

CHAPTER IV

EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this study. The chapter is divided into three sections, i.e., catalyst preparation, catalyst characterisation and reaction study in hydroxylation of benzene. The chemicals, apparatus and procedures for catalyst preparation are explained in section 4.1. The composition, structure and surface properties of the catalyst characterised by various techniques such as AAS, XRD, BET, SEM, and IR are discussed in section 4.2. Finally, the details of the reaction study are illustrated in section 4.3.

4.1 Catalyst preparation

4.1.1 Chemicals

The details of chemicals used in the preparation procedure of TS-1 are shown in Table 4.1.

Table 4.1 The chemicals used in the catalyst preparation

| Chemical | Grade | Supplier |
|---------------------------------|------------|----------|
| Titanium(IV) butoxide 97% | - | Aldrich |
| Tetrapropylammonium bromide 98% | - | Aldrich |
| Sodium chloride | Analytical | APS |
| Sodium hydroxide | Analytical | Merck |
| Sulfuric acid | Analytical | Aldrich |
| Sodium silicate solution | Extra pure | Merck |

4.1.2 Preparation Procedures

The preparation procedure of TS-1 by rapid crystallization method is shown in Figure 4.1, while the reagents used are shown in Table 4.2.

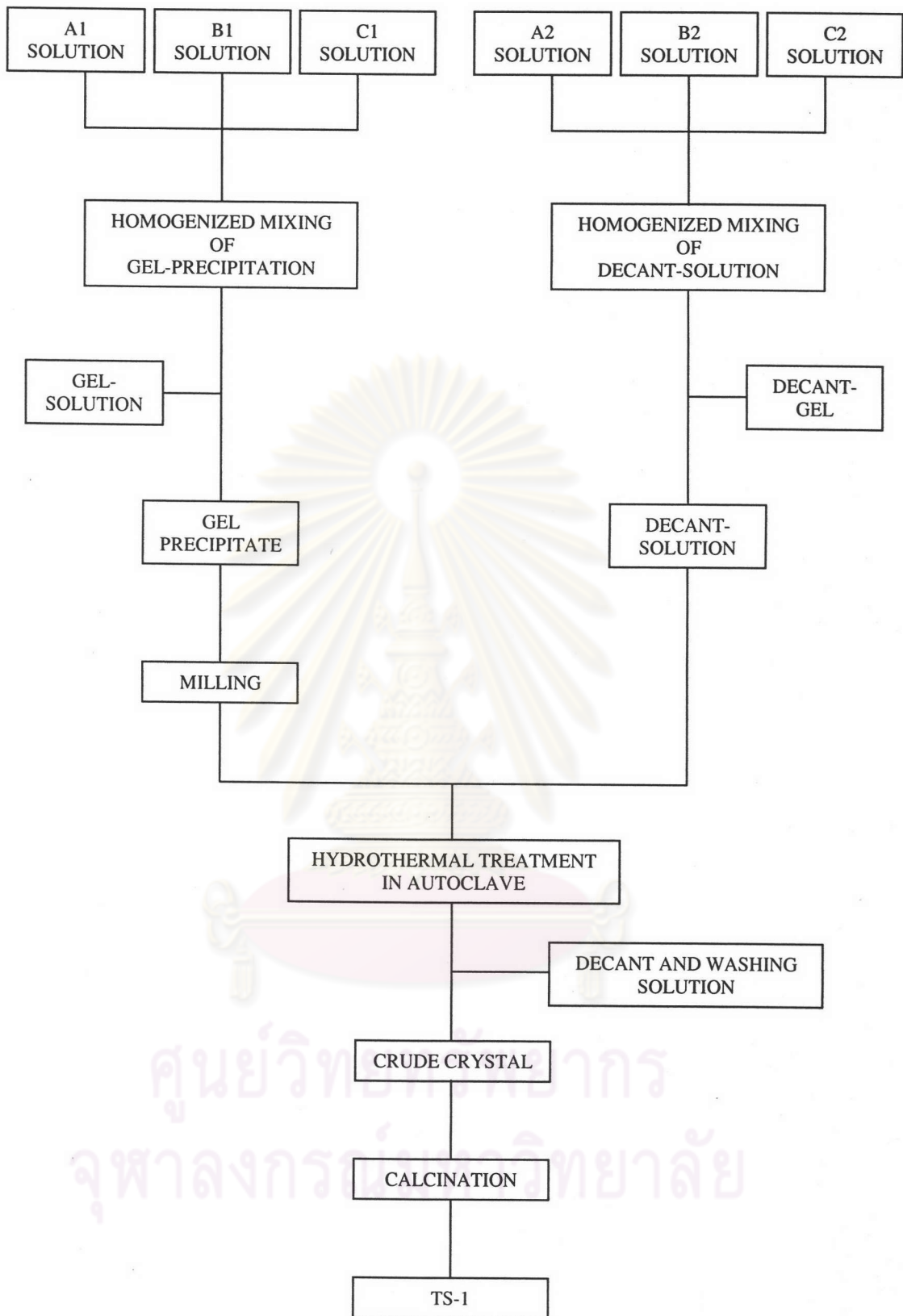


Figure 4.1 The preparation procedure of TS-1 by rapid crystallization method

Table 4.2 Reagents used for the preparation of TS-1 : Si/Ti = 52 (Appendix A)

| Solution for the gel preparation | | Solution for decant-solution preparation | |
|--|----------|--|----------|
| Solution A1 | | Solution A2 | |
| Ti[O(CH ₂) ₃ CH ₃] ₄ | 2.2085 g | Ti[O(CH ₂) ₃ CH ₃] ₄ | 2.2085 g |
| TPABr | 5.72 g | TPABr | 7.53 g |
| NaCl | 11.95 g | De-ionized water | 60 ml |
| De-ionized water | 60 ml | H ₂ SO ₄ (conc.) | 3.4 ml |
| H ₂ SO ₄ (conc.) | 3.4 ml | | |
| Solution B1 | | Solution B2 | |
| Sodium silicate | 69 g | Sodium silicate | 69 g |
| De-ionized water | 45 ml | De-ionized water | 45 ml |
| Solution C1 | | Solution C2 | |
| TPABr | 2.16 g | NaCl | 26.27 g |
| NaCl | 40.59 g | De-ionized water | 104 ml |
| NaOH | 2.39 g | | |
| De-ionized water | 208 ml | | |
| H ₂ SO ₄ (conc.) | 1.55 ml | | |

4.1.2.1 Preparation of Gel Precipitation and Decantation Solution

