## **CHAPTER IV**

## **EXPERIMENTAL**

The experimental in this chapter is divided into four major parts: (1) catalyst preparation, (2) catalyst characterization, (3) reaction study and. (4) adsorption of reactants on catalysts. The chemicals, apparatus and procedures for catalyst preparation are explained in section 4.1. The composition, structure, surface properties, acidity of the catalyst characterised by various techniques such as XRF, BET, XRD, FT-IR and NH<sub>3</sub>-TPD are discussed in section 4.2. The details of the reaction study are illustrated in section 4.3. Finally, the capable adsorptions of toluene and ethyl benzene on surface catalyst are presented in section 4.4.

## 4.1 Catalyst preparation

#### 4.1.1 Chemicals

All chemicals used in this preparation procedure of M-TS-1 catalysts are following 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
Cobalt(II)nitrate hexahydrate	Analytical	Aldrich
Vanadium(II)chloride	Analytical	Fluka
Iron(III)chloride hexahydrate	Analytical	Merck
Aluminium(III)nitrate nonahydrate	Analytical	APS

# 4.1.2 Preparation procedures

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

**Table 4.2** Reagents used for the preparation of M-TS-1 : Si/Ti = 50, Si/M = 150 (Appendix A)

Solution for the gel prep	oaration	1	Solution for decant-solution	ution	
Solution A1			Solution A2		
Ti[O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>4</sub>	2.208	35 g	Ti[O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>4</sub> 2	2.2085	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	50	ml
Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, VCl <sub>3</sub>	x	g	Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O, VCl <sub>3</sub>	x	g
FeCl <sub>3</sub> .6H <sub>2</sub> O, Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	)		FeCl <sub>3</sub> .6H <sub>2</sub> O, Al(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O	)	
De-ionized water	60	ml	$H_2SO_4$ (conc.)	3.4	ml
H <sub>2</sub> SO <sub>4</sub> (conc.)	3.4	ml			
Solution B1			Solution B2		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	15	ml
Solution C1			Solution C2		
TPABr	2.16	g	NaCl 2	26.27	g
NaCl	40.59	g	De-ionized water	04	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H <sub>2</sub> SO <sub>4</sub> (conc.)	1.55	ml			

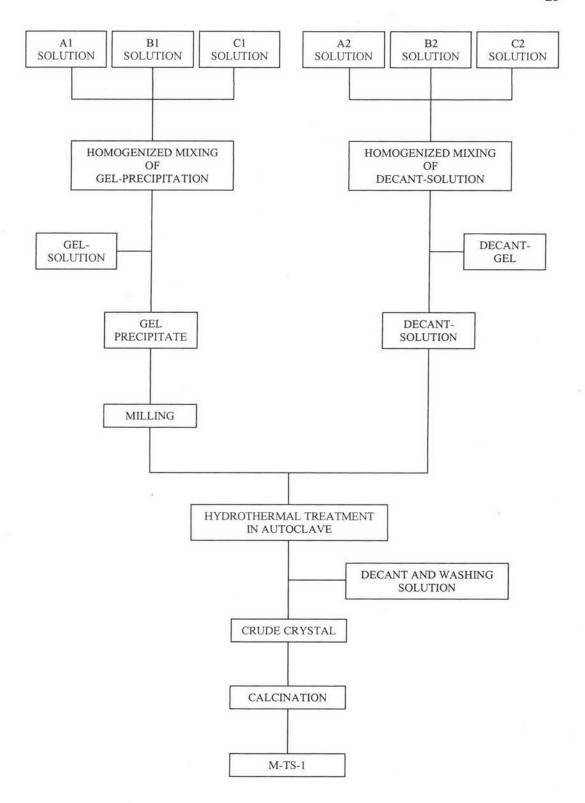


Figure 4.1 The preparation procedure of M-TS-1 by rapid crystallization method.

## 4.1.2.1 Preparation of gel precipitation and decantation Solution

The source of metals for preparation of decantation and gel solutions were Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O for Co, VCl<sub>3</sub> for V, FeCl<sub>3</sub>.6H<sub>2</sub>O for Fe, Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O for Al, Ti[O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sub>4</sub> for Ti, and sodium silicate for Si, respectively. TPABr (Tetra-npropyl ammonium bromide[(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N]Br) was used as organic template. The atomic ratio of Silicon/Titanium and Silicon/Metal were set at 50, 150, respectively. The preparation of supernatant liquid was separated from the gel, which is important for preparing the uniform crystals. The detailed procedures were as follows: Firstly, 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. H<sub>2</sub>SO<sub>4</sub> (conc.) or NaOH solution were used to adjust pH of the 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 totally 1 hour. the milling was done for 15 min and then the supernatant solution was removed by centrifugal separation 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  $\rightarrow$  centrifuge 15 min  $\rightarrow$  milled 30 min  $\rightarrow$  centrifuge 15 min.

Secondly, 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 supernatant liquids from A-2, B-2 and C-2 were mixed together with the milled gel mixture. However, before mixing, 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/cm<sup>2</sup> gauge. Then, the autoclave 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 temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization. The product crystals were washed with de-ionized water by centrifugation in order to remove chloride out of the crystals. Then the crystals were dried in an oven at 110 °C for at least 24 h.

#### 4.1.2.3 Calcination

The dry crystals were calcined in an air stream at 550 °C and held at that temperature for 7 h, by heating them from room temperature to 550 °C at a heating rate of 8.6 °C/min, to burn off the organic template and leave the cavities and channels in the crystals. Then, the calcined crystals were finally cooled down to room temperature in a dessicator.

## 4.1.3 Pretreatment catalysts

10 g of M-TS-1 and TS-1 were placed into a round bottom flask and then 150 ml of 5M HNO<sub>3</sub> 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 X-Ray Fluorescence Spectrometer (XRF)

The chemical composition analysis of elements of the catalyst was performed by X-ray fluorescence (XRF) using Siemens SRS3400.

#### 4.2.2 BET surface area measurement

The sample cell which contained 0.3 g of sample was placed into BET Micromeritrics 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 connected with a computer with Diffract ZT version 3.3 program for fully control of XRD analyzer. The experiments were carried out by using Cu K $\alpha$  radiation with Ni filter. Scans were performed over the 2 $\theta$  ranges from 6 $^{\circ}$  to 30 $^{\circ}$ .

## 4.2.4 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<sup>-1</sup> on a microcomputer

## 4.2.5 NH<sub>3</sub> Temperature programmed desorption (NH<sub>3</sub>-TPD)

Temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) was used to determine the acid properties of catalysts. NH<sub>3</sub>-TPD were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at 550°C in helium flow for 1h and then saturated with 15 %NH<sub>3</sub>/He mixture after cooling to 100°C. After purging with helium at 100°C for 1 h to remove weakly physisorbed NH<sub>3</sub>, the sample was heated to 550°C at therate of 10°C/min in a helium flow of 50 cm<sup>3</sup>/min. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH<sub>3</sub>. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer

The deconvlution of NH<sub>3</sub>-TPD peak was carried out with the "fityk" curve fitting programme. The peaks were assumed to be Gaussian with showness shape (using parameter 'SplitGaussian' in the programme).

## 4.3 Reaction study in the hydroxylation of alkyl benzene

The hydroxylation of alkyl benzene (toluene and ethyl benzene) with H<sub>2</sub>O<sub>2</sub> (30 wt% in water, Merk) was carried out in a 250 ml, paraffin oil jacketed, there-necked, glass flask fitted with a condenser and a mechanical stirrer placed in a stirring block heater as shown in Figure 4.2. The reaction was performed at atmospheric pressure. Typically, 1 g of a catalyst was reacted with reactant as alkyl benzene to H<sub>2</sub>O<sub>2</sub> molar ratio equals to 1 to 1 and 50 ml of water. First, the catalyst and water using for dispersion of a catalyst were added into a reactor at 90°C for 1 h so as to drive out gases in pores of catalyst. Then reactant and H<sub>2</sub>O<sub>2</sub> was added into reactor. For H<sub>2</sub>O<sub>2</sub> was slowly injected drop-wise using a 1 ml syringe at 70°C for 2 h. After the reaction has been stopped by cool down, 50 ml of ethanol was added into reactor to homogenize the aqueous phase and the organic phase. The products were analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The products obtained from ethyl benzene hydroxylation are also determined with the Gas Chromatography-Mass Spectrometry.

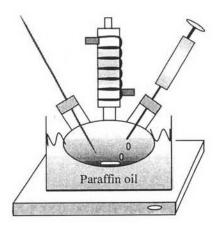


Figure 4.2 The hydroxylation reactor.

The operating conditions of the GC and GC-MS are listed in Table 4.3 and 4.4, respectively.

Table 4.3 Operating conditions for gas chromatograph

Gas chromatograph	SHIMADZU GC9A	
Detector	FID	
Packed column	GP 10% SP-2100	
Carrier gas	N <sub>2</sub> (99.999%)	
Carrier gas flow rate (ml/min)	30	
Injector temperature (°C)	250	
Detector temperature (°C)	250	
Initial column temperature (°C)	80	
Programme rate (°C/min)	2	
Final column temperature (°C)	240	
Analyzed chemical samples	Toluene and Ethyl benzene	

Table 4.4 Operating conditions for gas chromatograph mass spectrometry

Gas chromatography-Mass Spectrometry	Agilent Technology 5973	
Detector	MS	
Capillary column	HP-5ms	
Split ratio	50:01:00	
Carrier gas	He (99.999%)	
Carrier gas flow rate (cm/min)	24	
njector temperature (°C)	200	
etector temperature (°C)	350	
nitial column temperature (°C)	50	
Programme rate (°C/min)	10	
final column temperature (°C)	240	
analyzed chemical samples	Toluene and Ethyl benzene	

## 4.4 The adsorption of reactants on catalysts

The blank of toluene was prepared for a reference of the adsorption; 0.5 ml reactants as toluene and ethyl benzene, 70 ml ethanol and 40 ml water were added into 100 ml reactor (Scott duran) as showed in Figure 4.3 and stirred. The 0.5 g of TS-1 and M-TS-1 and 40 ml of water were carried out into reactor. The 0.5 g catalyst and 40 ml water were carried out into a reactor and stirred at 90 °C for 1hr after that cooled down at room temperature. The 0.5 ml of reactant and 70 ml ethanol were added and stir so as to combine phases of toluene and water. When the suppressible solution had deposited, the clear solution, which was a part of toluene non-absorption. It was analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The reactant adsorption on catalyst is determined in Appendix G.



Figure 4.3 The adsorption bottle