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นางสาวศราวดี มิตรพระพันธ์

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

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BENZENE HYDROXYLATION BY HYDROGEN PEROXIDE  
AT ELEVATED TEMPERATURE OVER TITANIUM SILICALITE-1 CATALYST



Miss Sarawadee Mitpapan

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย  
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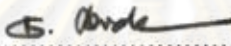
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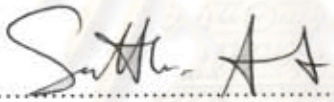
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By    Miss Sarawadee Mitpapan  
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Thesis Advisor                                Associate Professor Tharathon Mongkhonsi, Ph.D.


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Accepted by the Faculty of Engineering, Chulalongkorn University in Partial  
Fulfillment of the Requirements for the Master's Degree


  
.....Dean of the Faculty of Engineering  
(Associate Professor Boonsom Leardhirunwong, Dr.Eng)

THESIS COMMITTEE

  
.....Chairman  
(Professor Suttichai Assabumrungrat, Ph.D.)

  
.....Thesis Advisor  
(Associate Professor Tharathon Mongkhonsi, Ph.D.)

  
.....Examiner  
(Assistant Professor Suphot Phatanasri, Ph.D.)

  
.....External Examiner  
(Nattaya Comsup, D.Eng.)

ศราวดี มิตรพระพันธ์ : การไฮดรอกซิเลชันเบนซีนด้วยไฮโดรเจนเปอร์ออกไซด์ที่อุณหภูมิสูงด้วยตัวเร่งปฏิกิริยาไททานเนียมซิลิกาไลท์-1. (BENZENE HYDROXYLATION BY HYDROGEN PEROXIDE AT ELEVATED TEMPERATURE OVER TITANIUM SILICALITE-1 CATALYST) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร.ธราธร มงคลศรี, 70 หน้า.

งานวิจัยนี้ได้เพิ่มอุณหภูมิการทำปฏิกิริยาเบนซีนไฮดรอกซิเลชันบนตัวเร่งปฏิกิริยาไททานเนียมซิลิกาไลท์-1 ให้สูงเหนือจุดเดือดของเบนซีนที่ความดันบรรยากาศ เพื่อเพิ่มค่าการเปลี่ยนของไฮโดรเจนเปอร์ออกไซด์ จากผลจากการวิจัยพบว่าการเพิ่มค่าการเปลี่ยนเมื่อทำปฏิกิริยาที่อุณหภูมิสูงจะทำได้ก็ต่อเมื่อชั้นผิวหน้ามีชั้นเบนซีนเหลวปกคลุมผิวหน้าชั้นน้ำเอาไว้ตลอดเวลาการทำปฏิกิริยา ซึ่งกระทำได้โดยการลดปริมาตรที่ว่างเหนือผิวของเหลว (เพื่อลดการระเหยกลายเป็นไอของเบนซีนเหลว) และเพิ่มปริมาณเบนซีนที่ใช้ในการทำปฏิกิริยา นอกจากนี้ยังพบว่าเบนซีนเข้าทำปฏิกิริยานั้นคือเบนซีนที่ได้ละลายเข้าไปในเฟสน้ำแล้ว ไม่ใช่เบนซีนเหลวที่ลอยอยู่บนผิวหน้าเฟสน้ำ

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ภาควิชา..... วิศวกรรมเคมี..... ลายมือชื่อนิสิต..... ศราวดี..... มิตรพระพันธ์.....  
สาขาวิชา..... วิศวกรรมเคมี..... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..... รศ.ดร.ธราธร.....  
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ADVISOR : ASSOC.PROF.THARATHON MONGKHONSI, Ph.D., 70 pp.

This research has attempted to increase the hydroxylation of benzene over titanium silicate-1 catalyst over the boiling point of benzene at atmospheric pressure in order to increase the conversion of hydrogen peroxide. The research found that to achieve the increase in the conversion of hydrogen peroxide, the top surface of the water layer must be completely covered with a layer of liquid benzene through out the reaction period. This can be carried out by decreasing the volume of space above the liquid surface, in order to minimize the vaporization of liquid benzene, and increase the amount of benzene used in the reaction. Furthermore, this research also found that benzene that really involves in the hydroxylation reaction is the benzene already dissolved into the liquid phase, not the liquid benzene on the top surface of the water layer.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

Department : Chemical Engineering ..... Student's Signature Sarawadee Mitpapan  
Field of Study : Chemical Engineering ..... Advisor's Signature น น น  
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# CHAPTER I

## INTRODUCTION

### 1.1 Background of the research

Phenol is a versatile chemical used primarily in the formation of phenolic resins, as a solvent for petroleum refining, and in the production of nylon and other synthetic fibers. The well-known antiseptic properties of phenol promote additional industrial and medical applications, an important chemical intermediates. Most of the worldwide production of phenol is now based on the well established “cumene process”. The cumene process, however, comprises of several reaction steps beginning from the alkylation of benzene with propylene to form cumene. The oxidation of cumene to cumene hydroperoxide follows by the decomposition of cumene hydroperoxide to phenol and acetone. The major disadvantages of the cumene process are the formation of cumene hydroperoxide, which is an explosive substance, and its overall economics of the process strongly depends on the demand of the acetone byproduct in the chemical market.

From the disadvantages of the cumene process described above, attempts have been carried out to find a better alternative route. At present, the process which has the most potentially to be economical scale is the reaction called the hydroxylation of benzene. The hydroxylation of benzene to phenol by hydrogen peroxide using titanium silicalite-1 catalyst (commonly known in the name TS-1) can produce phenol in only one reaction step under mild conditions with much lesser amount of by-products. This reaction, however, still has several drawbacks to overcome. An important drawback is the low conversion due to the reaction system is a three-phase system. The reactants, benzene and hydrogen peroxide, are immiscible liquid which benzene present on the surface of hydrogen peroxide solution while the catalyst situates at the bottom of the reactor.

Even though vigorous stirring can homogenise the mixture, this technique works well only in a small laboratory reactor when only a small distance exists

between the benzene layer on the surface of the hydrogen peroxide solution and the catalyst at the bottom of the reactor. For a larger system, the larger distance between the benzene phase and the catalyst causes difficulty in homogenising the reactant mixture. Introducing a solvent to homogenise the polar and the non-polar reactants, though, can solve this problem, it poses new problems such as the recovery of the solvent and the adsorption of solvent on the catalyst surface which suppresses the reaction.

A better way to increase the conversion is to raise the system temperature. At a higher reaction temperature, the solubility of benzene in water increases. The increase concentration of benzene in the aqueous phase, hydrogen peroxide, accompany with the higher temperature should results in a higher conversion.

Reaction temperatures of previous research works are usually limit by the boiling point of benzene at atmospheric pressure (Bengoa et al. (1988), Bhaumik et al. (1998), Kumar et al. (1999), Zhang et al. (2004)). Some research (Chammingkwan et al. (2009)) has attempted to increase the system pressure, the pressure above the liquid surface, but without the increase of the system temperature which did not give any advantage on the conversion if the reaction temperature was not increased to gain the advantage of the increase pressure. Therefore, no benefit gained from such attempt.

In a research work of our group studying the oxidation of toluene to benzaldehyde by hydrogen peroxide over modified TS-1 catalyts, (Siridumrongdej (2009)) which was carried out in a pressurized autoclave reactor, it has been found that the conversion of the reaction can be significantly increased by raising the reaction temperature with the aid of pressure. This bring the idea of applying this technique to the benzene hydroxylation reaction.

In the present work, the reaction temperature is further increased beyond the boiling point of benzene at atmospheric pressure by increasing the system pressure. The reaction of the present work is, therefore, carried out in a pressurised autoclave reactor in order to raise the reaction temperature higher than the boiling point of benzene, the component having the lowest boiling point in the system, at atmospheric

pressure. However benzene and toluene have different boiling points which toluene has higher boiling point than water. Hence in the case of benzene, when the reactor temperature is increased over the boiling point of benzene, it vapourized into vapor phase but hydrogen peroxide in the water phase can interact with benzene in the liquid phase. The preliminary result found that the conversion is low despite the pressure and temperature of the system are increased.

In order to overcome the problem described in the above paragraph, this research is, therefore, set up to study operating parameters affecting the reaction at an elevated temperature. Some of the operating parameters investigated are volume of water used as solvent, volume of benzene used in the reaction, solubility rate of benzene in water, etc.

## 1.2 Objectives

The main objective of this research is to raise the productivity of phenol from the benzene hydroxylation reaction over TS-1 catalyst. The reaction is carried out in a pressurized autoclave reactor at reaction temperatures higher than used previously in any research work. The present research has the following steps.

1. Synthesizing TS-1 using hydrothermal technique synthesis.
2. The synthesized catalysts in characterized by using the following techniques.
  - X-ray Fluorescence Spectroscopy (XRF) to determine the composition of elements in the bulk of catalyst.
  - X-ray diffractometer (XRD) to determine the structure of catalysts.
  - Fourier Transform Infrared Spectrometer (FT-IR) to determine the incorporation of Ti atoms as a framework element.
  - Nitrogen adsorption based on Brunauer-Emmett-Teller method (BET) to determine surface area pore size and pore volume.



3. Investigate catalytic behavior of the synthesized catalyst by the direct hydroxylation of benzene using  $\text{H}_2\text{O}_2$  as an oxidant with different reaction temperature .

The present thesis is organised as follows:

Chapter I presents the background and scopes of the research.

Chapter II reviews the theory of this research and literature on the catalytic activity of TS-1 catalysts in the direct hydroxylation of benzene by  $\text{H}_2\text{O}_2$  the on previous works.

Chapter III consists of catalyst preparation procedure, techniques used in the characterization of catalysts and catalytic activity evaluation in the direct hydroxylation of benzene by  $\text{H}_2\text{O}_2$  at elevated temperature.

Experimental results, explanation and discussion are described in Chapter IV.

Chapter V summarized the conclusions emerged from the present work and recommendation for further study.

In addition, raw data related to the experimental works are collected in the appendices at the end of the thesis.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## CHAPTER II

### THEORY AND LITERATURE REVIEWS

This chapter gives background on phenol and the hydroxylation reaction of benzene by hydrogen peroxide in sections 2.1 and 2.2, respectively. Background on relationship between pressure, solubility and boiling point are given in Section 2.3. Section 2.4 gives some basic knowledge of titanium silicalite-1.

#### 2.1 Phenol

Phenol is one of the most important intermediates of the chemical industry. Its global capacity was about 8 million tons per year in 2008. Phenol demand growth was due to a robust polycarbonate industry and rapid growth of Asian economies, especially China. It has been reported that over 95% of commercial phenol synthesis is made by the cumene route. (Centi and Perathoner (2009)).

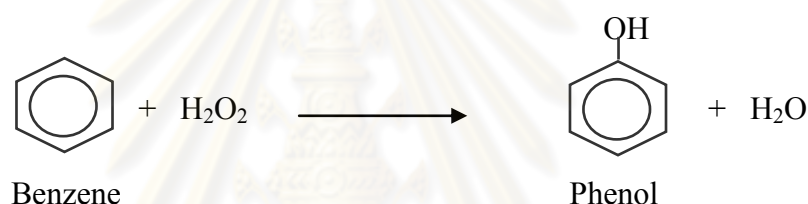
The cumene route is based on three different reactions: (i) Friedel-Crafts alkylation of benzene with propylene to produce cumene (isopropylbenzene); (ii) cumene oxidation with oxygen to cumyl hydroperoxide; and (iii) cleavage of cumyl hydroperoxide in an acidic medium to get phenol and acetone (usually about 0.62 tons acetone are formed per ton of phenol). The critical step of the cumene process is the second reaction, due to explosivity of cumyl hydroperoxide which requires to operate at low conversion per pass (typically 20%), limiting overall phenol yield per pass (typically in the 7–8% range).

In addition, competitive demand for propylene supply from steam crackers and refineries can negatively affect the cumene process. In addition, one of the disadvantages of the cumene route was the coproduction of acetone which had been reported that up to year 2000 had a good market. However, from that year the demand for phenol was outpacing the demand for acetone. In the year 2010, phenol demand was expected to grow 5.4% while global acetone demand was projected to grow only 2–3% per year (Centi and Perathoner (2009)). Furthermore, one of the main user

(over 30%) of acetone is the production of methyl methacrylate (MMA) via the acetone cyanohydrin route also come across environmental problems which can result negatively in the demand for acetone.

## 2.2 Hydroxylation of benzene by hydrogen peroxide

The hydroxylation of benzene by  $\text{H}_2\text{O}_2$  as an oxidant is an alternative route for the phenol production. Phenol is usually found as the main reaction product. Hydroquinone, catechol and 1,4-benzoquinone have also been observed as the consecutive products form from the further oxidation of phenol. The reaction of benzene and  $\text{H}_2\text{O}_2$  produces water as the by-product which is considered as a green process proceeding under mild conditions as shown in figure 2.1 below;



**Figure 2.1** Hydroxylation of benzene to phenol.

Catalytic testing results on the hydroxylation of benzene was reported by Bengoa et al in 1998. The reaction was carried out in a 250 ml batch glass reactor operated at atmospheric pressure at reaction temperature  $30^\circ\text{C}$  in a triphase system over TS-1 catalyst. Around 17% conversion based on  $\text{H}_2\text{O}_2$  with 74% phenol selectivity was reported.

Bhaumik et al. (1998) and Kumar et al. (1999) carried out the liquid phase hydroxylation reactions in a glass batch reactor under atmospheric pressure at 50 to  $80^\circ\text{C}$ . They reported the significant enhancement of reaction rate of benzene hydroxylation in a solvent-free system compared with bi-phase system. The increase 4-6 times activity when the reaction was performed in triphase instead of biphasic was reported. They suggested that this was due to the presence of solvent caused a diffusion hindrance of benzene molecule inside the TS-1 channel and such hindrance was not encountered in solvent-free system. The maximum conversion was reported

around 78% benzene conversion and 86% phenol selectivity at 70°C using benzene/H<sub>2</sub>O<sub>2</sub> molar ratio of 1:1.

Bhaumik et al. (1998) and Kumar et al. (1999) reported the increase of benzene conversion from 10.9% to 78.5% and the increase of phenol selectivity from 85% to 89% when water was used as solvent instead of acetonitrile. However, the repeated study under solvent-free conditions by Bianchi et al. (2007) was sensibly lower than that reported by Bhaumik et al. in 1998. The benzene conversion reported by Bianchi et al. (2007) was only at 4.5% with 42% phenol selectivity under the identical conditions. The work of Bianchi et al. (2007) and several works after 1999, which nobody can repeat the result of Kumar's research team, point out the problem on the confidence of the work of Kumar's research team.