A supernatant liquid was separated from the gel, which is important for preparing the uniform crystals. A gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the gel mixture was maintained within the range 9-11 because this pH range is suitable for precipitation. H₂SO₄ (conc.) or NaOH solution were used to adjust pH of gel mixture to an appropriate level if it was necessary. The gel mixture was separated from the supernatant liquid by a centrifuge. The precipitated gel mixture was milled for 1 h by a powder miller (Yamato-Notto, UT-22) before the hydrothermal treatment in order to obtain the uniform, fine crystals. The milling procedure was as follow: milled 15 min → centrifuge (to remove liquid out) 15 min → milled 15 min → centrifuge 15 min → milled 30 min → centrifuge 15 min.

A decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2 same as for the preparation of gel mixture. The pH of solution was maintained between 9-11. The colorless supernatant liquid was separated from the mixture by centrifugation.

4.1.2.2 Crystallization

The mixture of the milling precipitate and the supernatant of decant solution was filled in a 500 ml Pyrex glass. The glass container was placed in a stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm² gauge. The mixture was heated from room temperature to 160 °C with a heating rate of 2 °C/min, and then heating up to 210 °C with a heating rate of 12 °C/h while being stirred at 60 rpm, followed by cooling the mixture to room temperature in the autoclave overnight. The product crystals were washed with de-ionized water about 8 times by centrifugation in order to remove Cl⁻ from crystals. Then the crystals were dried in an oven at 110 °C for 24 h.

4.1.2.3 Calcination

The dry crystals were calcined in an air stream at 540 °C and held at that temperature for 7 h, by heating them from room temperature to 540 °C by heating rate 8.6 °C/min, to burn off the organic template and leave the cavities and channels in the crystals. The calcined crystals were finally cooled down to room temperature and stored in a dessicator for later use.

The catalysts were tableted by a tablet machine. The tableted catalysts were crushed and sieved to the range of 8-16 mesh.

