

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 characterization 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 characterized by various techniques such as XRF, BET, XRD, IR, NH₃-TPD, IR and UV-VIS 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.

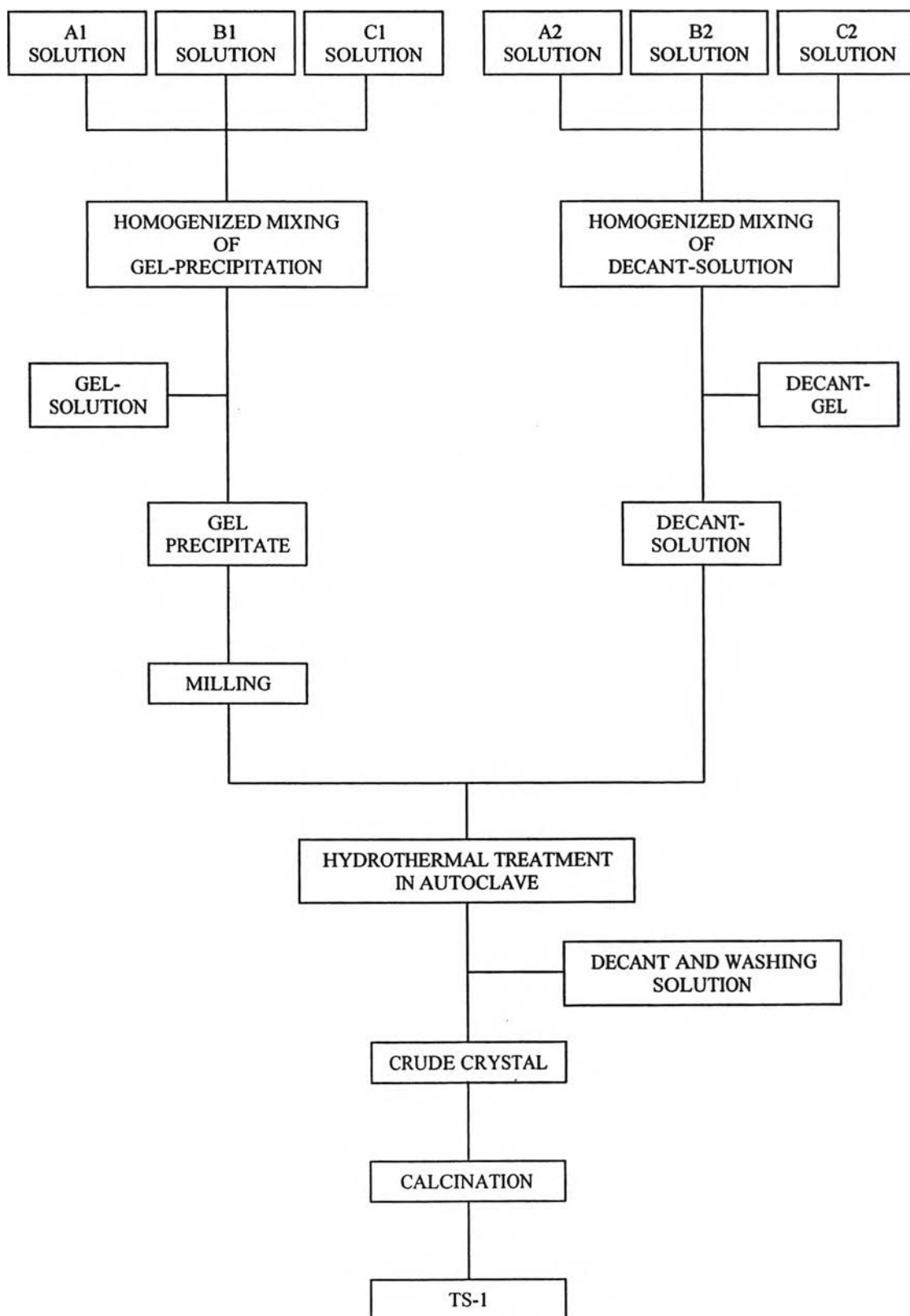


Figure 4.1 The preparation procedure of TS-1 by rapid crystallization method

Table 4.2 Reagents used for the preparation of TS-1 : Si/Ti = 60 (Appendix A)

