CHAPTER III

EXPERIMENT

3.1 Chemicals and Gases

A nitrogen gas of high purity grade was purchased from Thai Industrial Gases (TIG). Tetraethylorthosilicate (98 wt% TEOS), hexamethyleneimine (97 wt%), phenol (97 wt%) and catechol (>98 wt%) were available form Fluka. Hydrogen peroxide (30 wt%), hydroquinone (>99 wt%) and acetone (AR grade) were supplied from Merck. Tetrapropyl ammonium hydroxide (10 wt% in water, TPAOH) and tetrabutyl orthotitanate were purchased from TCI. Fumed silica was commercially available form Riedel-deHaën. Tetrapropyl ammonium bromide (98 wt%, TPABr), boric acid (99.7%) were purchased from Aldrich. Other chemicals were from BDH.

3.2 Synthesis of TS-1

3.2.1 Synthesis of TS-1 with Mixed TPAOH and TPABr Templates

TS-1 was synthesized in basic condition using a gel composition of SiO_2 : $0.025TiO_2$: 0.18TPAOH : 0.18TPABr : $36.5H_2O$ by modifying the recipe reported by Thangaraj [7] except for two different templates, *i.e.* tetrapropyl ammonium hydroxide (TPAOH) and tetrapropyl ammonium bromide (TPABr) were used instead. Three positions of solution were prepared separately. Solution A was prepared by dissolving 37.82 g TEOS in 66 g of 2-propanol. Solution B was prepared by dissolving 1.547 g of TBOT in 16.5 g of 2-propanol. Solution C was prepared by dissolving 8.892 g of TPABr 59 g in deionized water and mixed with 53.16 g of TPAOH. First, Into a 500-cm^3 four-neck round bottom flask containing Solution A in the ice bath and nitrogen atmosphere, 13.28 g of TPAOH template was added dropwise with continuous stirring for 1 h. After that solution B and C were added dropwise respective under vigorous stirring for 1 h in each step. The solution was heated at 80°C to remove the alcohol existing as solvent and by-products. The apparatus for alcohol removal was shown in Figure 3.2. The pH of resulting gel was adjusted to a value about of 11.7 with ammonia solution. Finally, water were added and stirred for 1 h. After homogeneously mixing, the resulted gel was transferred to a Teflon-lined autoclave and heated at 170°C in an oven designed to rotate the autoclaves at 60 rpm (rotating synthesis) for 4 days. The solid product was separated from the solution by centrifugation (6000 rpm, 15 min) and washed with deionized water before drying at 100°C overnight. The procedure was illustrated in Scheme 3.1 and apparatus for gel preparation was shown in Figure 3.1

