

CHAPTER IV

EXPERIMENT

This chapter is explanation about the experimental system and the experimental procedures that used in this work. The chemicals that used in the silica modified alumina preparation are presented in section 4.1. The lists of experimental equipment are shown in section 4.2. In section 4.3, the silica modified alumina preparation is presented. The characterization is presented in section 4.4.

4.1 Chemicals

The lists of chemicals used in these experiments were shown in the following.

1. Ultra high purity nitrogen gas (99.99%vol.) with oxygen and moisture content less than 3 ppm was supplied by Thai Industrial Gas Co. Ltd.
2. Aluminum isopropoxide (98+%) $[(CH_3)_2CHO]_3Al$ was manufactured by Aldrich Chemical Company. ,USA..
3. Tetraethyl orthosilicate (99+%) $Si(OC_2H_5)_4$ was manufactured by Aldrich Chemical Company ,USA..
4. Toluene (99%) $C_6H_5CH_3$ was supplied by Merck Co., Ltd., Germany.
5. 1-Butanol (99%) was supplied by Merck Co., Ltd., Germany.

4.2 Equipment

All equipment using in the catalyst preparation consisted of

1. Autoclave

The 1-L autoclave made from stainless steel. It could be operated at high temperature and pressure. The reaction was happened at 300°C and 6-14 MPa.

2. Iron jacket

The iron jacket was used to reduce the volume of autoclave to be 300 ml.

3. Beaker

The beakers were used to contain the reactant and collect the fluid separated from super critical drying made of the glass (3-mm thickness).

4. Cooling line

The cooling line made from stainless tube used in the vapor condensation of the vapor separated from the product when reaction was completed.

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4.3 Synthesis of silica modified alumina

In this research, the products were prepared by three different methods. First, the mixtures of aluminum isopropoxide (AIP, Aldrich) and tetraethyl orthosilicate (TEOS, Aldrich) were suspended in 100 ml of toluene in a beaker, and then set up in a 300 ml autoclave. In the gap between the beaker and the autoclave wall, 30 ml of toluene was added, After the autoclave was completely purged with nitrogen. The suspension was heated to 300°C at a rate of 2.3°C/min and held at this temperature for 2 h. During the reaction, the autogenous pressure gradually increased to 6-14 MPa. After the reaction, the autoclave valve was opened, and the fluid phase in the autoclave was released at that temperature condensing in a cooling coil. The condensed liquid was collected in a another beaker. After the autoclave was cooled, the white powder products were obtained. For the second method, the same procedures as the first one were followed except that 1-butanol was used in stead of toluene. In the third preparation, the same procedures as the first one were followed but a mixture of water and toluene was added instead of toluene in the gap between the beaker and the autoclave wall. Amount of water was varied as 10 and 30 ml. The AIP/TEOS weight ratios of the first and second preparation method were varied as 1,2,8,15,30,∞ but only the AIP/TEOS weight ratio of 8 was used for the third preparation method.

A part of the product was calcined in a box furnace by heating to the desired temperature (600°C, 1000°C and 1150°C) at a rate of 10°C/min and holding at that temperature for 1 h, and thus silica-modified aluminas were obtained.

The reaction products will be designated by abbreviations T, B and H meaning the solvents that used in the reaction: T means toluene B means 1-butanol, and H means the mixture of water and toluene in the gap between the beaker and the autoclave wall. The number followed H was the amount of water used in the gap (*10ml). The abbreviation followed by AS, which means the silica-modified alumina followed by a number for the AIP/TEOS weight ratio in the reaction mixture, which comes after the abbreviation and AS∞ was the product obtained by AIP alone. When

calcined samples are specified these abbreviation are followed by calcination temperature in the parenthesis. Therefore, TAS ∞ (1150) and TAl(1150) means the alumina sample prepared in toluene and calcined at 1150°C.

In this thesis we want to study in many conditions as following.

1. The effect of molar ratio of aluminum and silica of the product

One pot synthesis of silica modified alumina was further studied by varying the weight ratio of aluminum and silicon on the product 5 value (Al/Si = 1:1, 2:1, 8:1, 15:1, 30:1) and alumina alone for determining the suitable ratio. That had highest thermal stability.

2. The effect of solvent that used to prepare the products

One pot synthesis of silica modified alumina was further studied by varying the solvent that used in the preparation of products for study the effect of the solvent on the synthesis of products on the characteristics of products. And for study the mechanism of products in both solvents.

3. The mechanism of one pot synthesis

In the third preparation we tried to explain the mechanism of this reaction on the effect of water.

4.4 Characterization

The methods used to characterize the products were specified in the following.

1. X-ray Diffraction Patterns

X-ray diffraction (XRD) patterns of the products were performed with SIEMENS XRD D5000 at Petrochemical Engineering Research Laboratory, Chulalongkorn University, was employed to identify the crystal structure.

2. Fourier Transformed Infrared Spectroscopy (FT-IR)

NICOLET FT-IR Impact 400 spectroscopy at Petrochemical Engineering Research Laboratory, Chulalongkorn University, was employed to study the functional groups of the products.

