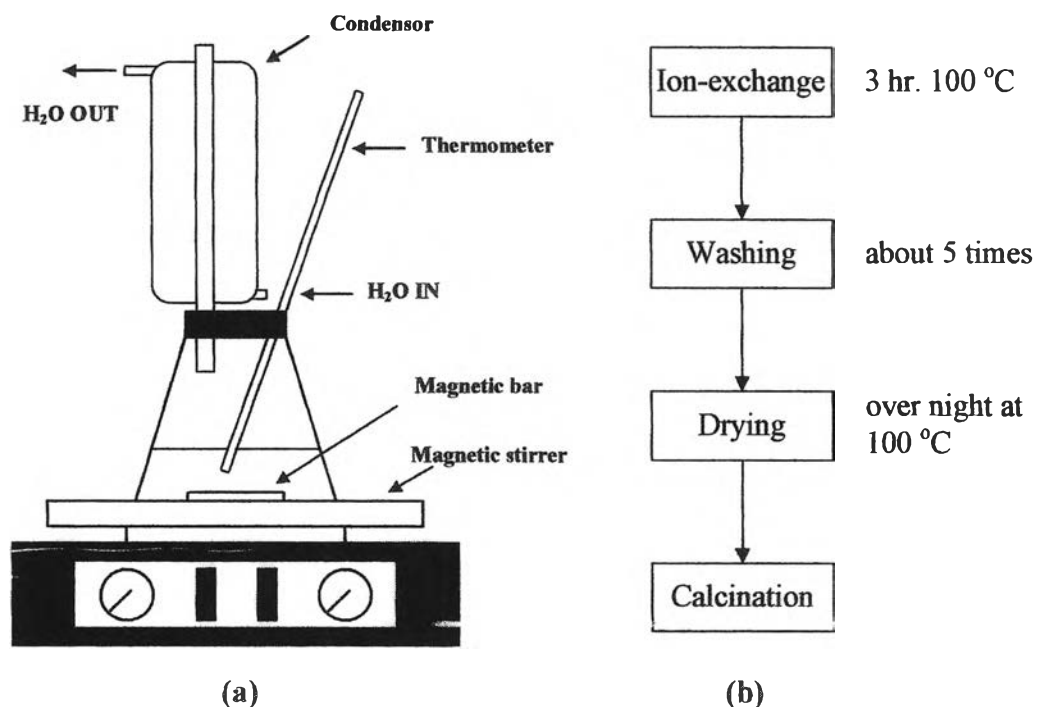
4.1.1.5 Second Calcination

The NH_4 -form crystal 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 3.5 hr. After this step the crystal thus obtained was called “H-form catalyst”.

4.1.1.6 Metal loading by Ion-Exchange

About 2 g of catalyst was immersed in 60 ml of metal salt aqueous solution about $80\text{ }^\circ\text{C}$ for 6 hr. It was washed with deionized water about 5 times, about 10 min for each time (as shown in Figure 4.2). The sample was dried overnight at 110°C . Finally, dry crystal was heated in air with the constant heating rate of $10\text{ }^\circ\text{C}/\text{min}$ up to $350\text{ }^\circ\text{C}$ and maintained for 2 hr.

Figure 4.2 Diagram of apparatus used for preparation of metal ion-exchange on catalyst



(a) A set of apparatus used for preparation of metal ion-exchange on catalyst

(b) A diagram for metal ion-exchange on catalyst

4.2 Preparation of silver cluster

Silver clusters were prepared by reducing Ag-ZSM5 catalysts of 0.25 g. in flow of 3% H₂/Ar and 100% H₂ at 300 °C , 0.5 hr.

4.3 Characterization of the catalysts

4.3.1 X-Ray Diffraction analysis (XRD)

The Crystallinity and X-Ray diffraction (XRD) patterns of catalysts were performed by a X-ray diffractometer SEIMENS D5000 connected with a personal computer with Diffract AT Version 3.3 program for fully control of the XRD analyzer. The experiment was carried out by using CuK α radiations with Ni filter and the operating condition of measurement are shown below:

2 θ range of detection: 4-70 °

Resolution : 0.04 °

Number of Scan : 10

The functions of base line subtraction and smoothing were used in order to get the well formed XRD spectra.

4.3.2 Scanning Electron Microscope (SEM)

The shape and size of the crystal of the prepared catalysts were observed by using JEOL JSM-5400 Scanning Electron Microscope (SEM) at The Analytical Instrument Center and Laboratory, Chulalongkorn University.

4.3.3 X-Ray Fluorescence analysis (XRF)

Percentage of metals was analyzed by X-Ray fluorescence spectrometer (XRF) technique. The silicon, aluminum and silver contents of prepared catalyst were analyzed by X-ray fluorescence spectrometer (XRF) at the Department of Science King Mongkut's Institute of Technology Ladkrabang.

4.3.4 Acidity Measurement

Temperature programmed desorption of ammonia (NH_3 -TPD) have been used to investigate the acidic properties of Ag-ZSM-5 zeolites. The acidity of catalysts was analyzed by NH_3 -TPD at Petrochemical Engineering Laboratory, Chulalongkorn University.

4.3.5 UV-Vis Spectroscopy

Characterizations of Ag clusters were determined by UV-Vis Spectroscopy Perkin-Elmer 650 at Petrochemical Engineering Laboratory, Chulalongkorn University. The prepared catalysts were measured in the range of 200-600 nm.