4.2 Catalyst characterization

4.2.1 Determination of composition content of catalysts

The composition analysis of elements in the bulk of the catalyst was performed by atomic absorption spectroscopy using Varian, Spectra A8000 at the Department of Science Service Ministry of Science Technology and Environment.

4.2.2 X-ray diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were performed by an X-ray diffractometer, SIEMENS D5000, using Cu K α radiation with Ni filter. The operating conditions of measurement are shown below :

| | |
|---------------------------------|-----------------|
| 2 θ range of detection : | 6-40 $^{\circ}$ |
| Resolution : | 0.04 $^{\circ}$ |
| Number of scan | 15 |

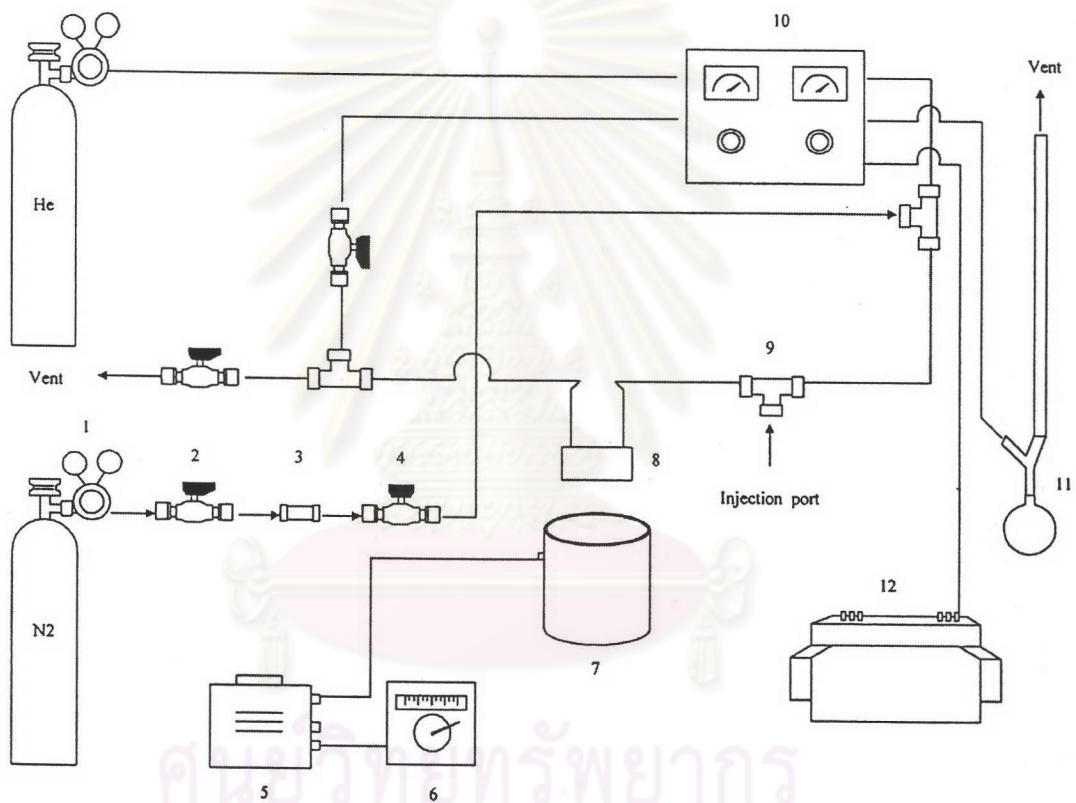
4.2.3 BET surface area measurement

4.2.3.1 Apparatus

The BET surface area measurement was carried out by using a conventional flow system shown in Figure 4.2. The apparatus consisted of two gas feed lines for helium and nitrogen. The flow rates of the gases were adjusted by means of fine-metering valves. The sample cell was made from pyrex glass. The operating conditions of the gas chromatograph (GOW-MAC) are shown in Table 4.3.

Table 4.3 Operating 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. Pressure Regulator | 2. On-Off Valve | 3. Gas Filter |
| 4. Needle Valve | 5. Voltage Transformer | 6. Temperature Controller |
| 7. Heater | 8. Sample Cell | 9. Three-way |
| 10. Thermal Conductivity | 11. Bubble flow meter | 12. Recorder |
- Detector

Figure 4.2 Schematic diagram of the single point BET specific surface area measurement

4.2.3.2 Procedure

The mixture of helium and nitrogen gas flowed through the system at the nitrogen relative gauge 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.