Nomiya et al. (2000) studied benzene hydroxylation with hydrogen peroxide catalyzed by selectively site-substituted vanadium (V) polyoxometalates. The reaction of benzene was carried out at 25°C in a 50 ml round bottom flask. The reaction system consisted of two liquid phases: an organic layer containing benzene and acetonitrile, and an aqueous layer containing acetonitrile and 30% H<sub>2</sub>O<sub>2</sub>. In a typical experiment, 0.10 mmol of catalyst precursor, 10 ml (113 mmol) of benzene, 2 ml (25.4 mmol) of aqueous 30% H<sub>2</sub>O<sub>2</sub>, and 5 ml of acetonitrile in a 50 ml round bottom flask with a serum cap were employed. A magnetic stirrer was also provided to stir the reaction medium.

The catalytic activity on the hydroxylation of benzene to phenol has been continuously studied by several research groups. He et al. (2001) reported the liquid phase hydroxylation of benzene which was performed in a 100 ml three necked glass flask batch reactor equipped with a magnetic stirrer, a reflux condenser stirred. The reaction was carried out under atmospheric pressure in air at 65°C over Ti-MCM-41 catalyst using acetone as solvent. It was believed that the large pore Ti-MCM-41 offered the great advantage of benzene substrate to diffuse and react on the active site and also phenol diffuse away from the active site. The selectivity of phenol close to 100% has been reported. The conversion of benzene increased when increased the titanium content and the introduction of Al. The best value of conversion was

reported at 98% with more than 95% phenol selectivity for [Si, Ti, Al]-MCM-41 (Si/Ti = 25 and Si/Al =  $\infty$ ) much better TS-1 catalyst which gave 10% benzene conversion and 63% phenol selectivity.

Several catalysts have also been developed for the benzene hydroxylation reaction. For example, Masumoto et al. (2002) carried out the reaction using a stainless steel reactor in a reaction temperature of 30°C and reaction time of 24 h under N<sub>2</sub> atmosphere (0.4MPa). They used a catalyst system containing vanadium (mainly vanadium catalyst supported on Al<sub>2</sub>O<sub>3</sub>) in aqueous solvent with high acetic acid concentration. The yield of phenol was found to be increased with the increase in the concentration of acetic acid in the aqueous solvent, the acetic acid concentration of around 80 vol.% was reported to be the maximum value.

Another study has been done by Lemke et al. (2003). The catalytic tests were carried out in a closed glass autoclave system and the mixture was stirred during the reaction. The autoclave was allowed to operate up to a pressure of 10 bar and the reaction temperature up to 70°C. Supported vanadium oxide catalysts were used in their study. The vanadium catalysts were prepared using various support materials such as MCM-41, MCM-48, SiO<sub>2</sub> and amorphous microporous mixed oxide. The best result was obtained at 8.3% phenol yield over VO<sub>x</sub>/SiO<sub>2</sub> catalyst with low percent of vanadium loading (0.14 wt.%) using acetic acid as co-solvent. They reported that consecutive oxidation reactions were suppressed on site isolated VO<sub>x</sub> catalysts. The reaction conditions to receive phenol selectivities >40% at a benzene conversion of >10%. However, high phenol selectivity was achieved at low benzene conversion.

Another study on the liquid-phase direct catalytic oxidation of benzene at room temperature and atmospheric pressure was carried out by Zhang et al. (2005). The reaction was performed in a 50 ml three-neck round bottom flask using vanadium-substituted heteropolyacids as catalysts. Various solvents, for example, formyl acid, glacial acetic acid, propyl acid, butyric acid and acetonitrile were tested and the best result was found by using glacial acetic acid. Different vanadium species such as NaVO<sub>3</sub>, H<sub>4</sub>PMo<sub>11</sub>VO<sub>40</sub>, H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> and H<sub>6</sub>PMo<sub>9</sub>V<sub>3</sub>O<sub>40</sub>, were reported to



be catalytically active for the hydroxylation of benzene with satisfactory results, 91% phenol selectivity and yield of 26%.

Another study was studied by Gao and Xu (2006). The reaction was performed in a 100 ml four-neck flask stirred reactor operated at atmospheric pressure at 40°C under stirring over clay supported vanadium oxide using acetic acid as solvent. The physical mixture of clay and V<sub>2</sub>O<sub>5</sub> catalyst exhibited lower activity than V<sub>2</sub>O<sub>5</sub>/clay prepared by impregnation method. High selectivity to phenol of 94% with 14% benzene conversion was achieved using the optimum 2.5% vanadium loading. They also reported that the excessive of vanadium oxide decomposed H<sub>2</sub>O<sub>2</sub> which resulted in low conversion.

Uddin et al. (2006) carried out liquid phase oxidation of benzene to phenol in a 100 ml three necked flat bottomed flask with O<sub>2</sub> at atmospheric pressure and reaction temperature 40°C. Catalysts based on carbon-based Fe-Pd and Cu-Pd catalyst, prepared by the technique they called “modified carbothermal reduction” of metal ion exchange method using cation exchange resin as a source of carbon, has been investigated. They reported that the bimetallic catalysts, Fe-Pd/carbon and Cu-Pd/carbon, showed much higher activity for phenol production than the monometallic catalysts. In addition, they also reported that a physical mixture of the single component catalysts such as Fe and Pd or Cu and Pd were not effective in the oxidation of benzene to phenol. They proposed that an intimate contact between Fe or Cu species with Pd species was necessary to formulate an active catalyst.

Fumin et al. (2007) studied the liquid phase hydroxylation of benzene in a 120 ml home-made glass reactor fitted with a water-cooled condenser and a magnetic stirrer. In a typical procedure, 0.06 mmol of catalyst (approximately accounting for 0.42% by mass in the reaction medium) was added to 40 mmol of benzene, which was dissolved in the mixed solvent of 10 ml of glacial acetic acid and 10 ml of acetonitrile, then the mixture was heated to 65°C. 120 mmol of hydrogen peroxide (30% aqueous solution) was added into the above suspension within 0.5 h by a syringe pump, followed by further vigorous stirring of 6 h. Using the mixed solvent for this reaction, a homogeneous phase was observed and the catalyst was well dissolved in the



reaction media due to the polarity of the solvent. The reaction mixture was sampled periodically, followed by the gas chromatography analysis with a flame ionization detector and a 30 m SE-54 capillary column.

Another study on the catalytic activity of TS-1 on the hydroxylation of benzene and toluene was performed by Sakullimcharoen et al. (2007). The reaction was carried out in a bubble reactor. The reactor was immersed in an oil bath in order to make the working temperature constant and performed at atmospheric pressure. The results showed that the conversion of benzene decreased when the volume of benzene feeding in each period increase. The amount of phenol increased when the reaction mixture was left for a period of time up to 4 hours.

Tanarungsun et al. (2007) reported the catalytic reaction between benzene and hydrogen peroxide at 30°C and atmospheric pressure in a 125 ml round flat bottomed flask. The reaction was catalyzed by Fe(III)/TiO<sub>2</sub> catalysts. The conversion were obtained as a result of the increased amount of metal active species. The benzene conversion increased, but the phenol selectivity decreased. It was found that acetone gave the highest benzene conversion, 10.8%, and phenol yield, 21.2%.

Kasemsiri et al. (2008) use a batch reactor, a 250 ml, water jacketed, three-necked, glass flask fitted with a condenser under stirring at 70°C, to carried out the catalytic properties of TS-1 modified Fe, Al, Co and V in the hydroxylation of benzene and alkyl benzene with hydrogen peroxide. The reaction was performed at atmospheric pressure. It has been reported that the addition of Fe, Al, Co and V can increase the catalytic activity of TS-1 on the hydroxylation of benzene in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1.

Abbo and Titinchi (2009) performed the hydroxylation of benzene at atmospheric pressure and reaction temperature 70°C in a two necked 50 ml glass round bottomed flask with a water condenser. The catalysts were prepared by ion-exchanged NaY zeolite with various valent cations. The highest conversion of benzene reported was 33% in a one-step process by using Cu–NaY with 100% selectivity to phenol.

Chammingkwan et al. (2009) studied the hydroxylation of benzene over TS-PQ<sup>TM</sup> catalyst using both a conventional stirred reactor operated at atmospheric pressure and an autoclave operated at 20 bar. The batch glass reactor equipped with a condenser was used for the operation under atmospheric pressure. The reaction was carried out in a three phase slurry reactor system. The catalytic activity of this catalyst was found to be higher than TS-1. The temperature effect was investigated at temperatures of 65°C, 70°C and 75°C at a fixed 1100 rpm stirring speed. They reported that the conversion of H<sub>2</sub>O<sub>2</sub> increased in a narrow range from 14.9% at 65°C to 19.4% at 70°C. The effect of pressure was also investigated in an autoclave using N<sub>2</sub> to pressurize the system. The molar ratio between benzene:H<sub>2</sub>O<sub>2</sub> was set at 5:1. The reaction temperature was studied at 60°C and 70°C. They reported that the system pressure did not have any significant effect on the H<sub>2</sub>O<sub>2</sub> conversion to organic compounds. Moreover the effect of additional water to the reaction mixture on H<sub>2</sub>O<sub>2</sub> conversion to organic compounds and product selectivity was also investigated. They reported that when increase the volume of additional water the conversion of H<sub>2</sub>O<sub>2</sub> could reach 22% at 40 ml additional water. Thereby, phenol selectivity of 96% could be achieved. They also reported that 60 ml additional water increased phenol selectivity up to 98%.

Qi et al. (2009) studied the benzene hydroxylation experiments carried out under atmospheric pressure in a stirred 25 ml batch glass reactor fitted with a water-cooled reflux condenser. A gas burette was installed to monitor possible molecular oxygen evolution from which H<sub>2</sub>O<sub>2</sub> effective conversion was calculated. The desired reaction temperature was achieved and maintained by a temperature-controlled water circulation system. In a typical run, 50 mg calcined catalyst powder was fully dispersed in 6 ml acetonitrile followed by the addition of 0.45 g benzene. After stabilization of the temperature, the required amount of H<sub>2</sub>O<sub>2</sub> was added in one lot and the benzene hydroxylation process was kept going with magnetic stirring for a period of time. After that, the used solid catalyst in the reaction system was separated and removed by centrifugation. The reaction products in the clear solution obtained above were analyzed by a Varian CP-3800 gas chromatograph equipped with a 25 m-long OV-17 capillary column and an FID detector.

Song et al. (2010) studies the hydroxylation of benzene to phenol over multi-walled carbon nanotubes supported  $\text{Fe}_3\text{O}_4$  catalyst. The reaction was performed in a 50 ml round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. In a typical procedure, 50 mg catalyst was suspended in 8 ml of acetonitrile, and 11.3 mmol of benzene was added. After the mixture was heated to the desired temperature under vigorously stirring, 13.5 mmol of  $\text{H}_2\text{O}_2$  (30 wt.%) was added within 15 min. The mixture of liquid phase products was analyzed by gas chromatography (GC-95).

Barbera et al. (2010) also studied the hydroxylation of benzene with hydrogen peroxide, catalyzed by TS-1. The selectivity to phenol was reported to be higher than 90% at low benzene conversion, but rapidly declined in conditions leading to benzene conversion higher than 3–4%. Catalytic tests were performed using the following procedure: first, the reactor was loaded with benzene, solvent, and TS-1 catalyst. Then the mixture was heated up to the desired reaction temperature; at this point, the aqueous hydrogen peroxide solution was fed to the reactor under stirring, for 30 min, by means of a peristaltic pump; after that, the reaction was left to proceed for 1.5 h more, for an overall reaction time that in standard conditions was 2 h. During this time, hydrogen peroxide was considered almost completely consumed, as confirmed by iodometric titration; this was important in order to avoid reactions due to residual unconverted hydrogen peroxide when injecting the solution containing the reaction products for GC analysis. The following amounts of reactants, solvent and catalysts were used, unless otherwise specified: solvent volume (either methanol, or methanol + water, or sulfolane + methanol) 52 ml; aqueous hydrogen peroxide solution (35 wt.%) 8.7 mL; benzene 0.1 mol; catalyst 1.17 g. The liquid phase reaction was conducted in a 150 ml batch autoclave made of glass, equipped with a stirrer; heating was provided by means of electric heating elements. The reactor operated at an autogenous pressure (4–5 bar for the reaction carried out at 80 °C).

From the literatures reviewed above one can see that the common problem many researchers confront is the low conversion of benzene. The methods normally employed are using solvent, adding a second metal to the TS-1, and catalyst modification by treatments. An important factor affecting the conversion has yet to be explored is increasing reaction temperature. Up to present, we have noticed that all the published papers carried out the reaction at a temperature lower than the boiling

point of benzene at atmospheric pressure. This factor becomes the interested topic of this study. In addition, many previous research did not exhibit the detail of the experimental procedures. Especially the detail of the time interval between the introduction of benzene following by hydrogen peroxide which is found in the present work that can significantly affect the conversion of  $\text{H}_2\text{O}_2$  at the end of the run.

### **2.3 Pressure, boiling point, and solubility relationship**

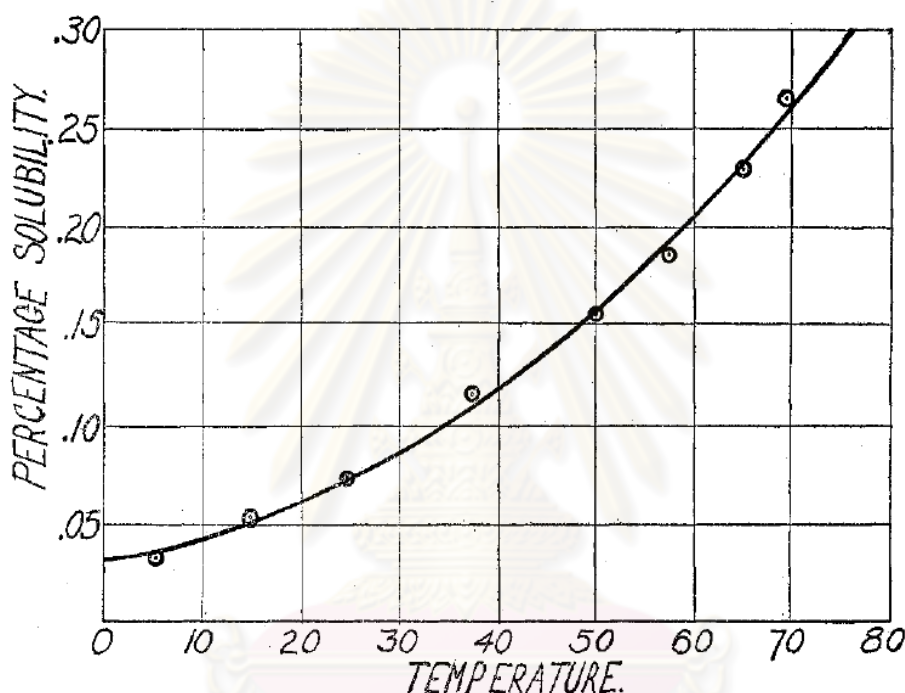
It is commonly known that the solubility of a non-polar molecule in water increases with the temperature of water. Due to the boiling point of benzene at atmospheric pressure is only  $80.1^\circ\text{C}$ , which is lower than the normal boiling point of water at the same pressure. Past experimental works on the hydroxylation of benzene, therefore, limited the reaction temperature at any temperature lower than  $80.1^\circ\text{C}$ .