3. Morphology

The shape and the size of the crystals were observe by JEOL Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

4. Chemical Analysis

Percentage of the components in the products was analyzed by X-ray fluorescence spectrometer (XRF) at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

5. BET Surface Area Measurement

5.1 Apparatus

The apparatus consisted of two gases feed lines for helium and nitrogen. The flow rate of gas was adjusted by means of fine-metering valve. The sample cell made from pyrex glass. The flow diagram of the BET surface area measurement is shown in Figure 4.1 and the operation conditions of gas chromatograph (GOW-MAC) is shown in Table 4.1

5.2 Procedure

The mixture of helium and nitrogen gas flowed through the system at the nitrogen relative pressure of 0.3. The sample was placed in the sample cell, which was then heated up to 150°C and held at this temperature for 2 h. The sample was cooled down to room temperature and ready to measure the surface area. There were three steps to measure the surface area.

Table 4.1 Operation conditions of gas chromatograph (GOW-MAC)

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml/min
Detector temperature	80°C
Detector current	80 mA

(1). Adsorption step

The sample cell was dipped in to the liquid nitrogen. Nitrogen was adsorbed on the surface of the sample until equilibrium was reached.

(2). Desorption step

The nitrogen-adsorbed sample was dipped in to the water at room temperature. The adsorbed nitrogen was desorbed from the surface of the sample. This step was completed when the recorder line became to the base line.

(3). Calibration step

1 ml of nitrogen at atmospheric pressure was injected at the calibration port and the area was measure. The area was the calibration peak

(4). The BET surface area calculation is in APPENDIX B.

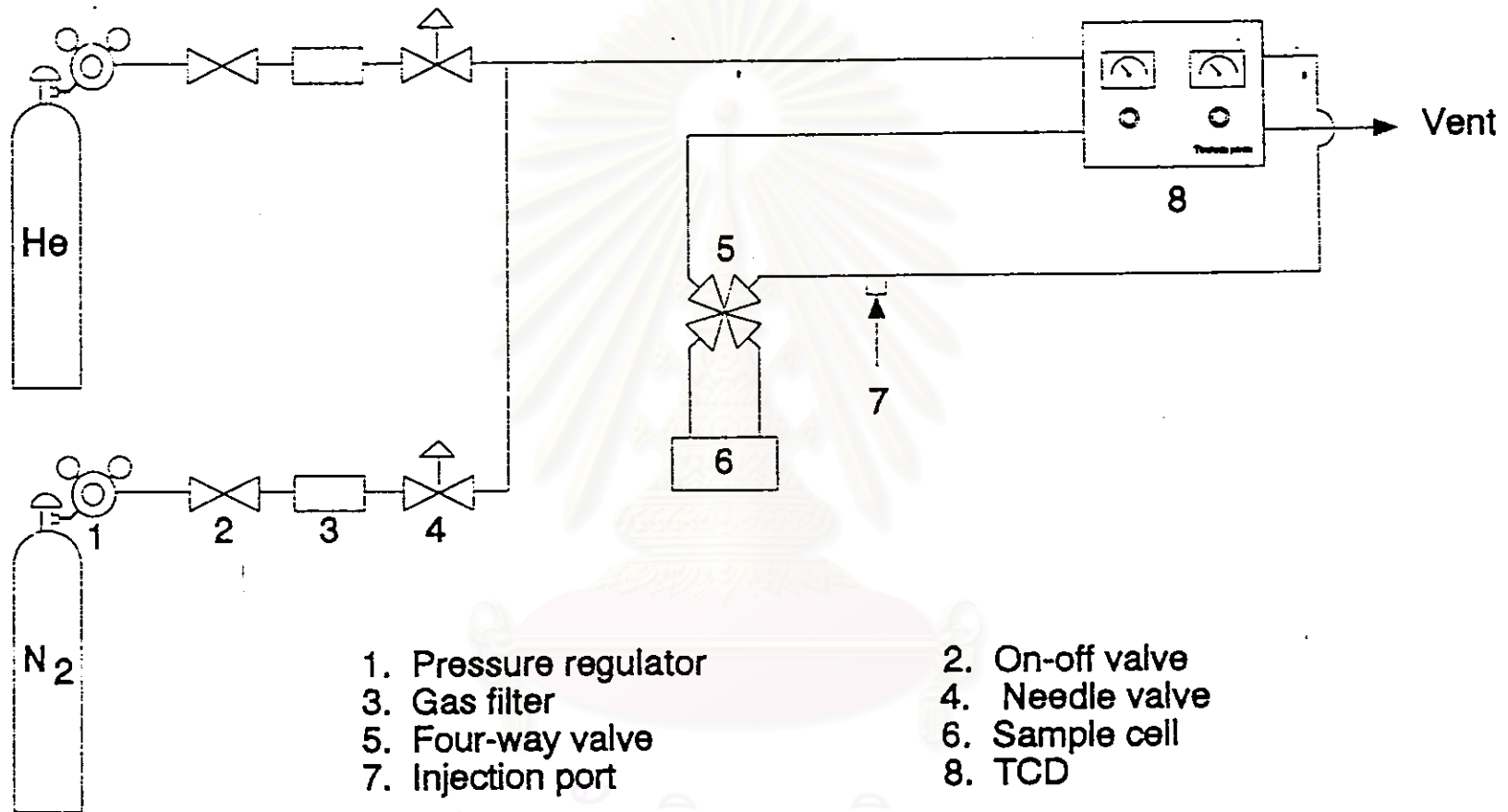


Figure 4.1 : BET instrument

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