1) Adsorption step

The sample cell was dipped into 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 into the water at room temperature. The adsorbed nitrogen was desorbed from the surface of the sample. This step was completed when the recorder line return back to the base line.

3) Calibration step

1 ml of nitrogen gas 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.

4.2.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to determine the catalyst granule morphology, using a JEOL JSM-35CF scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 20 kV at Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC).

4.2.5 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:100 and then pressed into a thin wafer. Infrared spectra were recorded between 400 and 1300 cm^{-1} on a microcomputer.

4.3 Reaction study in hydroxylation of benzene

4.3.1 Chemicals

The reactants used for the reaction study are shown in Table 4.4.

Table 4.4 The chemicals used for the reaction study.

| Chemical | Grade | Supplier |
|-----------------------|------------|----------|
| Benzene | Synthesis | Panreac |
| Hydrogen peroxide 30% | Analytical | APS |

4.3.2 Apparatus

The catalytic test was performed in a flow system as shown diagrammatically in Figure 4.3. The reaction system consists of a reactor, a saturator, an automatic temperature controller, an electrical heating tape and a gas controlling system. The instruments used in this system are listed and explained as follows:

4.3.2.1 Reactor

The reaction was performed in a conventional glass tubular reactor (inside diameter = 1 cm), at atmospheric pressure. Catalyst is placed between two quartz wool layers.

4.3.2.2 Automatic temperature controller

This unit consisted of a magnetic switch connected to a variable transformer and a Natto NT2438 temperature controller connected to a thermocouple attached to the catalyst bed in a reactor. The temperature control set point is adjustable within the range of 0 °C to 80 °C at the maximum voltage output of 220 volt.

4.3.2.3 Electrical heating tape

This supplies the required heated to the reactor for reaction. The reactor can be operated from room temperature up to 80 °C at the maximum voltage of 220 volt.

4.3.2.4 Gas controlling system

The gas supplying system consists of a cylinder of ultra high purity nitrogen that equipped with a pressure regulator (0-120 psig), an on-off valve and a needle valve was used for adjusting the flow rate.

4.3.2.5 Gas chromatography

The feed and products were analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The operating conditions of the GC are listed in Table 4.5.

4.3.3 Reaction procedure

The hydroxylation of benzene with hydrogen peroxide was carried out by using a conventional flow shown in Figure 4.2 under the following condition atmospheric pressure and reaction temperature 70 °C

Table 4.5 Operating conditions for gas chromatograph

| Gas chromatograph | SHIMADZU GC9A |
|---------------------------------|--------------------------|
| Detector | FID |
| Packed column | GP 10% SP-2100 |
| Carrier gas | N ₂ (99.999%) |
| Carrier gas flow rate (ml/min) | 30 |
| Injector temperature (°C) | 250 |
| Detector temperature (°C) | 250 |
| Initial column temperature (°C) | 110 |
| Programme rate (°C/min) | 10 |
| Final column temperature (°C) | 200 |
| Analyzed chemicals | Benzene and Phenol |

The procedure are described in the detail below.