For gaseous phase, the changing of pressure affects the density of the molecule of gas. If the pressure decreases, the space between the molecules is increased. The opportunity for the molecules to interact are less. Therefore, the reaction rate decreased. On the contrast, increasing pressure the molecules of a gas are made to come closer together. The space between the molecules is decreased. Therefore, the reaction rate is increased. As a result, in the gaseous phase, the changing of pressure obviously affects the reaction rate.

The behaviour of liquid is different from gas. Liquid is less compressible (may be not compressible if the applied pressure is not very high). For a reaction occurs in the liquid phase, the changing of pressure obviously does not affect the reaction if the temperature is not change. However, if one of the reactant or the product is gaseous or volatile, the changing of pressure can affect the reaction.

In our case, in order to keep benzene in the liquid state at a higher reaction temperature, the pressure above the liquid surface has to increase. The operation at a higher reaction temperature will allow more benzene to dissolve into the aqueous. Thus, better conversion is expected.

The solubility of water in benzene at different temperature is showed in Figure 2.2. From this figure, one can obviously see that water solubility in benzene increases rapidly when increasing the temperature (The boiling points of water and benzene can be increased by increasing the pressure of the system). Therefore, increasing the temperature of the reactor system will result in higher amount of benzene in the liquid phase. Thus providing more opportunity for benzene,  $H_2O_2$  and catalyst to contact altogether and convert into products.



**Figure 2.2** Percent solubility of water in benzene at different temperature( $^{\circ}C$ ) Aurther (1923).

#### 2.4 Titanium silicalite – 1

Titanium Silicalite (TS-1) catalyst, one of the most important innovation in heterogeneous catalysis over the last decades, was firstly reported by Taramasso et al (1983). It is a high performances composite material specifically designed for industrial oxidation reactions with hydrogen peroxide. The unique performances of the catalyst are due to the specific features of isolated Ti active sites, able to efficiently promote activity and selectivity in oxidation reactions with  $H_2O_2$ , while not isolated Titanium, such as segregated  $TiO_2$  “Anatase like” phase, is inactive for these reactions. Titanium Silicalite is a crystalline zeolite material in which tetrahedral



[TiO<sub>4</sub>] and [SiO<sub>4</sub>] units are arranged in a MFI structure. Owing to this structure TS-1 shows a three-dimensional system of channels having molecular dimension of 5.1-5.6 Å and which constitutes the zeolitic micropores of the material.

It was reported to be effective in the oxidation of a variety of organic compounds at low temperature, using diluted hydrogen peroxide as an oxidant such as the conversions of ammonia to hydroxylamine, of secondary alcohols to ketones and of secondary amines to dialkylhydroxylamines or reactions such as the phenol hydroxylation, the olefin epoxidation, the ketone ammoximation and also sulfide and disulfide oxidation. Eni polimeri europa company (2007).



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## CHAPTER III

### EXPERIMENTAL

The experimental procedures in this chapter are divided into three sections. The chemicals, apparatus and procedures for catalyst preparation are explained in section 3.1. The techniques used for the characterization of catalyst composition, surface properties etc. are detailed in section 3.2.

#### 3.1 Catalyst preparation

##### 3.1.1 Chemicals

The details of chemicals used in the preparation procedure of TS-1 are shown in Table 3.1. The reagents are summarized in Table 3.2 and the preparation procedure is shown in Figure. 3.1.

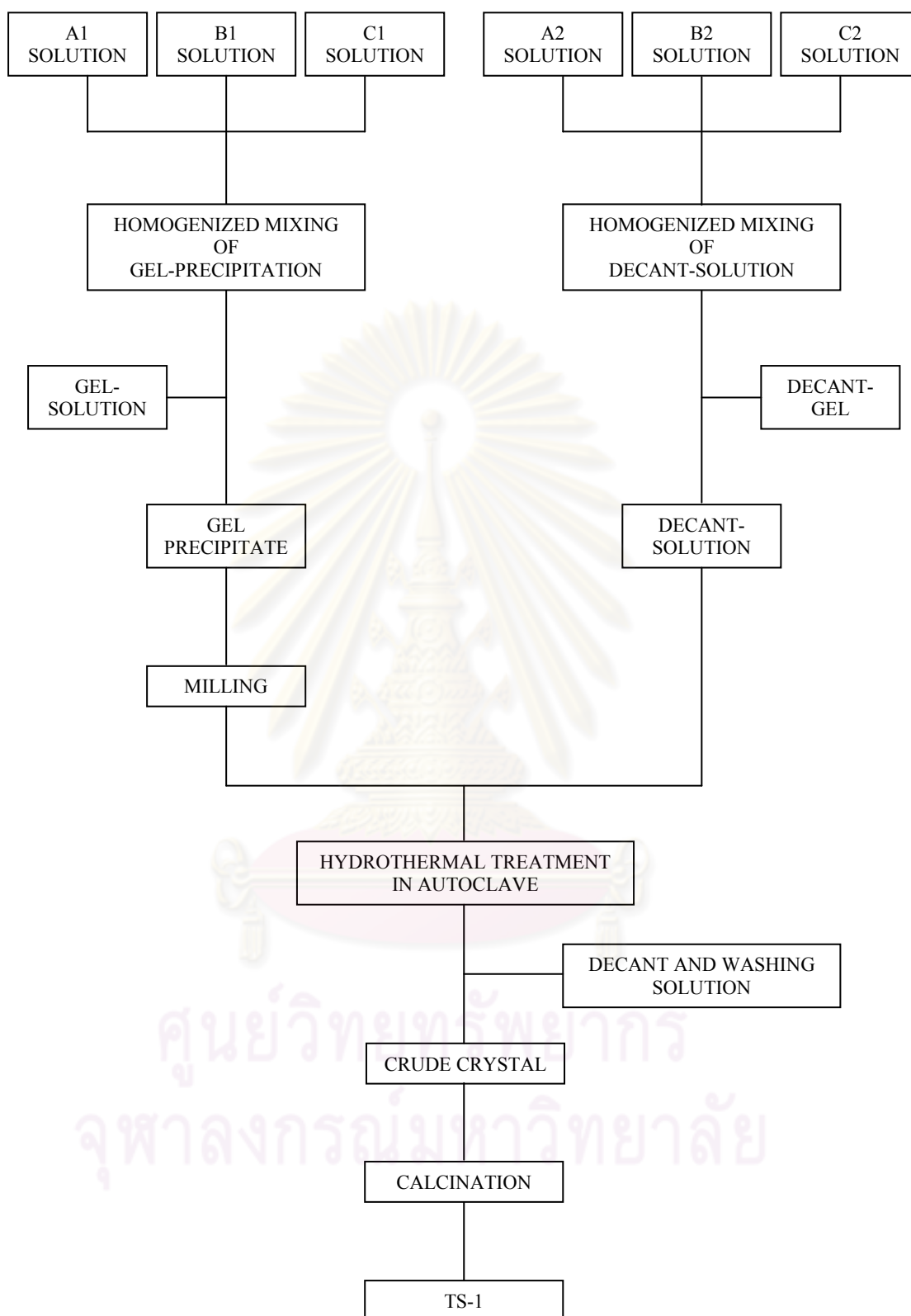
**Table 3.1** The chemicals use in the catalyst preparation.

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

**Table 3.2** Reagents use for the preparation of TS-1

Solution for the gel preparation		Solution for decant-solution preparation	
<u>Solution A1</u>		<u>Solution A2</u>	
Ti[O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>4</sub>	2.2970 g	Ti[O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> ] <sub>4</sub>	2.2970 g
TPABr	5.72 g	TPABr	7.53 g
NaCl	11.95 g	De-ionized water	60 ml
De-ionized water	60 ml	H <sub>2</sub> SO <sub>4</sub> (conc.)	3.4 ml
H <sub>2</sub> SO <sub>4</sub> (conc.)	3.4 ml		
<u>Solution B1</u>		<u>Solution B2</u>	
Sodium silicate	69 g	Sodium silicate	69 g
De-ionized water	45 ml	De-ionized water	45 ml
<u>Solution C1</u>		<u>Solution C2</u>	
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 <sub>2</sub> SO <sub>4</sub> (conc.)	1.55 ml		

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**Figure 3.1** The preparation procedure of TS-1 by rapid crystallization method.

The preparation of decantation and gel solutions comprises  $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$  for Ti and sodium silicate for Si, respectively. TPABr (Tetra-n-propyl ammonium bromide  $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]\text{Br}$ ) is used as organic template. The atomic ratio of Silicon/Titanium is in the recipicities set at 50. The preparation of supernatant liquid is separated from the gel, which is important for preparing the uniform crystals. The detail procedures are as follows: firstly, a gel mixture is 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 is maintained within the range 9-11 because this pH range is suitable for precipitation.  $\text{H}_2\text{SO}_4$  (conc.) or KOH solution are used to adjust pH of the gel mixture to an appropriate level if it is necessary. The gel mixture is separated from the supernatant liquid by a centrifuge. The precipitated gel mixture is milled for totally 1 hour. The milling is done for 15 min and then the supernatant solution is removed by centrifugal separation before the hydrothermal treatment in order to obtain the uniform, fine crystals. The milling procedure is as follows: mill 15 min  $\rightarrow$  centrifuge (to remove liquid out) 15 min  $\rightarrow$  mill 15 min  $\rightarrow$  centrifuge 15 min  $\rightarrow$  mill 30 min  $\rightarrow$  centrifuge 15 min.

Secondly, a decantation solution is 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 are mixed together with the milled gel mixture. However, before mixing, the pH of solution was maintained between 9-11. The colorless supernatant liquid is separated from the mixture by centrifugation.

In the step of crystallization, the mixture of the milling precipitate and the supernatant of decant solution are filled in a 500 ml Pyrex glass. The glass container is placed in a stainless steel autoclave. The atmosphere in the autoclave is replaced by nitrogen gas and pressurized up to 3  $\text{kg}/\text{cm}^2$  gauge. Then, the autoclave is heated from room temperature to 180  $^\circ\text{C}$  and kept at this temperature for 3 days, followed by cooling the mixture to room temperature in the autoclave.

The obtained product crystals are washed with de-ionized water decreased pH from about 12 to 7 by centrifugation in order to remove chloride out of the crystals. Then the crystals are dried in an oven at 110  $^\circ\text{C}$  for at least 24 h. The dry crystals are

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 at 10 °C/min. The calcined crystals are finally cool down to room temperature.

The obtained TS-1 is placed in a round bottom flask. Then 5 M of HNO<sub>3</sub> aqueous solution is added. After reflux at 80 °C for 3 h, the treated catalyst is filtered, washed with distilled water until pH 7, dried at 110 °C and calcined at 540 °C for 7 h in static air.

## **3.2 Catalyst characterization**

### **3.2.1 X-Ray Fluorescence Spectrometer (XRF)**

The chemical composition analysis of elements of the catalyst is performed by X-ray fluorescence (XRF) using Siemens SRS3400 at Scientific and Technological Research Equipment Centre, Chulalongkorn University.

### **3.2.2 X-Ray Diffraction (XRD)**

The crystallinity and X-ray diffraction patterns of the catalysts are 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 are carried out by using Cu K $\alpha$  radiation with Ni filter. Scans are performed over the 2 $\theta$  ranges from 6 ° to 30 ° with step size 0.04 °/sec.

### **3.2.3 Fourier Transform Infrared (FT-IR)**

The functional group on the catalyst surface is determined by FT-IR using Nicolet model Impact 6700 of the IR spectrometer. Infrared spectra are recorded between 400 and 4000 cm<sup>-1</sup> on a microcomputer.

### 3.2.4 BET surface area measurement

The total surface area, pore volume and pore size are calculated using BET Micromeritics ASAP 2020. The sample cell which contained 0.2 g of sample is placed into BET Micromeritics ASAP 2020. After degassing step, the surface area and pore volume of catalyst are measured.

## 3.3 Reaction study in the direct hydroxylation of benzene

### 3.3.1 Chemicals

The reactants used for the reaction study are shown in Table 3.3.

**Table 3.3** The chemicals use for the reaction study.

Chemical	Grade	Supplier
Benzene	Analytical	Panreac
Hydrogen peroxide 30%	Analytical	Merck
Ethanol	Analytical	Merck

### 3.3.2 Reaction procedure

The direct hydroxylation of benzene with molar ratio of reactant ( $\text{H}_2\text{O}_2$  : benzene) is 1:1 using TS-1 catalyst is carried out in a stainless steel reactor. The procedures are described in the detail below.

1. Catalyst 1 g, magnetic bar, water (50-140 ml). (for dispersion of the catalyst) and benzene 0.78 ml are added into the reactor and adjust the pressure to 2 bars by nitrogen gas.

2. Heat up the reactor by raising the oil bath temperature to 70 °C for 1 h to drive out gases in pores of the catalyst.

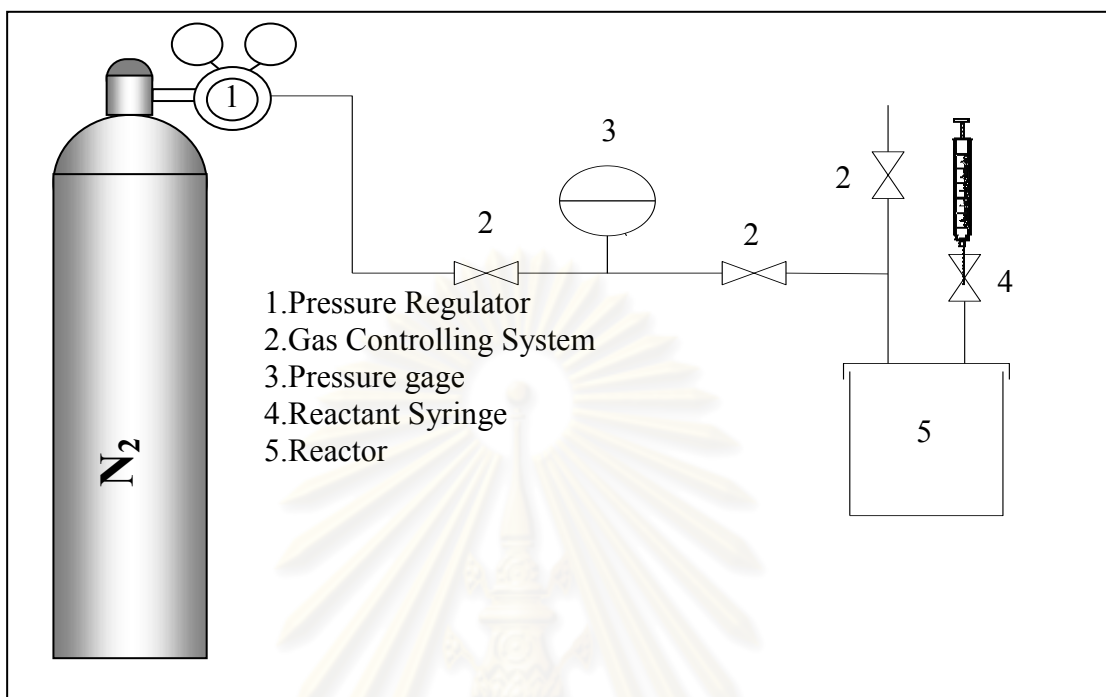


3. After degassing, adjust the oil bath temperature to the desired reaction temperature.
4. Start the reaction by injecting hydrogen peroxide 30 wt% 1 ml (for H<sub>2</sub>O<sub>2</sub>) to benzene molar ratio equals to 1:1) in a single injection into the reactor.
5. After 2 hrs, the mixture is immediately cooled down by removing the reactor from the oil bath and put into an ice bath in order to stop the reaction. After the reactor is cooled down, 50 ml of ethanol is injected into the reactor to homogenize the liquid mixture in the reactor.
6. The catalyst particle is separated from the homogeneous mixture by using the micro-centrifuge.
7. The liquid product is analyzed by the FID gas chromatography. The chromatogram data are converted into mole of products using a calibration curve.