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
Ti[O(CH ₂) ₃ CH ₃] ₄	1.91	g	Ti[O(CH ₂) ₃ CH ₃] ₄	1.91	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60.00	ml
De-ionized water	60.00	ml	H ₂ SO ₄ (conc.)	3.40	ml
H ₂ SO ₄ (conc.)	3.40	ml			
Solution B1			Solution B2		
Sodium silicate	69.00	g	Sodium silicate	69.00	g
De-ionized water	45.00	ml	De-ionized water	45.00	ml
Solution C1			Solution C2		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104.00	ml
NaOH	2.39	g			
De-ionized water	208.00	ml			
H ₂ SO ₄ (conc.)	1.55	ml			

Note * 2.87 g for Si/Ti= 40 , 3.58 g for Si/Ti = 32 , 4.25 g for Si/Ti = 22

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 drop wise 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 follows: 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 crystal products were washed with de-ionized water until pH 7 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 static air at 540°C and held at that temperature for 7 h, by heating them from room temperature to 540°C by heating rate 10°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.

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

4.1.3 Pretreatment catalysts

3 g of TS-1 was placed into a round bottom flask and then 14 ml of 3M and 5M HNO₃ aqueous solution was added. After reflux at 80°C for 3 h, the pretreated catalyst was filtered, washed with distilled water until pH 7, dried at 110°C and calcined at 540°C for 7 h in static air.

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 X-ray fluorescence (XRF) using Siemens SRS3400 at Scientific Instruments Service Centre, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang.

4.2.2 BET surface area measurement

The sample cell which contained 0.3 g of sample was placed into BET Micromeritics ASAP 2020. After degassing step, the surface area and pore volume of catalyst were measured

4.2.3 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 :	0.01 $^{\circ}$
Number of scan :	15

4.2.4 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 6700 with SMART DIFFUSE REFLECTANCE. Infrared spectra were recorded between 400 and 1200 cm $^{-1}$ on a microcomputer.

4.2.5 Ammonia Temperature Program Detector (NH₃-TPD)

4.2.5.1 Measuring procedure

Sample cell which contained 0.1 g of sample was placed into Micromeritics Chemisorb 2750. Helium gas with flow rate at 15 ml/min was released to flow through our sample. The sample was heated from room temperature to 540°C with heating rate of 10°C/min and held at this temperature for 1 h. The sample was cooled down to 80°C and ready to measure the surface area. There were three steps to measure the surface area.

1) Adsorption step

The 15 vol% ammonium gas with flow rate at 15 ml/min was flowed through the sample instead of helium, and held for 15 minutes.

2) Desorption step

2.1) Physi-sorption

The helium gas at the same flow rate was flowed through the sample instead of ammonium and also hold for another hour.

2.2) Chemi-sorption

Our sample was heated from 80°C to 540°C with a heating rate of 10°C/min. The signal from this step was recorded every 1 second and reported on a microcomputer.

4.2.6 Ultraviolet-Visible Spectroscopy (UV-Vis)

4.2.6.1 Measuring procedure

The harsh black holder which contained 0.3 gram of sample was placed into Perkin Elmer Lambda 650, UV/VIS spectrometer. The measurement was performed in reflectant mode.

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 4.3 The chemicals used for the reaction study.

Chemical	Grade	Supplier
Benzene	Analytical	PS
Hydrogen peroxide 30%	Analytical	Merck
Nitric acid 70%	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, a mass flow control, a timer, an automatic temperature controller, an electrical heating tape and 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. Pellet catalysts 0.5 gram are placed between two quartz wool layers in the glass tubular reactor.

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 70°C at the maximum voltage output of 220 volt.

4.3.2.3 Electrical heating tape

This unit supplies the required heated to the reactor for reaction. The reactor can be operated from room temperature up to 70°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 mass flow control 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 4.4 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)	170
Analyzed chemicals	Benzene and Phenol

The procedures are described in the detail below.