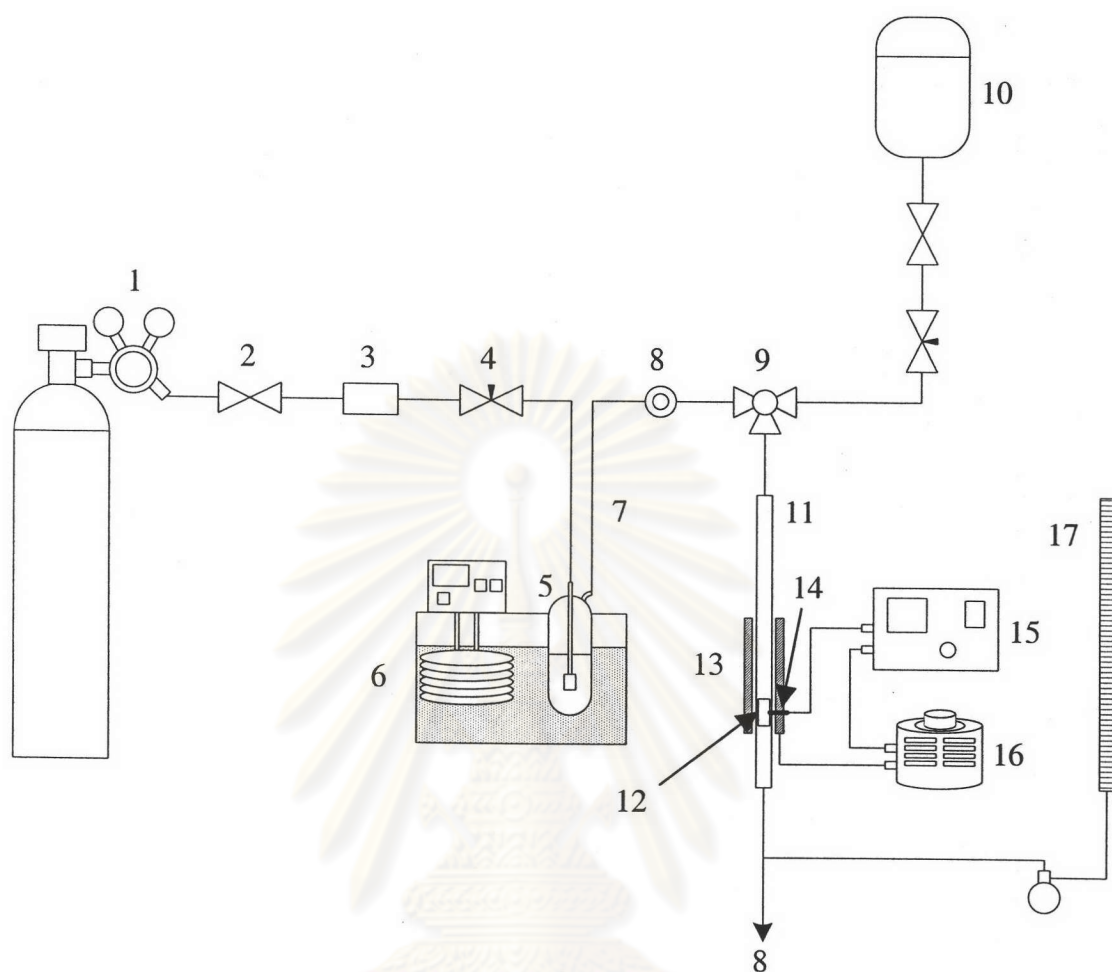
- 1) 1 gram of catalyst was packed in the glass tubular reactor and then heat up the reactor by raising the temperature from room temperature to 70 °C
- 2) Put benzene in the saturator and set the temperature of the water bath at 70 °C. Heat up the line to 100 °C.
- 3) Adjust the outlet pressure of nitrogen to 1.5 bar and turn on the on-off valve to allow nitrogen gas to pass through benzene inside the saturator set in the water bath. Measure the outlet gas flow rate by using a bubble flow meter. The flow rate was 30 ml/min.
- 4) The feed gas was analyzed by using the FID gas chromatograph. The chromatograph data were changed into mole of benzene using a calibration curves (Appendix C). Wait until the mole of benzene in the feed gas becomes constant.
- 5) Start the reaction by adjusting the three-way valve to allow hydrogen peroxide to pass through the reactor for the required period time. Then adjust the

three-way valve to benzene side for the required period time. Switching the three-way valve periodically.

6) Take sample for analyzed at the bottom of reactor. The reaction product was analyzed by the FID gas chromatograph.



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|---|-----------------------|----------------------------|
| 1. Pressure Regulator | 2. On-Off Valve | 3. Gas Filter |
| 4. Needle Valve | 5. Saturator | 6. Water Bath |
| 7. Heating Line | 8. Sampling Point | 9. Three-way Valve |
| 10. H ₂ O ₂ Storage | 11. Reactor | 12. Catalyst Bed |
| 13. Heating Tape | 14. Thermocouple | 15. Temperature Controller |
| 16. Variable Voltage Transformer | 17. Bubble flow meter | |

Figure 4.3 Schematic diagram of the reaction apparatus for the hydroxylation of benzene with hydrogen peroxide