**Table 3.4** 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)	60
Injector temperature (°C)	250
Detector temperature (°C)	250
Initial column temperature (°C)	70
Initial hold time (min)	5
Program rate (°C/min)	6
Final column temperature (°C)	170 for phenol 230 for catechol and quinones
Final hold time (min)	10
Analyzed chemical	Phenol

The presence of over hydroxylation products such as catechol and quinone are also tested by raising the final column temperature to 230 °C, but none are observed.



**Figure 3.2** Schematic diagram of the reaction system.

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## CHAPTER IV

### RESULTS AND DISCUSSION

This chapter reports and gives explanation to experimental results of the present study. The experimental results reported are arranged in a sequence which is believed to be able to give a clear vision of the development of the experimental procedure.

During the progress of the research work, we have found that several operating parameters should be studied before raising the reaction temperature above the boiling point of benzene at atmospheric pressure. It is observed that difference in operating parameters such as volume of water used as solvent, ratio between benzene and  $H_2O_2$ , waiting period (time between feeding benzene and  $H_2O$ ) results in different  $H_2O_2$  conversions. Therefore, these parameters have to be specified before carrying out the hydroxylation reaction at elevated temperature.

It should be noted here that the conversion of  $H_2O_2$  reported in this chapter are the conversion of  $H_2O_2$  to “organic product”. It is unavoidable that during the reaction, part of  $H_2O_2$  decomposed. In practice, what we really concern is the highest amount of  $H_2O_2$  can be converted to organic product(s).  $H_2O_2$  molecules remained in the system can not be recovered. Therefore, the unreacted  $H_2O_2$  and the decomposed  $H_2O_2$  are treated as the same since we can not use it.

#### 4.1 Characterization of catalyst

##### 4.1.1 Catalyst composition (XRF)

The chemical compositions of TS-1 batch 1 and batch 2 determined by X-Ray Fluorescence Spectrometer (XRF) are illustrated in Table 4.1 below.

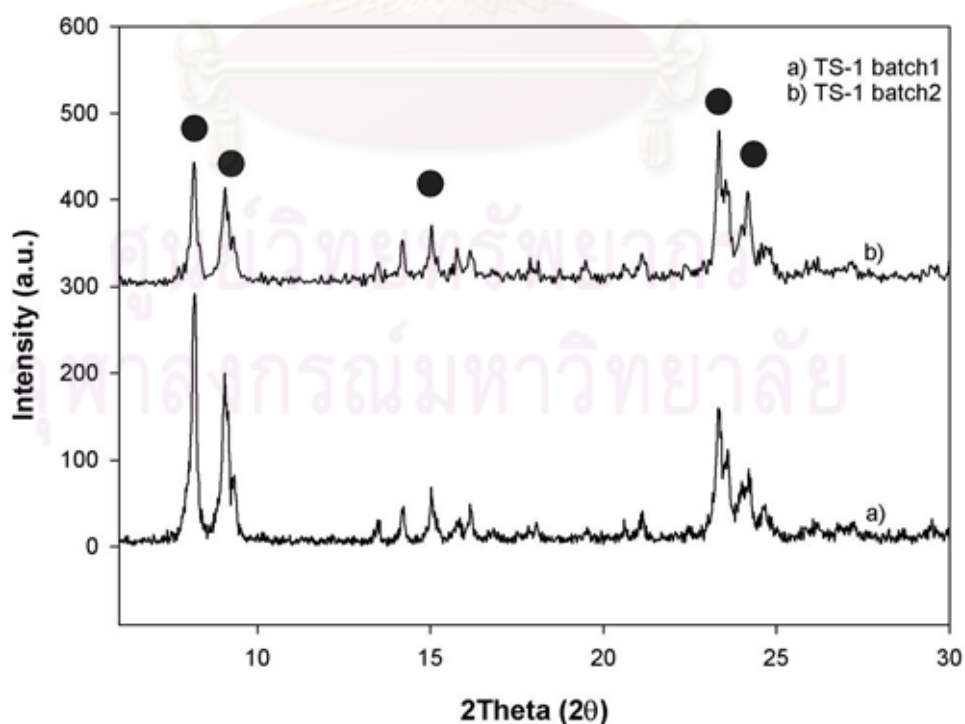
**Table 4.1** The chemical compositions of TS-1 batch 1 and batch 2.

Catalysts	%Si	%Ti	Si/Ti
TS-1 batch1	96.42	2.16	44.63
TS-1 batch2	97.03	1.62	59.89

Due to the amount of catalyst needed to complete all experiments is larger than expected. Catalysts prepared from 2 batches are used in the present study. Though the catalyst obtained from both batches are slightly different in composition, this parameter should not affect the operations parameter comparison. Because in each operations parameter comparison, the catalyst from the same batch is used.

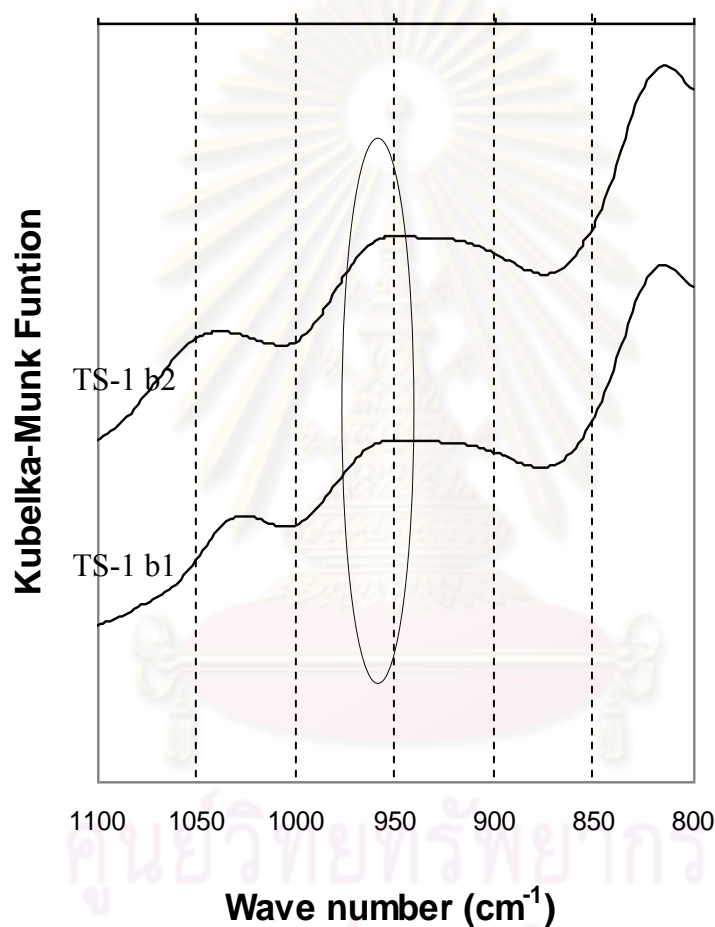
#### 4.1.2 Crystal structure (XRD)

The X-ray diffraction analysis demonstrates that the sample have the MFI crystal structure (see the XRD pattern showed in Fig 4.1). One can see that both specimens exhibit a set of diffraction peaks at 2-Theta = 7.9°, 8.8°, 14.8°, 23.9° and 24.4° in their XRD patterns, indicating the presence of TS-1 (Huang et al., 2010).

**Figure 4.1** XRD pattern of TS-1 batch 1 and batch 2.

### 4.1.3 Fourier Transform Infrared (FT-IR)

The absorption band at  $960\text{ cm}^{-1}$ , being attributed to the stretching mode of  $[\text{SiO}_4]$  units bonded to a  $\text{Ti}^{4+}$  ion ( $\text{O}_3\text{SiOTi}$ ), indicates the incorporation of titanium in the MFI framework (Huang et al., 2010) also appears in the IR spectra of both sample. These results confirmed that both samples have  $\text{Ti}^{4+}$  cation the catalyst framework.



**Figure 4.2** The FTIR spectra for TS-1 batch 1 and batch 2.

### 4.1.4. Data from $\text{N}_2$ -physorption (BET)

Data in Table 4.2 show that BET surface area of TS-1 from both batch are not so different. Therefore, the difference observed during catalytic testing should not be the result of the different in catalyst surface area.

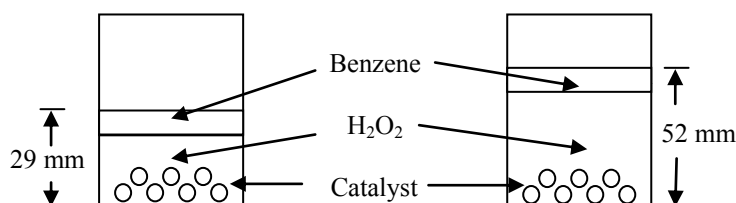
**Table 4.2** The data from N<sub>2</sub>-physisorption .

Catalysts	BET surface Area (m <sup>2</sup> /g)
TS-1 (batch1)	351.1
TS-1 (batch2)	362.49

## 4.2 The effect of operating parameters on conversion of H<sub>2</sub>O<sub>2</sub>

### 4.2.1 The effect of volume

In the present study, the reaction is carried out in a pressurized autoclave reactor. The inside diameter of the reactor is 50 mm. The internal volume is approximately 150 ml. If 50 ml of water is used as solvent, the benzene layer will be about 29 mm from the magnetic bar situated at the bottom of the reactor. If a larger amount of water is used, i.e. 90 ml, the benzene layer will be about 52 mm from the magnetic bar situated at the bottom of the reactor. Initially before the magnetic stirrer is turned on, the catalyst will deposit at the bottom of the reactor while the benzene reactant is on the top surface of water. For the reaction to occur, both benzene and H<sub>2</sub>O<sub>2</sub> must present on the catalyst surface. If a larger volume of water is used, the distance between the catalyst and benzene will increase. From this point of view, the chance for the catalyst to contact with benzene phase should decrease with the increase in the volume of water. Therefore, one may expect that if we increase the volume of water, the conversion of H<sub>2</sub>O<sub>2</sub> should decrease. This phenomenon is described graphically in Figure 4.3. From Figure 4.3, one can clearly see that the distance between catalyst and benzene increases with the volume of water. This should result in less chance for the catalyst to contact with benzene. The experimental results obtained from using 50 ml and 90 ml of water at 70 °C and 90°C are summarized in Table 4.3 below.



**Figure 4.3** (Left) when 50 ml of water is used and (Right) when 90 ml of water is used.



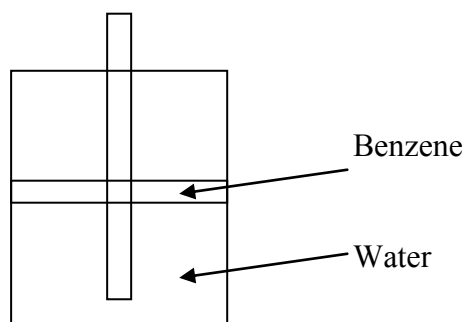
**Table 4.3** The effect of volume of water with the ratio of H<sub>2</sub>O<sub>2</sub>:benzene (1:1).

Temp (°C)	Volume of water (ml)	Conversion of H <sub>2</sub> O <sub>2</sub> (%)
70	50	13.13
70	90	21.86
90	50	6.84
90	90	15.35

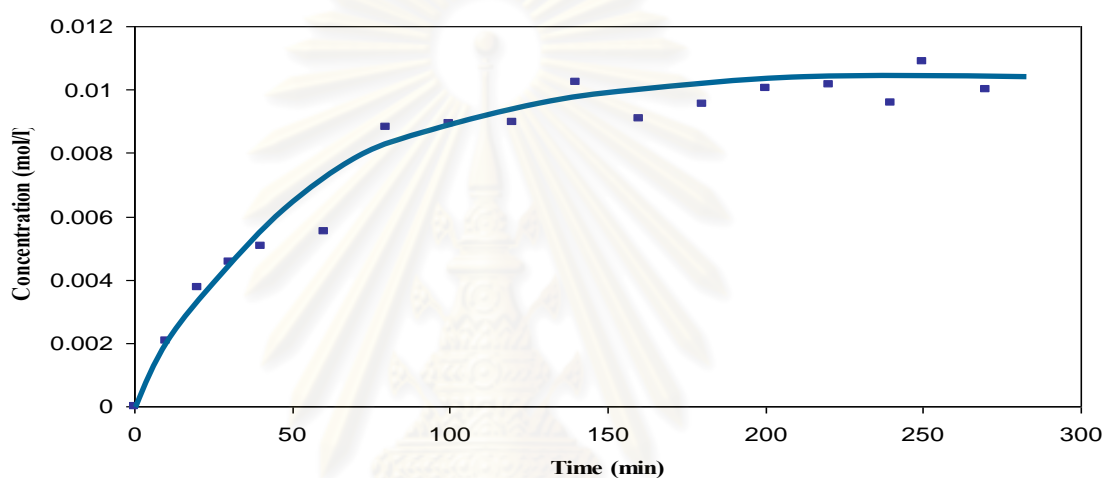
The results reported in Table 4.3, however, contrast to what is expected above. It is found that when we increase the volume of water used as solvent, the conversion of H<sub>2</sub>O<sub>2</sub> increases even though the chance for the catalyst to contact with benzene is lower. When the volume of water is increased from 50 ml to 90 ml (1.8 time increase), the conversion of H<sub>2</sub>O<sub>2</sub> increases from 13.55% to 22.53% (about 1.7 time) at 70°C and from 7.10% to 13.91% (about 1.96 time) at 90°C. Because of these results, it is hypothesized that the benzene in the liquid phase (benzene on the top surface of water) may not directly involve in the reaction with H<sub>2</sub>O<sub>2</sub>. The benzene directly reacts with H<sub>2</sub>O<sub>2</sub> is most likely the benzene dissolved into the water phase.