1) 0.5 g of catalyst pellet 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) Fill benzene in the saturator and set the temperature of the water bath at 40°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. The flow rate was adjusted at 30 ml/min by mass flow control. The outlet gas flow rate can be checked by using a bubble flow meter.

4) The feed gas was analyzed by using the FID gas chromatograph. The chromatogram data were converted into mole of benzene using a calibration curves (Appendix C). Then, wait until the mole of benzene in the feed gas becomes constant.

5) Start the reaction by turn on the timer that is auto switching (cyclic experiment) of liquid H_2O_2 and gas benzene with 1 second and 899 second, respectively. Allow hydrogen peroxide to pass through the reactor for the required period time and follow to benzene side for the required period time.

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

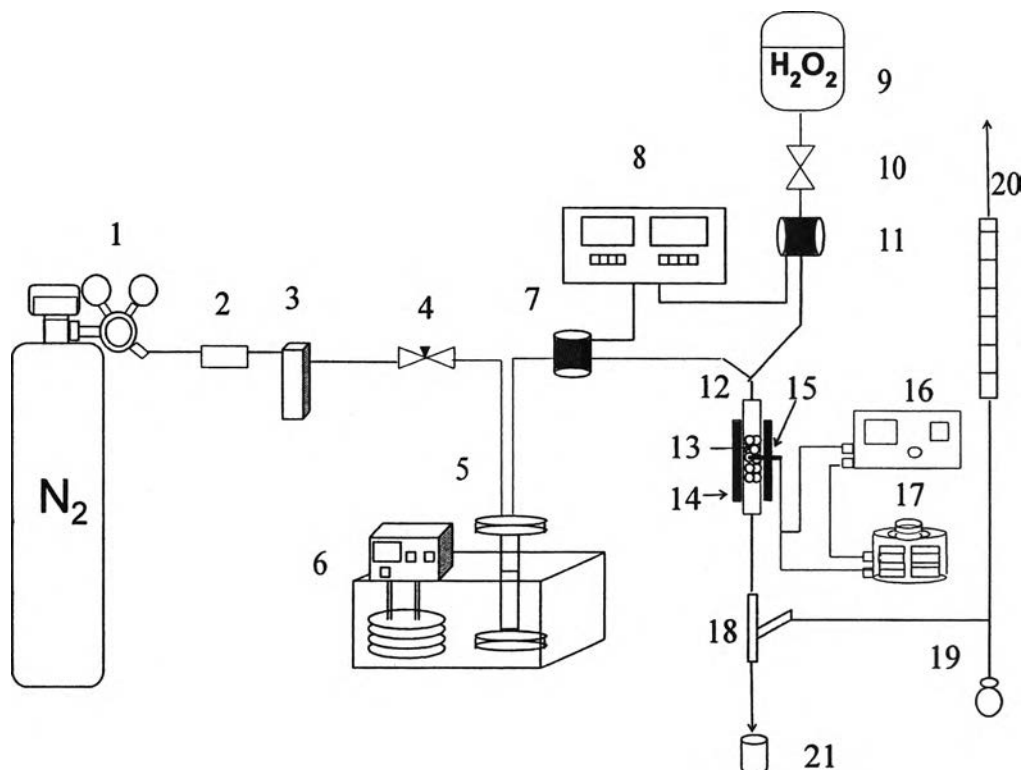


Figure 4.2 Schematic diagram of the reaction apparatus for the hydroxylation of benzene with hydrogen peroxide.

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|----------------------------|----------------------------------|--|
| 1. Pressure Regulator | 2. Gas Filter | 3. Mass Flow Control |
| 4. On-Off Valve | 5. Saturator | 6. Water Bath |
| 7. Solenoid Valve | 8. Timer | 9. H ₂ O ₂ Storage |
| 10. On-Off Valve | 11. Solenoid Valve | 12. Glass Reactor |
| 13. Catalyst Bed | 14. Heating Tape | 15. Thermocouple |
| 16. Temperature Controller | 17. Variable Voltage Transformer | 18. Y-Tube |
| 19. Bubble Flow Meter | 20. Vent Gas Benzene | 21. Sampling Point |