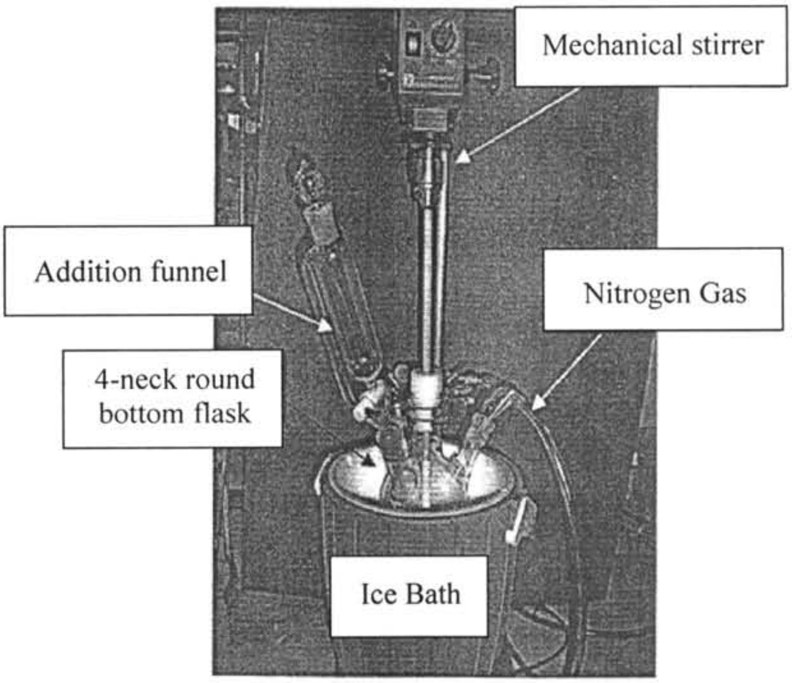
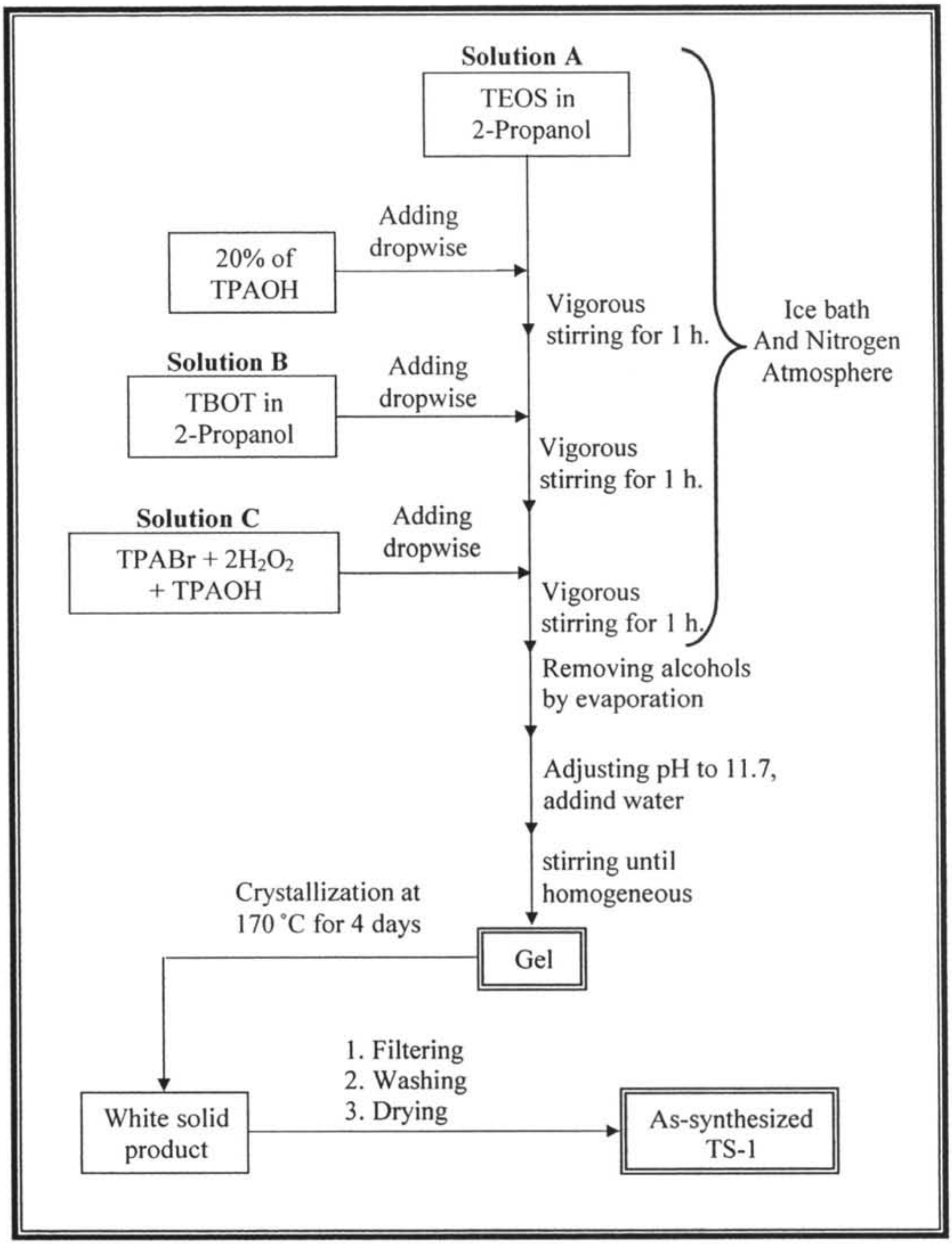


Figure 3.1 Apparatus for the gel preparation of TS-1 catalysts.

3.2.2 Synthesis of TS-1 with Pure TPAOH Template

TS-1 with pure TPAOH template was also synthesized using the procedure described in section 3.2.1 but no ammonia solution was added. The first part of template was 10% of total TPAOH and the other was used in the solution C. TPABr was replaced by TPAOH of equivalent mole. A typical molar composition of the mixture corresponded to the formula SiO_2 : $0.025TiO_2$: 0.36TPAOH : $36.5H_2O$.



Scheme 3.1 Preparation diagram for TS-1.

3.2.3 Synthesis of TS-1 with Pure TPABr Template

TS-1 with pure TPABr template was also synthesized using the procedure described in section 3.2.1 but TPABr was used instead TPAOH of equivalent mole. More water was added in order to dissolve TPABr completely. The molar composition of the gel mixture was SiO_2 : $0.025TiO_2$: 0.36TPABr : $51H_2O$.

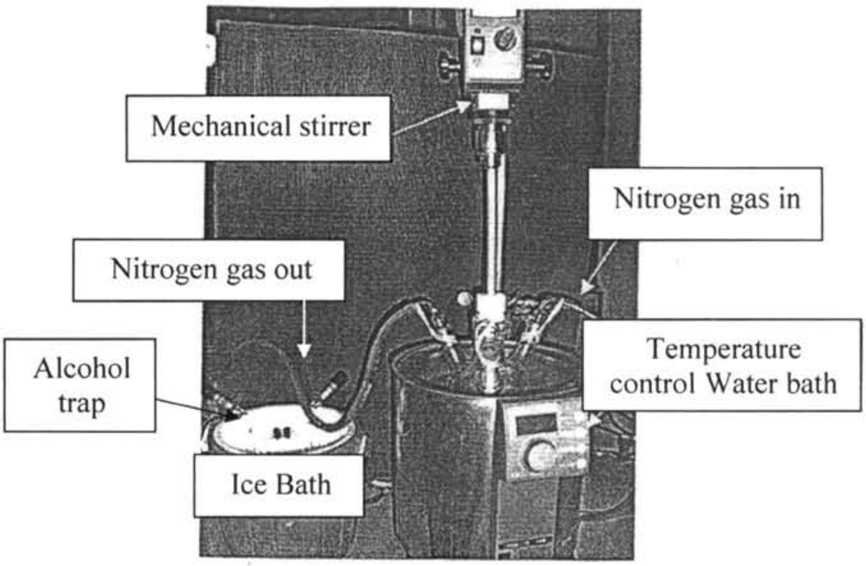


Figure 3.2 Apparatus for removing alcoholic solvent and by-products.

3.2.4 Synthesis of Ti-MWW

Ti-MWW catalyst was synthesized following the conventional procedure [6]. Template solution was prepared by dissolving 28.63 g of hexamethyleneimine (HM) in 67.45 g of deionized water at room temperature in a 500-cm^3 four-neck round bottom flask with continuous stirring for 15 min. This solution was divided into two equal parts, to one of which 1.70 g of TBOT was added under vigorous stirring, and to the other 16.73 g of H_2BO_3 was added under vigorous stirring. The stirring was maintained for 30 min to hydrolyze TBOT. 12.02 g of fumed silica was also divided into two equal parts which were separately transferred gradually to the solutions containing titanium (Mixture A) and boron (Mixture B). Further stirring for 1 h was performed to form two homogeneous gels. The gels were then mixed together and stirred for 1.5 h to obtain a gel with a molar composition of SiO_2 : $0.025TiO_2$: $0.67B_2O_3$: 1.4HM : $19H_2O$. The resulting gel was transferred into a Teflon-lined autoclave and crystallized in an oven specially designed to rotate the autoclaves in pair at 60 rpm (rotating synthesis) at 130°C for 1 day, then 150°C for 1 day, and subsequently at 170°C for 7 days. After cooling, the solid product was filtered off and washed with deionized water. The product was then dried at 60°C for 1 day. The procedure for preparing the Ti-MWW was shown in Scheme 3.2.

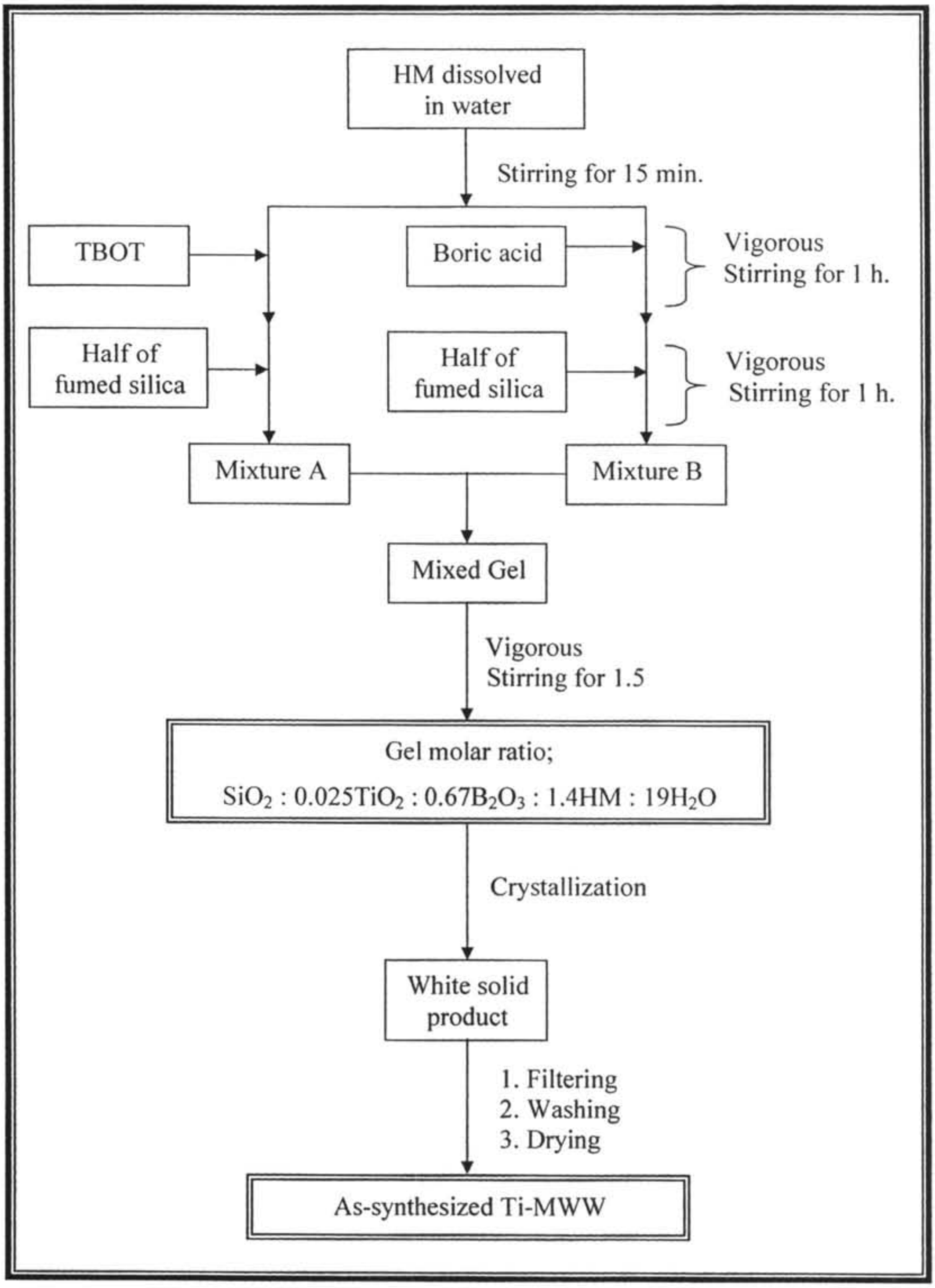
To remove boron and extraframework titanium species, an acid treatment of the as-synthesized products with 2 M HNO_3 solution was carried out at 100°C for 20 h under reflux in a silicone oil bath. The volume of acid is 20 mL per 1 g of sample. The solid product was separated from the solution by filtration and washed with deionized water before drying at 60°C for 10 h.

3.2.5 Conditions for Crystallization of Ti -MWW

There are two methods for crystallization of Ti -MWW.

Method I: The gel Ti-MWW precursor was crystallized with rotation of the autoclave by multistep heating at 130°C for 1 day, then 150°C for 1 day and subsequently 170°C for different time from 5 to 7 days.

Method II: The gel Ti-MWW precursor was crystallized with rotation of the autoclave by isothermal heating at 170°C for different time from 7 to 9 days.



Scheme 3.2 Preparation diagram for Ti-MWW.

3.3 Catalysts Characterization

XRD patterns of samples were measured using a Rigaku DMax-2200/Utima$^+$ X-ray powder diffractometer equipped with Cu target and graphite single crystal monochromater. The scan speed was 5°/min and the scan step was 0.02°. The three slits (scattering, divergent and receiving slits) were fixed at 0.5°, 0.5° and 0.3 mm, respectively.

The specific surface area was obtained by nitrogen adsorption at -196°C using a BELSORP-mini apparatus. The sample weight was near 40 mg, and weighed exactly after pretreatment at 400C under vacuum of 10^{-4} Pa for 3h to ensure a dry clean surface, free from any loosely held adsorbed species. The specific surface areas were determined by application of BET equation and Langmuir equation at relative pressure between 0.02 and 0.15 P/P°. The external surface area was determined by application of t-plots using Harkins-Jura equation. The dead volume correction of was applied with all measurements.

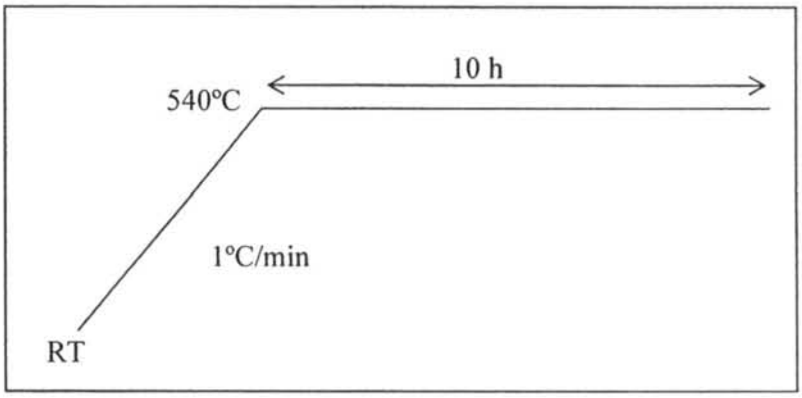
SEM images for determination of morphology and particle size of catalysts were taken using a JEOL JSM-5410LV scanning electron microscope. Powder samples were coated with spluttering gold under vacuum prior to analysis.

Titanium coordination sites in the catalysts were measured by the diffused reflectance-ultraviolet (DR-UV) in the range of 190-400 nm using a Shimadzu UV-2550 UV-Visible spectrophotometer equipped with a 60° integrating sphere and pressed powder of $BaSO_4$ was used as background.

Titanium and boron contents in the catalysts were analyzed using a Perkin Elmer PLASMA-1000 inductively coupled plasma atomic emission spectrometer (ICP-AES). The solid catalysts were digested by hydrofluoric acid in a 100-cm^3 Teflon beaker. An amount of 0.0400 g of a calcined catalyst was soaked with 10 cm^3 of 37% HCl and subsequently with 10 cm^3 of 48% hydrofluoric acid to get rid off silica in the form of volatile SiF_4 species. The solid was heated not boiled to dryness on a hot plate. The hydrofluoric acid treatment was repeated twice more. An amount of 10 cm^3 of the mixture of 6 M HCl : 6M HNO_3 at a ratio of 1 : 3 was added and further heated to dryness. An amount of 10 cm^3 deionized water was added to the beaker and warmed for 5 minutes to complete dissolution. The solution was transferred to a 50-cm^3 polypropylene volumetric flask. The solution in the flask was brought to the mark with deionized water. The flask was capped and shook thoroughly. If the sample is not analyzed immediately, the solution was then transferred into a plastic bottle with a treaded cap lined with a polyethylene seal.

3.4 Organic Template Removal

The organic templates used in the synthesis of the catalysts were removed from the catalyst pores by conversion to carbon dioxide at high temperature. The as-synthesized catalyst samples were calcined in a muffle furnace from room temperature to 540°C with programmable heating rate of 1°C/min for 10 h. The heating program was shown in Scheme 3.3.