In order to prove the proposed hypothesis, the solubility of benzene in water is measured. The measurement is carried out at room temperature and pressure. In this experiment 160 ml of water and 10 ml of benzene is used. The explanation why we used higher volume of water because during each sampling, a significant volume of water (about 1 ml) is withdrawn from the system. If too low volume of water is used, the experiment will be affected from the sampling volume.

In this experiment, 160 ml of water is filled into a 250 ml beaker. Then, a 1/4" tube is vertically placed in the beaker. This tube is used as sampling point. Then 10 ml of liquid benzene is added into the beaker and the magnetic stirrer is turned on. The experimental period is started from this point. The concentration of benzene in the aqueous is measured by from samples of water via the 1/4" tube. To collect the sample, a rubber balloon is used to purge the water inside the tube 3-4 time in order to make sure that the water inside the tube and the water outside the tube have the same concentration of benzene. After that an 1 microliter of syringe is used to collect the water. The collected water is analyzed by an FID gas chromatograph to determine the concentration of benzene. The experimental system and experimental results are exhibited graphically in Figures 4.4 and 4.5 respectively.



**Figure 4.4** The experimental of the solubility benzene in water.



**Figure 4.5** The concentration of benzene in H<sub>2</sub>O by added the benzene covered the above of liquid surface.

Please be reminded that the solubility of benzene in water depends on temperature. At a temperature, there is only one saturated concentration of benzene in water. The amount of benzene dissolved into the water is the product between the concentration of benzene in the water phase and total volume of water. Therefore, at a temperature, if larger volume of water is used, higher amount of benzene in the aqueous phase also higher. This means that higher amount of benzene can react with H<sub>2</sub>O<sub>2</sub> on the catalyst surface. This explanation can well explain the experimental result reported in Table 4.3.

At this point, it can be concluded that benzene dissolved in the water phase plays an important role for the hydroxylation reaction. Therefore, another attempt to

increase the concentration of benzene in the water phase is carried out by increasing the reaction temperature. The results of this attempt are discussed in section 4.1.1.

#### 4.2.2 The effect of temperature

It is known that the solubility of a non-polar molecule (such as hydrocarbons) in water increases with the temperature of water. In the present study, an attempt has been carried out to increase the concentration of benzene in the aqueous phase by raising the reaction temperature. Since the boiling point of benzene is only 80°C, the reactor system has to be pressurized in order to keep benzene remain in the liquid state. With this technique, the reaction can be carried out at 90°C which is higher than the normal boiling point of benzene and any reaction temperature used by any researchers before.

In our first attempt, the volume of water used as solvent is kept at 50 ml, the volume of H<sub>2</sub>O<sub>2</sub> used is 1.0 ml and the volume of benzene used is 0.89 ml. Benzene was firstly injected into the reactor filled with water and catalyst. After 60 min of stirring the mixture (the waiting period), H<sub>2</sub>O<sub>2</sub> was injected into the reactor. The reaction time began from the time H<sub>2</sub>O<sub>2</sub> was injected into the reactor. The reaction was carried out for 120 min before stopping by placing the reactor into an ice-bath. In this experiment, the reaction was carried out at 70°C and 90°C. The results obtained are shown in Table 4.4 below.

**Table 4.4** The effect of temperature/volume with the ratio of H<sub>2</sub>O<sub>2</sub>:benzene (1:1).

Temp (°C)	Volume of water (ml)	Conversion of H <sub>2</sub> O <sub>2</sub> (%)
70	50	13.13
90	50	6.84
90	90	15.35

It is found that the obtained result was not as expected. In this case, increasing reaction temperature from 70°C to 90°C resulted in lower H<sub>2</sub>O<sub>2</sub> conversion. It is hypothesized that at higher reaction temperature, higher amount liquid of benzene vaporized into gaseous phase. Thus, lesser amount of benzene was available for the reaction in the aqueous phase. In order to test this hypothesis, the volume of water used as solvent was increased from 50 ml to 90 ml. This will decrease the free space

above the liquid surface. It should be emphasized here that at a temperature, a liquid has only one equilibrium pressure. Lesser free space means that lesser amount of liquid has to vaporize until the system pressure reaches the equilibrium pressure is lesser. Because of this reason, it was expected that after the volume of water was increased from 50 ml to 90 ml, higher amount of benzene will remain in liquid phase. The conversion of  $\text{H}_2\text{O}_2$  should, therefore, increase.

The results reported in Table 4.4 show that at  $90^\circ\text{C}$ , when the volume of water is increased from 50 ml to 90 ml, the conversion of  $\text{H}_2\text{O}_2$  really increases as expected.

This experiment reveals that the free space above the liquid surface play some role during the reaction by controlling the amount of benzene stay in liquid phase.

#### 4.2.3 The effect of ratio of benzene: $\text{H}_2\text{O}_2$

At a temperature there is only one saturated concentration of hydrocarbon in water. In our system, benzene exists in two phases. The first one is liquid benzene on the top layer of the water surface. The second one is the benzene already dissolved into the water phase. In order to verify which part of benzene really important for the reaction, experiments with different amount of benzene ( $\text{H}_2\text{O}_2$  was kept constant at 1.0 ml) were carried out. If the liquid benzene is really important for the reaction, the observed conversion of  $\text{H}_2\text{O}_2$  should increase with the increase in the benzene volume used. If the dissolved benzene is really important for the reaction, the observed conversion of  $\text{H}_2\text{O}_2$  should not increase with the increase in the benzene volume used. The experimental results obtained from using benzene per  $\text{H}_2\text{O}_2$  molar ratio 1:1, 5:1, and 10:1 are reported in Table 4.5 In all experiments, the volume of water used is 90 ml, the reaction temperature is  $70^\circ\text{C}$ , and the waiting period is 60 min.

**Table 4.5** The reaction at  $70^\circ\text{C}$ , the volume of water 90 ml, the ratio of benzene : $\text{H}_2\text{O}_2$  are 1:1, 5:1 and 10:1 respectively.

Ratio of Benzene: $\text{H}_2\text{O}_2$	Conversion of $\text{H}_2\text{O}_2$ (%)
1:1	18.68
5:1	19.28
10:1	19.99

From the results in Table 4.5 one can say that the conversion of  $\text{H}_2\text{O}_2$  is insignificantly affected by the increase amount of benzene. These result suggested that benzene molecules which play the important role in the hydroxylation reaction is the benzene molecules already dissolved into the water phase.

From this finding, it is expected that if the amount of benzene in the water phase can be increased, the conversion of  $\text{H}_2\text{O}_2$  will increase also. In the present work, the amount of benzene dissolved in the water phase can be increased by :

(a) Increase the volume of water used as solvent. The reason is the amount of benzene dissolved in the water phase equals to the product between the volume of water and the concentration of benzene. At a reaction temperature, there is only one equilibrium concentration of benzene in water regardless of the amount of water. Therefore increasing the volume of water used will also increase the amount of benzene dissolved in the water phase.

(b) Increase the waiting period. Here the "waiting period" means the time between the injection of benzene into the reactor and the injection of  $\text{H}_2\text{O}_2$  into the reactor. The solubility of benzene in water testing showed in Figure 4.5 reveals that at room temperature benzene takes a significant period, about 120 min, to dissolve into the aqueous phase until the aqueous phase becomes saturated with benzene. If we allow the liquid benzene to have time to dissolve into the aqueous phase, we can expect that for the same reaction period, the time from the injection of  $\text{H}_2\text{O}_2$  till the reaction is stopped, the conversion of  $\text{H}_2\text{O}_2$  will increase. The experimental results of this testing will be discussed later in Section 4.2.5.

(c) Increase the reaction temperature. It is knowed that the solubility of a non-polar molecule in water increase with water temperature. Raising reaction temperature will increase not only the solubility of benzene but also the reaction rate. Using this technique to achieve the increase in the conversion of  $\text{H}_2\text{O}_2$ , however, is not straight forward. This is because raising the reaction temperature not only increases the parameter positively affects the reaction (the solubility of benzene) but also increases the parameter negatively affected the reaction (the vaporization of



benzene). The experimental results obtained from increasing reaction temperature using different operating parameters (volume of water, volume of benzene) are reported and discussed in Section 4.2.4 below.

This section demonstrates what happens when the reaction temperature is raised beyond the boiling point of benzene at atmospheric pressure (80 °C). Firstly, the results obtained from 70°C and 90°C are compared in Table 4.6. In both experiments, the volume of water used is 90 ml. The waiting period is 60 minutes. The molar ratio of benzene to H<sub>2</sub>O<sub>2</sub> used is 1:1 (or 0.89 ml of benzene per 1.0 ml of H<sub>2</sub>O<sub>2</sub> solution).

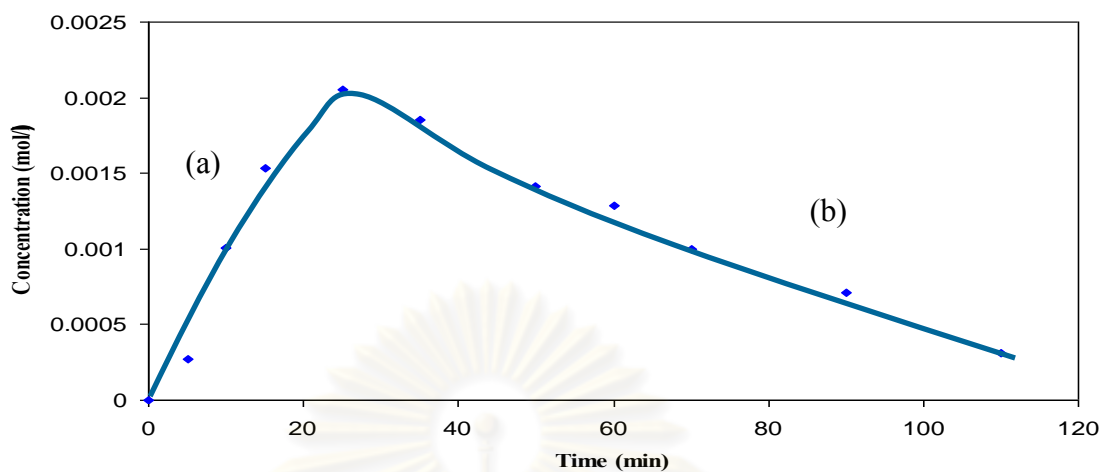
**Table 4.6** The effect of volume of water with the ratio of H<sub>2</sub>O<sub>2</sub>:benzene (1:1) at volume of water 90 ml.

Temp (°C)	Conversion of H <sub>2</sub> O <sub>2</sub> (%)
70	21.86
90	15.35

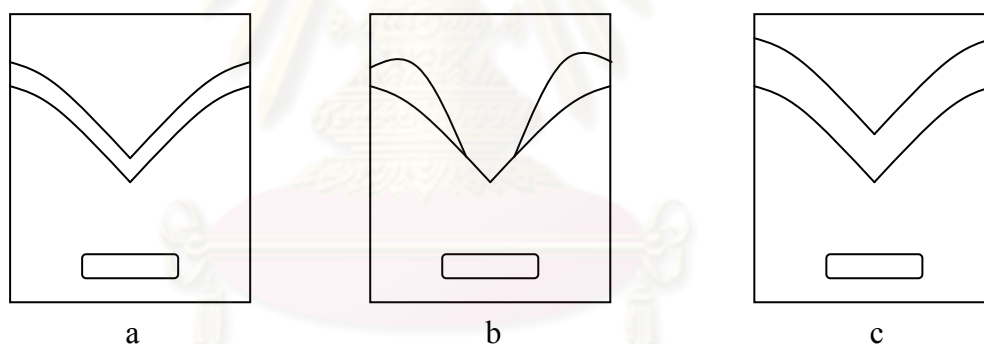
The results in Table 4.6 show that raising the reaction temperature from 70°C to 90°C, using the above mentioned parameters, results in a drop in the H<sub>2</sub>O<sub>2</sub> conversion. This means that the concentration of benzene in the aqueous phase, under the above mentioned parameters, at 90°C is lower than at 70°C. It is suspected that during the progress of the reaction, under vigorous stirring, the water layer is not completely covered by the liquid benzene. Part of the top surface of the water layer has a direct contact with the gaseous phase. The concentration of benzene in the aqueous phase, therefore, is not only depended on the existence of the liquid benzene, but also the partial pressure of benzene above the top surface of the water layer directly contact with the gaseous phase. On the other hand, the benzene molecules already dissolved into the aqueous phase can diffuse directly into the gaseous phase if the top surface of the water layer is not covered by the liquid benzene. In order to clarify this effect, another benzene solubility in water experiment is set up. The procedure of the experiment is the same as previously described in Section 4.2.4 but only 0.89 ml of benzene is used. The experimental result obtained is graphically demonstrated in Figure 4.6 below.



#### 4.2.4 The effect of the solubility of benzene in water which the benzene is not covered the surface of aqueous



**Figure 4.6** Concentration of benzene in water at room temperature added water 160 ml and benzene 0.89 ml a) initial during the testing b) after a period of time.



**Figure 4.7** The benzene layer was stirred a) initial during the testing b) after a period of time c) excess benzene.

During the experiment it is observed that initially during the testing in (a), the top layer of the water surface is completely or nearly completely covered by the liquid benzene. During this period, the benzene concentration measured from the aqueous sample increases with time. Since benzene can vaporize easily at room temperature, after a period of time in (b), there will be no enough liquid benzene to cover all the top surface of the water layer. At this moment the top surface of water layer begins to expose directly to the air above the surface. As the time goes by, larger and larger surface area of the top surface of the water layer becomes directly expose to air. This

allows the benzene molecules already dissolved in the aqueous phase to escape from the aqueous phase. The following result is a steady decrease of the benzene concentration in the aqueous phase as show in Figure 4.6 in (a) and (b).

One should not confuse the trend in Figure 4.6 with the trend in Figure 4.5. The trend in Figure 4.5 which shows that the concentration of benzene increases up to an equilibrium concentration comes from the experiment which the amount of benzene used is controlled to be able to totally cover the top surface of the water layer. Therefore, the benzene molecules already dissolved into the aqueous phase can not escape to the gaseous phase. The excess benzene as show in Figure 4.7 in (c).

#### 4.2.5 The period time of mixing between benzene and water

At room temperature, one can see from Figure 4.5 that the water takes about 120 min to become saturated with benzene. As we have explained earlier that the benzene molecules really involve in the reaction are the benzene molecules already dissolve into the water phase. For a fixed reaction time, e.g. 120 min in our case, one can expect if benzene and  $\text{H}_2\text{O}_2$  are mixed simultaneously the conversion of  $\text{H}_2\text{O}_2$  should not high because there is only a little amount of benzene in the water phase. If benzene is allowed to dissolve into the water phase until the water phase becomes saturate with benzene before the injection of  $\text{H}_2\text{O}_2$ , the conversion of  $\text{H}_2\text{O}_2$  should higher than the former case. In order to confirm this expectation, two experiments are performed. In the first experiment benzene are injected first following by  $\text{H}_2\text{O}_2$  immediately. In the second experiment  $\text{H}_2\text{O}_2$  are injected 60 min after the injection of benzene in order to allow the water phase becomes saturate with benzene first. The results from both experiments are tabulated in Table 4.7.

**Table 4.7** The reaction at temperature 70 °C, the volume of water 90 ml, ratio of benzene : $\text{H}_2\text{O}$  is 5:1.

Time (min)	Conversion of $\text{H}_2\text{O}_2$ (%)
0	17.21
60	19.28

It is observed that the conversion of  $\text{H}_2\text{O}_2$  increases significantly if the water phase is allowed to saturate with benzene first. The slight increase, only 2%, possibly due to at this reaction temperature,  $70^\circ\text{C}$ , benzene can dissolve into the water phase faster than at room temperature. However, it is proved that it will be better if one allows the water phase to become saturated with benzene before the introduction of  $\text{H}_2\text{O}_2$ . Therefore, in the followed experiments carried out at higher reaction temperatures, the injection of  $\text{H}_2\text{O}_2$  will be performed 60 min after the injection of benzene.

#### **4.2.6 The reaction at temperature higher than the boiling point of benzene at atmospheric pressure**

From the experimental results reported in Sections 4.2.1 to 4.2.6 we can expect that in order to achieve a higher  $\text{H}_2\text{O}_2$  conversion at a reaction temperature higher than the boiling point of benzene at atmospheric pressure, the following operating conditions should be practiced

(a) Possibly largest volume of water used as solvent should be used. Because the benzene molecules which control the progress of the reaction are the benzene molecules dissolved in the aqueous. Larger volume of water mean larger amount of dissolved benzene to react with  $\text{H}_2\text{O}_2$ . In our case, from the size of the reactor used in this study, the possibly largest volume of water can be used is about 120 ml. Therefore, the volume of water used in the experiments at elevated temperature from this point is 120 ml. The remaining volume is reserved for the volume of benzene and  $\text{H}_2\text{O}$  used, as well as, for the expansion of liquid at high temperature. The increase of volume of water also reduces the space above the liquid surface. This will also minimize the loss of benzene (from the liquid benzene) via vaporization into gaseous phase.

(b) Long enough waiting time should be allowed for benzene to dissolve into the aqueous phase. Since the experiments are carried out at reaction temperatures higher than room temperature (which the solubility testing is performed). 60 min hour waiting time is considered to be sufficient.

(c) A large amount of benzene is required to completely cover the top surface of the water phase overall the reaction period. This is to prevent the benzene molecules already dissolved in the aqueous phase escape into the gaseous phase. Therefore, 8.9 ml of benzene is used in the subsequent experiments at elevated temperature.

Please be reminded again that the boiling point of benzene and water at atmospheric pressure is 80°C and 100°C respectively. The result at 70°C is reported as base case. The results obtained from the reaction temperature 90, 100, and 110°C are summarized in Table 4.8.

**Table 4.8** The reaction at the volume of water 120 ml, the ratio of benzene 10:1, the waiting time for 60 min.

Temp (°C)	Conversion of H <sub>2</sub> O <sub>2</sub> (%)
70	17.21
90	27.52
100	31.99
110	34.47

It is showed experimentally that with proper operating procedures the conversion of H<sub>2</sub>O<sub>2</sub> to phenol can be enhanced significantly by raising the reaction temperature. Thus, the main objective of this work is finally achieved.

#### 4.2.7 Conclusions

This chapter has demonstrated the suitable operating procedures for the reaction to be carried out at temperature higher than the boiling point of benzene at atmospheric pressure. It has been demonstrated that the benzene molecules dissolved in the water phase are the molecules play the important role during the hydroxylation reaction. The liquid benzene float above the water layer does not directly involve in the reaction. The liquid benzene only supplies benzene molecules to the water phase. If the amount of liquid benzene used is high enough to totally cover the top surface of water layer, the conversion of H<sub>2</sub>O<sub>2</sub> will not depend on the volume of benzene used any more. In previous works which showed that the conversion of H<sub>2</sub>O<sub>2</sub> increased with the amount of benzene used may be because in those experiments the top surface

of water layer was not completely covered during the entire period of the reaction. Therefore, the progress of the reaction should be evaluated from the conversion of  $\text{H}_2\text{O}_2$  because all  $\text{H}_2\text{O}_2$  molecules have chance to access to the catalyst surface.

The higher amount of benzene dissolved in the water phase, the higher conversion achieved. In order to increase the amount of benzene dissolved in the water phase, the following procedures should be followed.

- (i) The largest volume of water used as solvent should be used. This will not only increase the amount of dissolve benzene but also reduce the space above the liquid surface.
- (ii) Benzene should allow to be dissolved into the water phase before  $\text{H}_2\text{O}_2$  is introduced.
- (iii) During the progress of the reaction, the top surface of the water layer should be completely covered with liquid benzene.
- (iv) The possible highest reaction temperature should be used.

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## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

The present work investigates the hydroxylation of benzene by hydrogen peroxide at elevated temperature over TS-1 catalyst having. The conclusions and recommendations for future study which can be drawn from the experimental results are summarized in Sections 5.1 and 5.2, respectively.

#### 5.1 Conclusions

1. Benzene which dissolved in the water phase is the part that directly involves in the reaction and control the progress of the reaction.
2. The following procedures should be followed to maximise the amount of benzene dissolved in the water phase.
  - (i) The largest volume of water used as solvent should be used.
  - (ii) During the progress of the reaction, the top surface of the water layer should be completely covered with liquid benzene.
  - (iii) The possible highest reaction temperature should be used.
3. The conversion of  $H_2O_2$  does not depend on the volume of benzene used.
4. The progress of the reaction should be evaluated from the conversion of  $H_2O_2$  because all  $H_2O_2$  molecules have chance to access to the catalyst surface.

#### 5.2 Recommendations

From the previous conclusions, the following recommendations for future studies are proposed.



1. Further study on catalyst stability and regeneration is still needed. In the experiments, the fresh catalysts are only used in the reaction.
2. Adding other metal on the catalyst TS-1 for increase the conversion.
3. In this study, examine the catalytic activity of the catalyst at elevated pressure. It is possibly study at vacuum pressure.
4. Experiment in a bigger reactor should be studied in order to study the possibility to increase the productivity.



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**APPENDICES**

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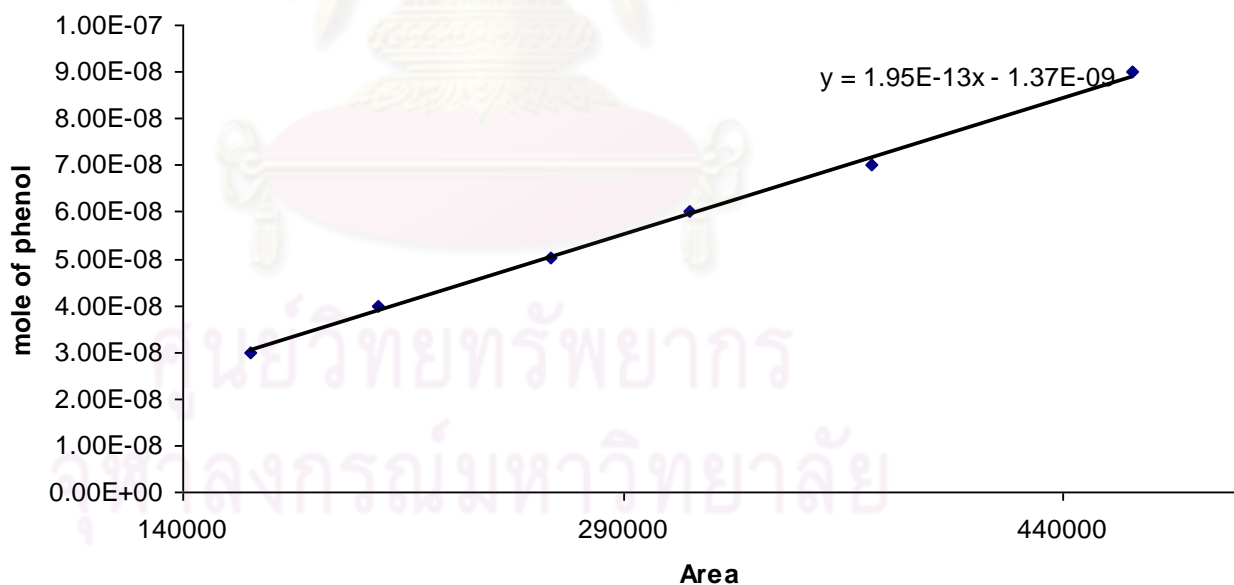
## APPENDIX A

### CALIBRATION CURVES

This appendix shows the calibration curves for calculation of products in the hydroxylation of benzene reaction. The only product observed is phenol. The reactant is benzene.

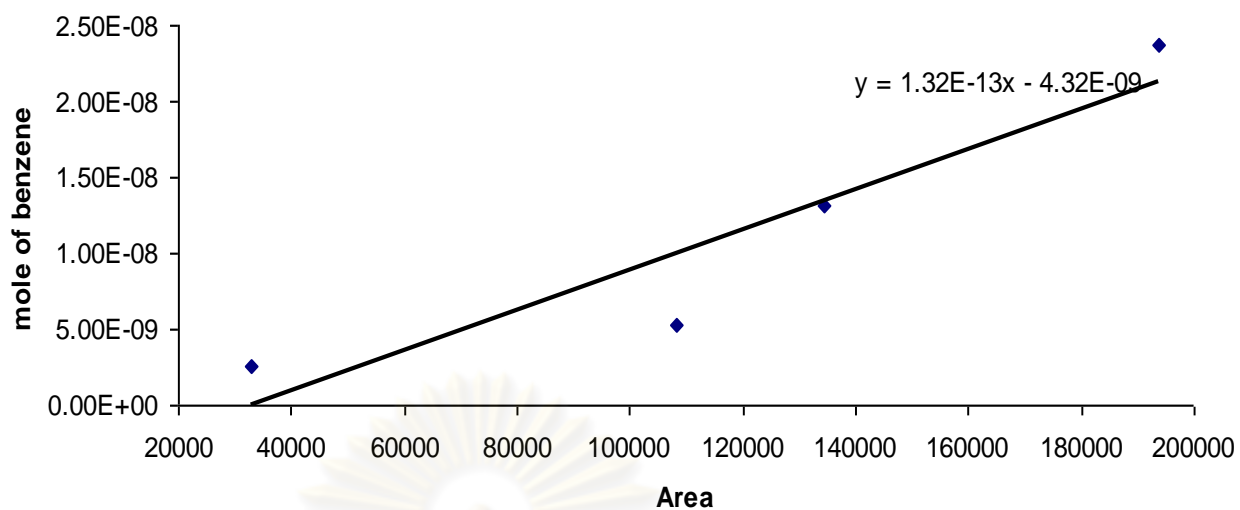
The flame ionization detector, gas chromatography Shimadzu model 9A was used to analyze the concentration of phenol and benzene by using GP 10% SP-2100 column.

Mole of phenol and benzene in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of phenol, benzene are illustrated in the following figures.

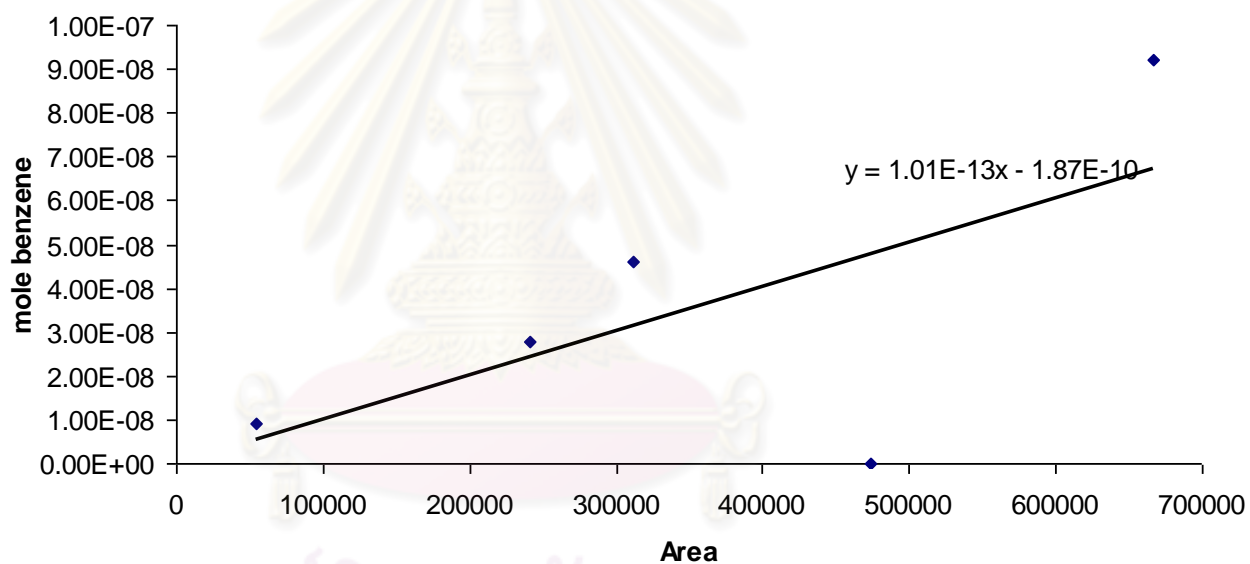


**Figure A1** The calibration curve of phenol.





**Figure A2** The calibration curve of benzene at low concentration.



**Figure A3** The calibration curve of benzene at high concentration.

## APPENDIX B

### CALCULATION FOR PERCENTAGE OF CONVERSION OF H<sub>2</sub>O<sub>2</sub> TO PHENOL

$$\text{Amount of sample injected} = 5\mu\text{l}$$

$$\text{Area of phenol peak} = 343718 \quad \text{A.U.}$$

$$\text{From Calibration curve; mole of phenol} = 1.95 \times 10^{-13} X - 1.37 \times 10^{-9}$$

Substitute area (X) into equation we obtain

$$\begin{aligned} \text{mol of phenol} &= 1.95 \times 10^{-13} (343718) - 1.37 \times 10^{-9} \\ &= 6.5655 \times 10^{-8} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Concentration} &= \frac{\text{The area (mol) / amount of sample inject (5}\mu\text{l)}}{5\mu\text{l}} \\ &= \frac{6.5655 \times 10^{-8} \text{ mol}}{5\mu\text{l}} \\ &= 0.01313 \quad \text{mol/l} \end{aligned}$$

volume of; H<sub>2</sub>O 50 ml, EtOH 50 ml, Benzene 0.89 ml, H<sub>2</sub>O<sub>2</sub> 1 ml

$$\begin{aligned} \text{Total volume of solution} &= \text{H}_2\text{O} + \text{EtOH} + \text{Benzene} + \text{H}_2\text{O}_2 \\ &= \text{H}_2\text{O}_2 + \text{EtOH (ml)} ; \text{ Because the reactant reacted} \end{aligned}$$

$$\begin{aligned} \text{Amount of phenol product} &= \text{Total vol} \times \text{concentration} \\ &= 100 \text{ ml} \times 0.01313 \text{ mol/l} \\ &= 0.001313 \text{ mol} \end{aligned}$$

Mole of H<sub>2</sub>O<sub>2</sub> feed in the system 0.01 mol

$$\begin{aligned} \% \text{ Conversion of H}_2\text{O}_2 \text{ to organic product(s)} &= \frac{\text{Mol of Phenol}}{\text{Mol of H}_2\text{O}_2 \text{ feed}} \times 100 \\ &= \frac{0.001313}{0.01} \times 100 \end{aligned}$$

$$\% \text{ Conversion of H}_2\text{O}_2 \text{ to organic product(s)} = 13.13\%$$

## APPENDIX C

### CALCULATION OF METAL QUANTITY

#### Example of the calculation of the metal quantity in catalyst (TS-1)

The XRF results were reported in the amount of metal oxide as shown in Table C1 and C2.