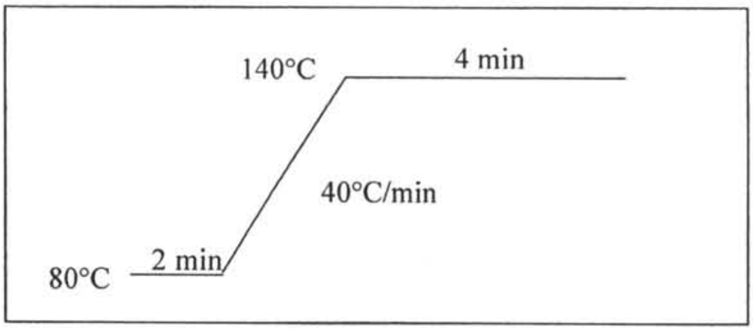
Scheme 3.3 The heating program for calcination of the catalysts (RT = Room Temperature).

3.5 Catalytic Activity Test for Phenol Hydroxylation

3.5.1 Activity of Various Catalysts

The reactions of phenol oxidation or hydroxylation catalyzed by various calcined catalysts were carried out in a 50-ml round-bottom flask under reflux. For a typical run, a mixture containing 0.05 g of catalysts, 0.47 g of phenol (5 mmol), and 5 mL of solvent was mixed in the flask and heated at the desired reaction temperature under stirring. To start the reaction 0.284 g of 30 wt% hydrogen peroxide (2.5 mmol) was added. The apparatus for phenol hydroxylation was shown in Figure

3.3. After 5 h of the reaction, the flask was cooled to room temperature. The solid was separated from the solution by filtration. Liquid products from catalytic test were analyzed using a VARIAN GC-3800 gas chromatograph equipped with a 30-m long and 0.32-mm outer diameter CP sil 8CB (0.25 μm film thickness) column and flame ionization detector (FID). Cycloheptanone was used as internal standard. A sample volume is 1 mL. The column heating program is shown in Scheme 3.4. Injector and FID were heated to 200°C before sample injection.



Scheme 3.4 The GC column heating program for liquid sample analysis.

3.5.2 Effect of Solvent Types

To investigate the effect of solvent types on the catalytic activity and selectivity, the experiment was performed as described in the section 3.5.1 using different solvents: water, methanol, acetone and acetonitrile. TS-1-Mix and Ti-MWW-acid were chosen as catalysts. The reaction time was fixed at 5 h.

3.5.3 Effect of Reaction Time

To investigate the effect of **reaction** time on the catalytic activity and selectivity, the experiment was performed as described in the section 3.5.1 using different reaction time, 1, 3 and 5 h. TS-1-Mix and Ti-MWW-acid were chosen as catalysts.

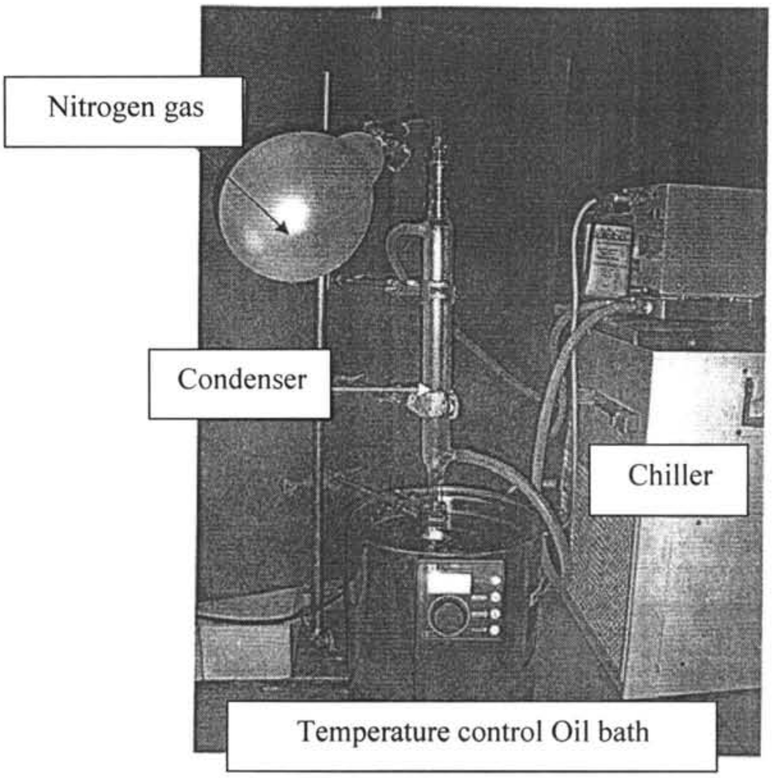


Figure 3.3 Apparatus for phenol hydroxylation reaction.