**Table C1** Data of TS-1 from XRF technique batch1.

Metal oxide	Concentration (%wt)
Al <sub>2</sub> O <sub>3</sub>	0.18
SiO <sub>2</sub>	95.51
P <sub>2</sub> O <sub>5</sub>	0.751
SO <sub>3</sub>	0.489
CaO	0.159
TiO <sub>2</sub>	2.85
Fe <sub>2</sub> O <sub>3</sub>	0.0044
ZrO <sub>2</sub>	0.0156

**Table C2** Data of TS-1 from XRF technique batch2.

Metal oxide	Concentration (%wt)
Al <sub>2</sub> O <sub>3</sub>	0.21
SiO <sub>2</sub>	95.45
P <sub>2</sub> O <sub>5</sub>	0.848
SO <sub>3</sub>	0.25
CaO	0.153
TiO <sub>2</sub>	2.12
ZrO <sub>2</sub>	0.0181

**Table C3** Molecular weight of the metal oxides

Metal oxide	MW
Al <sub>2</sub> O <sub>3</sub>	101.96
SiO <sub>2</sub>	60.08
P <sub>2</sub> O <sub>5</sub>	141.97
SO <sub>3</sub>	80.06
CaO	56.07
TiO <sub>2</sub>	79.86
Fe <sub>2</sub> O <sub>3</sub>	159.69
ZrO <sub>2</sub>	123.23

Mole of metal oxide, mole of cation and mole% of cation are calculated from follow equation.

### 1. Mole of metal oxides

$$\text{Mole of Al}_2\text{O}_3 = \frac{\text{weight of Al}_2\text{O}_3}{\text{molecular weight of Al}_2\text{O}_3}$$

$$\text{Mole of Al}_2\text{O}_3 = \frac{0.18}{101.9613} = 0.001765 \text{ mole}$$

### 2. Mole of cation (e.g. Aluminium: Al)

$$\text{Mole of cation} = \text{number of cation atom} \times \text{mole of metal oxide}$$

$$\begin{aligned} \text{Mole of Al} &= 2 \times 0.001765 \\ &= 0.003530 \text{ mole} \end{aligned}$$

### 3. Mole percent of cation (e.g. Aluminium: Al)

$$\text{Mole\% of Al} = \frac{\text{mole of Al}}{\text{total mole of cations}}$$

$$\text{Mole\% of Al} = \frac{0.003530}{1.6485} = 0.00214 \text{ mole\%}$$

**Table C4** Calculated composition of TS-1 batch1.

Compound	%wt	MW	mole of metal oxide	mole of cation	mole % of cation	Mol%
Al <sub>2</sub> O <sub>3</sub>	0.18	101.961	0.001765	0.003530	0.00214	0.21
SiO <sub>2</sub>	95.51	60.0843	1.589599	1.589599	0.96425	96.42
P <sub>2</sub> O <sub>5</sub>	0.751	141.974	0.005289	0.010579	0.00641	0.64
SO <sub>3</sub>	0.489	80.0632	0.006107	0.006107	0.00370	0.37
CaO	0.159	56.078	0.002835	0.002835	0.00171	0.17
TiO <sub>2</sub>	2.85	79.8658	0.035684	0.035684	0.02164	2.16
Fe <sub>2</sub> O <sub>3</sub>	0.0044	159.692	2.7553E-05	5.51061E-05	3.34276E-05	0.003
ZrO <sub>2</sub>	0.0156	123.224	0.000126	0.000126	7.67954E-05	0.007

**Table C5** Calculated composition of TS-1 batch2.

Compound	%wt	MW	mole of metal oxide	mole of cation	mole % of cation	Mol%
Al <sub>2</sub> O <sub>3</sub>	0.21	101.961	0.002059	0.004119	0.00251	0.25
SiO <sub>2</sub>	95.45	60.0843	1.588601	1.588601	0.97031	97.03
P <sub>2</sub> O <sub>5</sub>	0.848	141.974	0.005972	0.011945	0.00729	0.73
SO <sub>3</sub>	0.25	80.0632	0.003122	0.003122	0.00190	0.19
CaO	0.153	56.078	0.0027283	0.002728	0.00166	0.16
TiO <sub>2</sub>	2.12	79.8658	0.0265445	0.026544	0.01621	1.62
ZrO <sub>2</sub>	0.0181	123.224	0.0001468	0.000146	8.97179E-05	0.008

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## APPENDIX D

### DATA FROM TEMPERATURE PROGRAMED DESORTION OF AMMONIA (NH<sub>3</sub>-TPD)

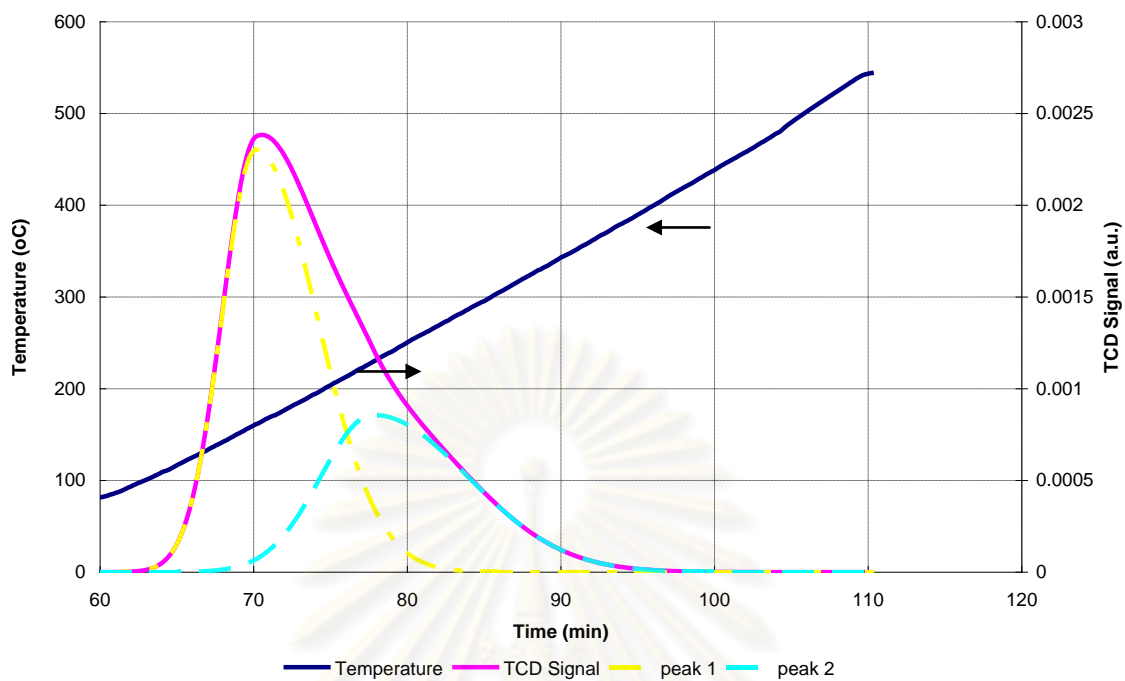
Temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) is used to determine the acid properties of catalysts. NH<sub>3</sub>-TPD is carried out using a flow apparatus. The catalyst sample (0.1 g) is treated at 550 °C in helium flow for 1 h and then saturated with 15 %NH<sub>3</sub>/He mixture after cooling to 80 °C. After purging with helium at 80 °C for 1 h to remove weakly physisorbed NH<sub>3</sub>, the sample is heated to 550 °C at the rate of 10 °C/min in a helium flow of 50 ml/min. The amount of acid sites on the catalyst surface is calculated from the desorption amount of NH<sub>3</sub>. It is determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer.

The deconvolution of NH<sub>3</sub>-TPD peak is carried out with the “fityk” curve fitting programme. The peaks are assumed to be Gaussian with showiness shape (using parameter „SplitGaussian“ in the programme).

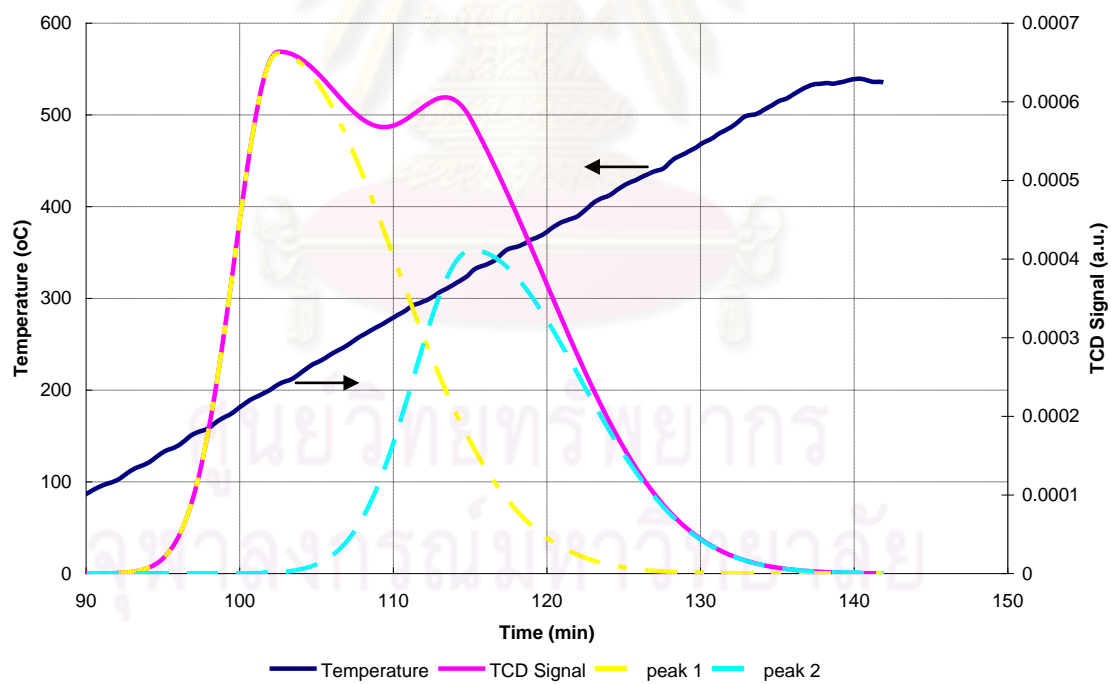
**Table D1** The strength and amount of the acid site of the catalysts.

Catalysts	Weak acid strength		Strong acid strength		Total acid site (μmol/g)
	Temp	Site	Temp	Site	
	(°C)	(μmol/g)	(°C)	(μmol/g)	
TS-1 batch1	160	70.27	230	39.69	109.96
TS-1 batch2	209	32.77	350	20.41	53.18





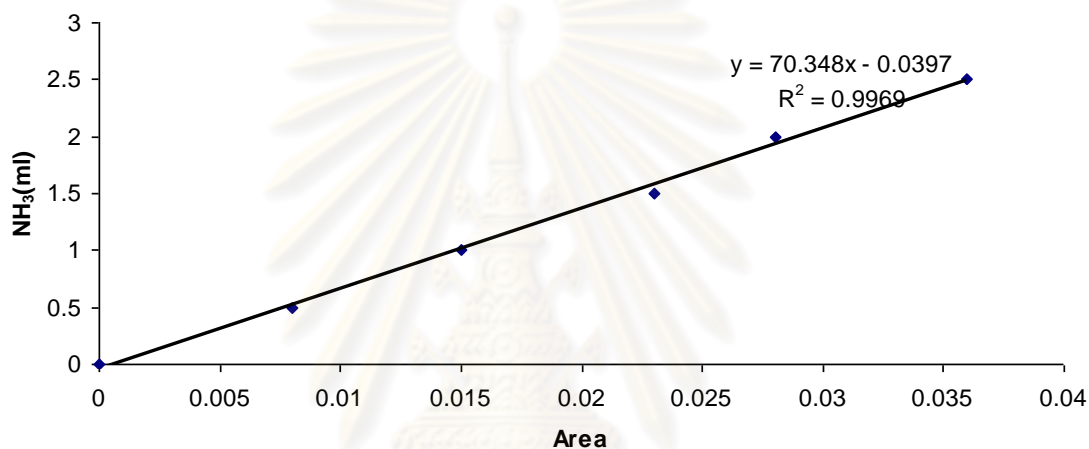
**Figure D1** NH<sub>3</sub>-TPD of TS-1 catalyst batch1.



**Figure D2** NH<sub>3</sub>-TPD of TS-1 catalyst batch2.

**Table D2** Data from fityk program for calculation of acid site

Sample	Area	
	Weak acid strength	Medium acid strength
TS-1 batch1	0.0178	0.0103
TS-1 batch2	0.0086	0.00557

**Figure D3** The calibration curve of ammonia.

From example, TS-1 batch1 sample, total acid site is calculated from the following step.

1. Calculation of total peak to peak volume

From Figure G1 below, the volume of NH<sub>3</sub> calculates from equation  $y=70.348x - 0.0397$ .

$$\text{The volume of NH}_3 = 70.348 \times \text{area} - 0.0397$$

$$\text{The volume of NH}_3 = 70.348 \times \text{area} - 0.0397$$

$$(\text{Weak acid strength}) = 70.348 \times 0.0178 - 0.0397$$

$$= 1.2124 \text{ ml}$$

$$\begin{aligned}
 \text{The volume of NH}_3 &= 70.348 \times \text{area} - 0.0397 \\
 \text{(Medium acid strength)} &= 70.348 \times 0.0103 - 0.0397 \\
 &= 0.6848 \text{ ml}
 \end{aligned}$$

2. Calculation for adsorbed volume of 15% NH<sub>3</sub>

$$\begin{aligned}
 \text{Adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume} \\
 \text{(Weak acid strength)} &= 0.15 \times 1.2124 \text{ ml} \\
 &= 0.1818 \text{ ml}
 \end{aligned}$$

$$\begin{aligned}
 \text{Adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume} \\
 \text{(Medium acid strength)} &= 0.15 \times 0.6848 \text{ ml} \\
 &= 0.1027 \text{ ml}
 \end{aligned}$$

3. The acid sites are calculated from the following equation

$$\text{The acid sites} = \frac{\text{Adsorbed volume (ml)} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}} \times 298 \text{ K} \times \text{weight of catalyst (g)}}$$

For TS-1 sample, 0.1058 g of this sample was measured, therefore

$$\begin{aligned}
 \text{The acid sites (Weak acid strength)} &= \frac{0.0303 \times 10^{-3} \text{ ml} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}} \times 298 \text{ K} \times 0.1058 \text{ g}} \\
 &= 70.27 \mu\text{mol/g}
 \end{aligned}$$

$$\begin{aligned} \text{The acid sites (Medium acid strength)} &= \frac{0.0176 \times 10^{-3} \text{ ml} \times 101.325 \text{ Pa}}{8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}} \times 298 \text{ K} \times 0.1058 \text{ g}} \\ &= 39.69 \mu\text{mol/g} \end{aligned}$$

$$\begin{aligned} \text{The total acid sites} &= 70.27 + 39.69 \\ &= 109.96 \mu\text{mol/g} \end{aligned}$$



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**APPENDIX E****MATERIAL SAFETY DATA SHEET****Benzene****General**

Synonyms: (6) annulene, benzin, benzol, benzole, benzolene, phene, phenyl hydride, pyrobenzole, coal naphtha

Molecular formula: C<sub>6</sub>H<sub>6</sub>

**Physical data**

Appearance	: colourless liquid
Melting point	: 5.5 °C
Boiling point	: 80 °C
Specific gravity	: 0.87
Vapour pressure	: 74.6 mm Hg at 20 °C
Flash point	: -11 °C
Explosion limits	: 1.3 % - 8 %
Autoignition temperature	: 561 °C

**Stability**

Stable. Substances to be avoided include strong oxidizing agents, sulfuric acid, nitric acid, halogens. Highly flammable.

**Toxicology**

This material is a known carcinogen. The risks of using it in the laboratory must be fully assessed before work begins. TLV 10 ppm. Short-term exposure may cause a variety of effects, including nausea, vomiting, dizziness, narcosis, reduction in blood pressure, CNS depression. Skin contact may lead to dermatitis. Long-term exposure may lead to irreversible effects. Severe eye irritant. Skin and respiratory irritant.

### Personal protection

Safety glasses, gloves, good ventilation. Thought should be given to using an alternative, safer product.

## Phenol

### General

Synonyms: benzenol, carbolic acid, hydroxybenzene, monohydroxybenzene, monophenol, oxybenzene, phenic acid, phenylic acid, phenyl alcohol, phenyl hydrate, phenyl hydroxide, phenylic alcohol

Molecular formula:  $C_6H_5OH$

### Physical data

Appearance	: colourless crystals with a characteristic odour
Melting point	: 40 - 42 °C
Boiling point	: 182 °C
Specific gravity	: 1.07
Vapour pressure	: 0.35 mm Hg at 20 °C
Flash point	: 79 °C
Explosion limits	: 1.5 % - 8.6 %
Autoignition temperature	: 715 °C



**Stability**

Stable. Substances to be avoided include strong oxidizing agents, strong bases, strong acids, alkalies, calcium hypochlorite. Flammable. May discolour in light.

**Toxicology**

This material is a systemic poison and constitutes a serious health hazard. The risks of using it in the laboratory must be fully assessed before work begins. Vesicant. Typical MEL 2 ppm; typical OEL 1 ppm. Acute poisoning by ingestion, inhalation or skin contact may lead to death. Phenol is readily absorbed through the skin. Highly toxic by inhalation. Corrosive - causes burns. Severe irritant.

**Personal protection**

Safety glasses, gloves, good ventilation.

**Hydrogen peroxide****General**

Synonyms : Peroxide, 100 volume peroxide, Hydrogen dioxide solution, Hydrogen peroxide, 30%, unstabilized, Hydrogen Peroxide, 30%

Note : Typical concentrations lie in the range 3%-35%. Solutions of much higher concentration (e.g. 60% and above) present significantly increased risks, and should not be used unless such strength is absolutely essential.

Molecular formula :  $H_2O_2$

**Physical data**

Appearance : colourless liquid

Melting point :  $-28\text{ }^{\circ}\text{C}$

Boiling point	: 114 °C
Specific gravity	: typically near 1.19
Vapour pressure	: 23.3 at 30 °C

### **Stability**

Unstable - readily decomposes to water and oxygen. Light sensitive. May develop pressure in the bottle - take care when opening. Forms potentially explosive compounds with ketones, ethers, alcohols, hydrazine, glycerine, aniline, sodium borate, urea, sodium carbonate, triethylamine, sodium fluoride, sodium pyrophosphate and carboxylic acid anhydrides. Materials to avoid include combustibles, strong reducing agents, most common metals, organic materials, metallic salts, alkali, porous materials, especially wood, asbestos, soil, rust, strong oxidizing agents.

### **Toxicology**

Toxic. Corrosive - can cause serious burns. Eye contact can cause serious injury, possibly blindness. Harmful by inhalation, ingestion and skin contact. Typical OEL 1 ppm.

### **Hazards Identification**

Strong oxidizer. Contact with other material may cause a fire. Harmful if inhaled. Corrosive. Causes eye and skin burns. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns.

### **Potential Health Effects**

Inhalation : Vapors are corrosive and irritating to the respiratory tract. Inhalation of mist may burn the mucous membrane of the nose and throat. In severe cases, exposures may result in pulmonary edema and death.

Ingestion : Corrosive and irritating to the mouth, throat, and abdomen. Large doses may cause symptoms of abdominal pain, vomiting, and diarrhea as well as blistering or tissue destruction. Stomach distention (due to rapid liberation of oxygen),

and risk of stomach perforation, convulsions, pulmonary edema, coma, possible cerebral edema (fluid on the brain), and death are possible.

Skin Contact : Corrosive. Symptoms of redness, pain, and severe burn can occur.

Eye Contact : Vapors are very corrosive and irritating to the eyes. Symptoms include pain, redness and blurred vision. Splashes can cause permanent tissue destruction.

### Personal protection

Safety glasses are essential; acid-resistant gloves are suggested. Suitable ventilation.

## Titanium (IV) n-butoxide

### General

Synonyms : Tetra-n-butyl titanate, TNBT, Titanium (IV) n-butoxide (TYZOR TNBT), Tetra-n-butyl orthotitanate for synthesis, titanium tetrabutanolate, Titanium(IV)n-butoxide (TYZOR TBT), Butyl Titanate, Titaniumbutoxide colorlessliq, Titanium n-butoxide, Titanium (IV) n-butoxide, 99+%Tetra-n-utoxytitanium (IV) ~Tetra-n-butylorthotitanate, Titanium tetrabutoxide, Triethoxy Methane, Titanium tetrabutylate, Orthotitanic acid tetrabutyl ester

Molecular formula :  $C_{16}H_{36}O_4Ti$

Chemical formula :  $Ti[O(CH_2)_3CH_3]_4$

### Physical data

Boiling point : 310-314 °C

Flash point : 78 °C

Density ( $g\ cm^{-3}$ ) : 1.486

## Toxicology

Irritating to eyes, respiratory system and skin.

## Personal protection

Avoid contact with skin and eyes.

## Tetrapropylammonium bromide

### General

Synonyms : 1-Propanaminium, N, N, N-tripropyl, bromide or Tetra-n-propylammonium bromide or TPBr or TPABr

Molecular formula :  $C_{12}H_{28}N.Br$

Chemical formula :  $(C_3H_7)_4NBr$

### Physical data

Solubility in Water	: 60% (20 °C)
pH	: 5 - 10 for solution
Melting Point	: 275 - 278 °C (decomposes)

### Stability and reactivity

Stable at ambient temperatures. Do not expose to high temperatures. Oxidizers should be tested for compatibility before use.

### Hazardous decomposition

In fire conditions : Carbon monoxide, Hydrobromic acid and Nitrogen oxides. If heated to decomposition, tripropylamine may be released.

### Potential health effect

Inhalation	: May cause irritation.
Eye Contact	: May cause irritation.
Skin Contact	: May cause irritation.
Ingestion	: No toxicity or other health effects information available.
Chronic	: May cause irritation. No additional information available.

### **First aid measure**

Inhalation : Remove to fresh air. If breathing has stopped, give artificial respiration. Consult a physician.

Eye Contact : Immediately flush with water until no evidence of chemical remains (at least 15-20 minutes) and consult a physician.

Skin Contact : Immediately flush with water with sufficient volume until there is no evidence of the chemical on the affected area.

Ingestion : If person is conscious and able to swallow, have them drink a large volume of water and milk and induce vomiting. Contact a physician.

### **Fire fighting measures**

Wear S.C.B.A. May use water spray, carbon dioxide, dry chemical or chemical foam to fight fire.

### **Hazardous product combustion**

May emit Nitrogen oxides, Hydrobromic acid and Carbon monoxide.

## Sodium chloride

### General

Synonyms : extra fine 200 salt, extra fine 325 salt, H.G. blending, salt, sea salt, table salt, common salt, dendritis, rock salt, top flake, white crystal, saline, halite, purex, USP sodium chloride

Molecular formula : NaCl

### Physical data

Appearance	: colorless crystals or white powder
Melting point	: 804 °C
Boiling point	: 1,413 °C
Vapor pressure	: 1 mm Hg at 865°C
Specific gravity (g cm <sup>-3</sup> )	: 2.16
Solubility in water	: 35.7 g/100g at °C

### Stability

Stable. Incompatible with strong oxidizing agents.

### Toxicology

May cause skin, eye or respiratory irritation.

### Personal protection

Not believed to present a significant hazard to health.



## Sodium hydroxide

### General

Synonyms : caustic soda, soda lye, lye, white caustic, aetznatron, ascarite, Collo-Grillrein, Collo-Tapetta, sodium hydrate, fotofoil etchant, NAOH, STCC 4935235, sodium hydroxide pellets, Lewis red devil lye  
Molecular formula: NaOH

### Physical data

Appearance : colorless white solid (often sold as pellets)  
Melting point : 318 °C  
Boiling point : 1,390 °C  
Vapor pressure : 1 mm Hg at 739 °C  
Specific gravity (g cm<sup>-3</sup>) : 2.12  
Water solubility : high (Note: dissolution in water is highly exothermic)

### Stability

Stable. Incompatible with a wide variety of materials including many metals, ammonium compounds, cyanides, acids, nitro compounds, phenols, combustible organics. Hygroscopic. Heat of solution is very high and may lead to a dangerously hot solution if small amounts of water are used. Absorbs carbon dioxide from the air.

### Toxicology

Very corrosive. Causes severe burns. May cause serious permanent eye damage. Very harmful by ingestion. Harmful by skin contact or by inhalation of dust.

### Personal protection

Safety glasses, adequate ventilation, Neoprene or PVC gloves.

## Sodium silicate

### General

Synonyms : silicic acid sodium salt, water glass, sodium water glass, soluble glass, silicate of soda, silicon sodium oxide, sodium orthosilicate, sodium sesquisilicate, sodium silicate glass, agrosil S, barasil S, britesil, carsil 2000, chemfin 60, chemsilicate, crystal 79, crystal 96, ineos 140, inosil Na 4237, portil A, pyramid 8, vitrosol N40, ZhS 3, very large number of further trade names

Molecular formula :  $\text{Na}_4\text{O}_4\text{Si}$

### Physical data

Appearance : colourless liquid as usually supplied (solution)

Boiling point : ca. 102 °C for a 40% aqueous solution

Specific gravity : approximately 1.3 for a ca. 40% solution

### Stability

Stable. Incompatible with acids, most metals, many organic materials.

### Toxicology

Harmful by ingestion. Corrosive - may cause burns through skin or eye contact. Very destructive of mucous membranes.

### Personal protection

Safety glasses, gloves.

## Aluminium (III) nitrate nonahydrate

### General

Synonyms : aluminum nitrate 9-hydrate, aluminium nitrate nonahydrate, aluminum nitrate nonahydrate, nitric acid aluminium salt

Molecular formula :  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

### Physical data

Appearance : white crystalline powder

Melting point : 73 °C

Water solubility : appreciable

### Stability

Strong oxidizer - contact with combustible material may lead to fire.  
Incompatible with water, most common metals, organics. Moisture-sensitive.

### Toxicology

May be harmful if swallowed. Skin, eye and respiratory irritant. May cause serious eye irritation.

### Personal protection

Safety glasses, adequate ventilation.

## Ethanol

### General

Synonyms : ethanol, grain alcohol, fermentation alcohol, alcohol, methylcarbinol, absolute alcohol, absolute ethanol, anhydrous alcohol, alcohol dehydrated, algrain, anhydrol, cologne spirit, ethyl hydrate, ethyl hydroxide, jaysol, jaysol s, molasses alcohol, potato alcohol, sekundasprit, spirits of wine.

Molecular formula :  $C_2H_5OH$

### Physical data

Appearance	: colourless liquid
Melting point	: -144 °C
Boiling point	: 78 °C
Specific gravity	: 0.789
Vapour pressure	: 1.59
Flash point	: 14 °C (closed cup)
Explosion limits	: 3.3% - 24.5%
Autoignition temperature	: 363 °C
Water solubility	: miscible in all proportions

### Stability

Stable. Substances to be avoided include strong oxidizing agents, peroxides, acids, acid chlorides, acid anhydrides, alkali metals, ammonia, moisture. Forms explosive mixtures with air. Hygroscopic.

### Toxicology

Causes skin and eye irritation. Ingestion can cause nausea, vomiting and inebriation; chronic use can cause serious liver damage. Note that "absolute" alcohol, which is close to 100% ethanol, may nevertheless contain traces of 2-propanol,

together with methanol or benzene. The latter two are very toxic, while "denatured" alcohol has substances added to it which make it unpleasant and possibly hazardous to consume.

### **Personal protection**

Safety glasses. Suitable ventilation.



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## APPENDIX F

### LIST OF PUBLICATION

Sarawadee Mitpapan and Tharathon Mongkhonsi, “Hydroxylation of benzene to phenol at elevated temperature”, The 17<sup>th</sup> Regional Symposium on Chemical Engineering (RSCE 2010), November, 2010.



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## VITA



Miss Sarawadee Mitpapan was born on April 30<sup>th</sup>, 1986 in Chonburi, Thailand. She finished high school from Saint Paul Convent School in April, 2005 and received the bachelor's degree of Chemical Engineering from Faculty of Engineer, Burapha University in May, 2009. She continued her master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in June, 2009.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย