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บนตัวเร่งปฏิกิริยา AI-TS-1

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EFFECT OF IONS IN ELECTROLYTE SOLUTION ON THE OXIDATION
REACTION OF TOLUENE TO BENZALDEHYDE OVER AI-TS-1 CATALYST

Miss Sunantha Kaenthong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

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Thesis Title EFFECT OF IONS IN ELECTROLYTE SOLUTION
 ON THE OXIDATION REACTION OF TOLUENE TO
 BENZALDEHYDE OVER Al-TS-1 CATALYST

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สุนันทา แก่นทอง : ผลของไอออนในสารละลายอิเล็กโทรไลต์ต่อปฏิกิริยาการออกซิไดซ์
โทลูอินไปเป็นเบนซัลดีไฮด์บนตัวเร่งปฏิกิริยา Al-TS-1. (EFFECT OF IONS IN
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วิทยานิพนธ์หลัก: รศ.ดร.ชราธร มงคลศรี, 80 หน้า.

งานวิจัยนี้ได้ทำการศึกษาผลของไอออนในสารละลายอิเล็กโทรไลต์ต่อปฏิกิริยาการ
ออกซิเดชันระหว่างโทลูอินและไฮโดรเจนเปอร์ออกไซด์โดยใช้ตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไล่ต์-1
ที่ได้รับการปรับปรุงด้วยโลหะอะลูมิเนียมเป็นตัวเร่งปฏิกิริยา ตัวเร่งปฏิกิริยาเตรียมโดยวิธีไฮโดร
เทอร์มอลและทำการวิเคราะห์คุณลักษณะด้วย XRD, FT-IR, XRF และ BET ปฏิกิริยาคำเนินการ
ที่อุณหภูมิ 110 และ 120 องศาเซลเซียส ในเครื่องปฏิกรณ์แบบอัดความดัน กรดไฮโดรคลอริก กรด
ไนตริก แอมโมเนียมคลอไรด์ แอมโมเนียมไนเตรต โซเดียมคลอไรด์ หรือโซเดียมไนเตรต ถูกเติม
ลงไปในพื้นที่ความเข้มข้นของสารละลายเท่ากับ 0.1 โมลาร์ ผลที่ได้จากการศึกษาความว่องไว
ในการทำปฏิกิริยาพบว่าการเติมสารละลายอิเล็กโทรไลต์ไม่เพียงแต่เป็นการเพิ่มความเข้มข้นของ
โทลูอินในพื้นที่แต่ยังคงเป็นการเพิ่มการเกิดเบนซัลดีไฮด์ที่เป็นผลิตภัณฑ์หลักในปฏิกิริยา ค่าร้อยละ
การเปลี่ยนแปลงของไฮโดรเจนเปอร์ออกไซด์ในปฏิกิริยาที่มีไอออนในพื้นที่จะให้ค่าสูงกว่า
ปฏิกิริยาในพื้นที่ที่ไม่มีไอออน นอกจากนี้ค่าการเปลี่ยนแปลงของไฮโดรเจนเปอร์ออกไซด์จะ
ยังคงมีค่าเพิ่มขึ้นเมื่ออุณหภูมิในการทำปฏิกิริยาเพิ่มสูงขึ้น

ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อนิสิต.....
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SUNANTHA KAENTHONG: EFFECT OF IONS IN ELECTROLYTE
SOLUTION ON THE OXIDATION REACTION OF TOLUENE TO
BENZALDEHYDE OVER Al-TS-1 CATALYST. ADVISOR: ASSOC.
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This research studies effect of ions in electrolyte solution on the oxidation reaction between toluene and hydrogen peroxide to benzaldehyde over titanium silicalite-1 catalyst modified with metallic aluminum (Al-TS-1). The catalyst is prepared by hydrothermal method and characterized by XRD, FT-IR, XRF and BET. The reaction is carried out at reaction temperatures 110°C and 120°C in a pressurized autoclave reactor. Hydrochloric acid, nitric acid, ammonium chloride, ammonium nitrate, sodium chloride or sodium nitrate is added into the aqueous phase which the concentration of solution is 0.1 M. The catalytic activity testing found that the addition of electrolyte solution not only increases the concentration of toluene in the aqueous phase but also increases the formation of benzaldehyde as main product in the reaction. The conversion of hydrogen peroxide in the reaction which has the presence of ions in the aqueous phase is higher than the reaction in the neutral aqueous phase. In addition, the conversion of hydrogen peroxide is also increases with the increasing of reaction temperature.

Department :.....~~Chemical Engineering~~..... Student's Signature

Field of Study :..~~Chemical Engineering~~..... Advisor's Signature

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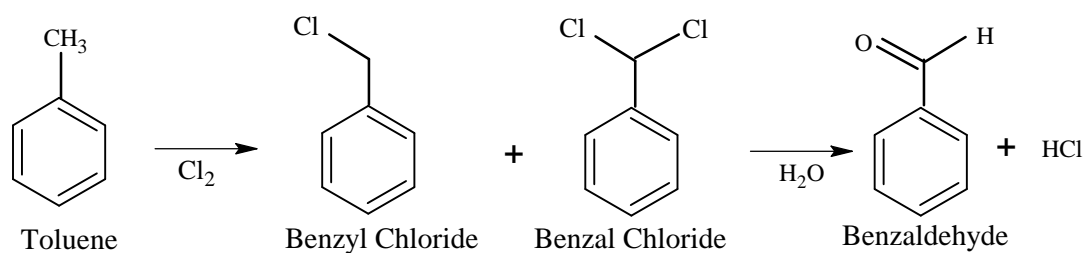
CHAPTER I

INTRODUCTION

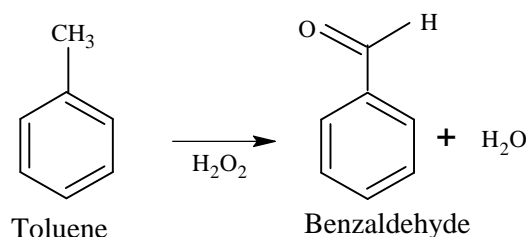
1.1 Rational

Benzaldehyde (C_6H_5CHO) is an organic compound consisting of a benzene ring which a hydrogen atom is substituted with formyl group (COH). Benzaldehyde is used widely in industrial. The characteristic chemical property of benzaldehyde is colorless liquid with odor of oil of bitter almond. In deed, benzaldehyde is the primary compounds of almonds oil. Besides, it can be extracted from natural sources such as apricot, cherry and peach seeds and favor to use in commercial food flavorant, dyestuff, perfumery, and pharmaceutical industries.

In the conventional processes, benzaldehyde is produced by processes comprise of the liquid phase oxidation of toluene, the vapor phase oxidation of toluene and chlorination of toluene. At present, the chlorination of toluene is the major for the production of benzaldehyde. In this process, chlorine is reacted with toluene in presence of light to give benzalchloride that benzylchloride as intermediates. Subsequently, benzylchloride is hydrolysed to give benzaldehyde. The disadvantages of this route are the process has two steps, need to use light to initiate the reaction, and produce by products. Another processes in are the liquid phase and vapor phase oxidation route that begin from reacting toluene with oxygen in the presence of a homogeneous catalyst. The disadvantages of this route are the reaction only occurs in the presence of homogeneous catalyst and use high energy in separation. The vapor phase oxidation also gives benzoic acid, carbon dioxide, anthraquinone, carbon monoxide and water as byproducts. Both benzaldehyde production routes are shown schematically in Figure 1.1.



(a) The chlorination of toluene route.



(b) The oxidation of toluene route.

Figure 1.1 The synthesis route of benzaldehyde from toluene.

The synthesis of titanium silicalite-1 (TS-1) was firstly reported by Taramasso in 1983. Titanium silicalite-1 (TS-1) has gained interest from several researchers owing to its effectiveness on the oxidation reaction of a variety of organic compounds using hydrogen peroxide. Many researchers studied synthesis benzaldehyde from toluene using H_2O_2 as oxidant over TS-1 and TS-1 promoted with metal.

Attempt to study the catalytic of titanium silicalite-1 modified with metal on the hydroxylation of toluene by H_2O_2 was carried out at 70°C and 95°C in glass three-necked flask that fitted with a condenser by using TS-1, Co-TS-1, V-TS-1, Al-TS-1 and Fe-TS-1 as catalyst. The experimental results are reported that TS-1, Co-TS-1 and V-TS-1 gave two products: o-cresol and p-cresol at 70°C while Al-TS-1 and Fe-TS-1 gave three major products: o-cresol, p-cresol and benzaldehyde as main product. The catalytic activity of TS-1 and titanium silicalite-1 catalyst modified with metal follows the order: Fe-TS-1 > Al-TS-1 > TS-1 > Co-TS-1 > V-TS-1. Besides, benzaldehyde was also main product when the reaction temperature increased. The

catalytic activity of TS-1 and titanium silicalite-1 catalyst modified with metal at 95°C follows the order: Al-TS-1 > TS-1 > V-TS-1~ Co-TS-1[1].

In addition, direct synthesis of benzaldehyde from toluene over TS-1 and TS-1 promoted with aluminium cation (Al-TS-1) as catalysts in glass three-necked flask that fitted with a condenser at reaction temperature 70°C and 90°C was carried out. It was reported that Al-TS-1 could oxidize toluene to benzaldehyde using hydrogen peroxide in a one step reaction and could increase the formation of benzaldehyde as main product and inhibit the formation of cresol. In addition, the conversion of H₂O₂ increases with increasing the reaction temperature [2]. However, the important disadvantage is the low conversion owing to decomposition of H₂O₂ before reacting with toluene.

Another study on the effect of acidity of solution on reaction between toluene and hydrogen peroxide over TS-1 catalyst and TS-1 modified with different amount of Co catalysts found that increasing reaction temperature and adjusting the pH of aqueous in range of acidity can enhance the formation of benzaldehyde significantly [3]. At the same time, the toluene oxidation by hydrogen peroxide at elevated temperature over TS-1 and TS-1 modified with aluminium cation was investigated. It is found that the increasing reaction temperature of the system beyond the normal boiling of water with the help of pressure could also increase the conversion of toluene to benzaldehyde, Besides, Al-TS-1 catalyst was also promotes production of benzaldehyde [4].

Some research studied benzene hydroxylation by hydrogen peroxide at elevated temperature over TS-1 catalyst. It was reported that benzene already dissolving into the liquid phase play the important role in the hydroxylation reaction, do not benzene on the top surface of liquid phase thus the increase volume of water as a medium can to raise quantity of benzene dissolve in aqueous phase [5].

Subsequently, effect of acidity on the oxidation of toluene to benzaldehyde by hydrogen peroxide using TS-1 catalyst modified with metallic aluminium was

studied. The result showed that the reactions added with appropriate amount of hydrochloric acid can increase the productivity of benzaldehyde and decreases the productivity of o-cresol and p-cresol. In addition, hydrochloric acid can increase the toluene solubility in water [6].

In the present work, effects of ions in acidic/salt solutions on the oxidation reaction of toluene to benzaldehyde by using hydrogen peroxide as oxidant in a stirred reactor under tri-phase condition are investigated. The Al-TS-1 catalyst is used in this study because Al significantly improves the catalytic activity and promoted produce benzaldehyde. In addition, the reaction is also carried out at temperature higher than the boiling point of toluene and water at atmospheric pressure.

1.2 Objective

This research studies effect of ions in aqueous electrolyte solutions on the oxidation reaction of toluene over Al-TS-1 by using H_2O_2 as the oxidizing agent in liquid phase condition at elevated temperature.

1.3 Scope of this research

1) Synthesizing in the ratio Si/Al 150 using incorporation technique to introduce second metal during hydrothermal synthesis.

2) The synthesized catalysts are characterized by using the following techniques.

- X-ray Fluorescence Spectroscopy (XRF) to determine the composition of elements in the bulk of catalyst.
- X-ray Diffractometry (XRD) to determine the structure of catalysts.
- Fourier Transform Infrared Spectrometer (FT-IR) to determine the incorporation of Ti atoms as a framework element.

- N_2 adsorption based on Brunauer-Emmett-Teller method (BET) to determine surface area pore size and pores volume.

3) Investigate the solubility of toluene in acidic/salt solutions at room temperature and atmospheric pressure.

4) Investigate the influence of ions in acidic/salt solutions by carried out the oxidation reaction as adding acids/salt solutions: HCl, HNO₃, NH₄Cl, NH₄NO₃, NaCl, and NaNO₃ compare with the reaction carried out without acid/salt solution by using H₂O₂ as an oxidant with differences temperature reaction but pressure constant.

The present thesis is organized as follows:

Chapter I presents the rational and scopes of the research.

Chapter II presents the theory of this research and literature on the catalytic activity on the oxidation reaction between toluene and hydrogen peroxide over TS-1 catalyst on the previous works.

Chapter III consists of the catalyst preparation, catalyst characterization and reaction study in the oxidation reaction between toluene and hydrogen peroxide.

Chapter IV reveals the experimental results and discussion of the reaction.

Chapter V presents the conclusions and recommendations for future study.

Finally, data relate to the research are compiled in the appendices at the end of the thesis.

CHAPTER II

THEORY AND LITERATURE REVIEW

The partial oxidation reaction between toluene and hydrogen peroxide is widely used in production of benzaldehyde. The titanium silicalite-1 (TS-1) has received considerable interest owing to its unique catalytic properties in oxidation reactions with diluted hydrogen peroxide as the oxidant. This chapter gives background of titanium silicalite-1 (TS-1), production of benzaldehyde, the decomposition of hydrogen peroxide, the bi-phase and tri-phase and literature reviewed in sections 2.1-2.5 respectively.

2.1 Titanium silicalite-1

The synthesis of titanium silicalite-1 (TS-1) was firstly reported by Taramasso in 1983 [7]. TS-1 is a silica rich molecular sieve with MFI structure in which isolated titanium species in the zeolite framework function as catalytic sites. It is interested from several researchers due to its effectiveness in the oxidation of a variety of organic compounds using hydrogen peroxide at low temperature. Examples of such reactions are the hydroxylation of phenol, the olefin epoxidation, the ketone ammoximation and also sulfide and disulfide oxidation.

Titanium silicalite is a crystalline zeolite material in which tetrahedral $[\text{TiO}_4]$ and $[\text{SiO}_4]$ units are arranged in a MFI structure. The MFI structure is a common pattern of crystalline zeolite that is built up by 5-1 secondary building unit (SBU: the smallest number of TiO_4 units, where T is Si or Al but in case of TS-1 at T position is replacing with Si or Ti, from which zeolite topology is built) which are link together to form chain and the interconnection of these chains leads to the formation of the channel system in the structure. The MFI structure has a three dimensional pore system consisting of sinusoidal 10-ring channels ($5.1 \times 5.5 \text{ \AA}$) and intersecting straight 10-ring channels ($5.3 \times 5.6 \text{ \AA}$). The MFI structure is showed in Figure 2.1.

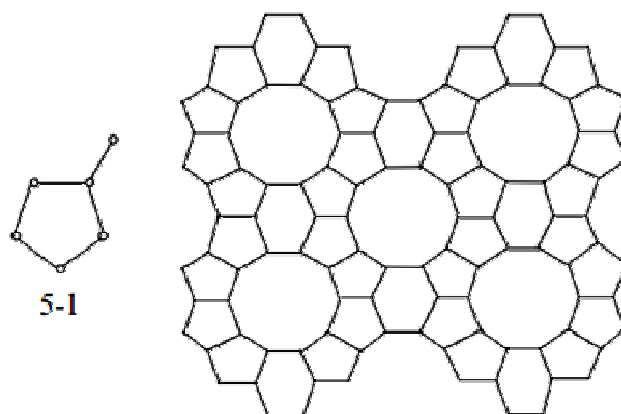


Figure 2.1 MFI structure [8].

2.2 Production of benzaldehyde

Benzaldehyde is a main product of the hydrolysis of benzal chloride and the partial oxidation of toluene. The hydrolysis of mixture of benzyl chloride and benzal chloride occurs in sulfuric acid using vanadium pentoxide as a catalyst but this process is not important in industrial because the presence of sulfuric acid causes waste products. Therefore, the partial oxidation of toluene is a commercial process for the production of benzaldehyde.

2.2.1 The partial oxidation of toluene

The partial oxidation of toluene with oxygen give benzaldehyde as main product can be carried out in either the gas phase or liquid phase. Benzaldehyde is easily further oxidized to benzoic acid and other products thus conditions must be appropriate control.

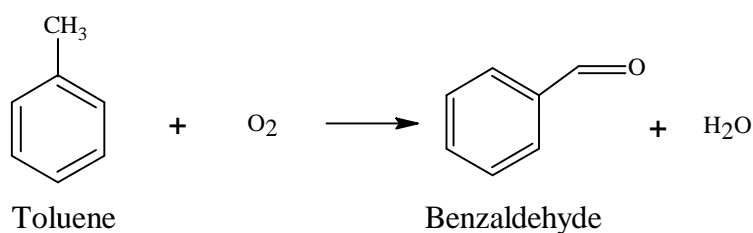


Figure 2.2 The partial oxidation of toluene.

In the gas phase, the partial oxidation is carried out by passing toluene vapor together with gaseous mixture such as air through a catalyst bed in a tube bundle or fluidized-bed reactor at the reaction temperature 250-650°C. Since the reaction is highly exothermic, cooling water system is necessary. The catalysts widely used are vanadium pentoxide promoted with potassium sulphate and promoted uranium oxide catalyst. Benzoic acid, carbon dioxide, anthraquinone, carbon monoxide and water are by products of this synthesis route. Furthermore, the oxidation of toluene in the liquid phase is also carried out by the reaction between toluene and oxygen obtained from hydrogen peroxide decomposition.

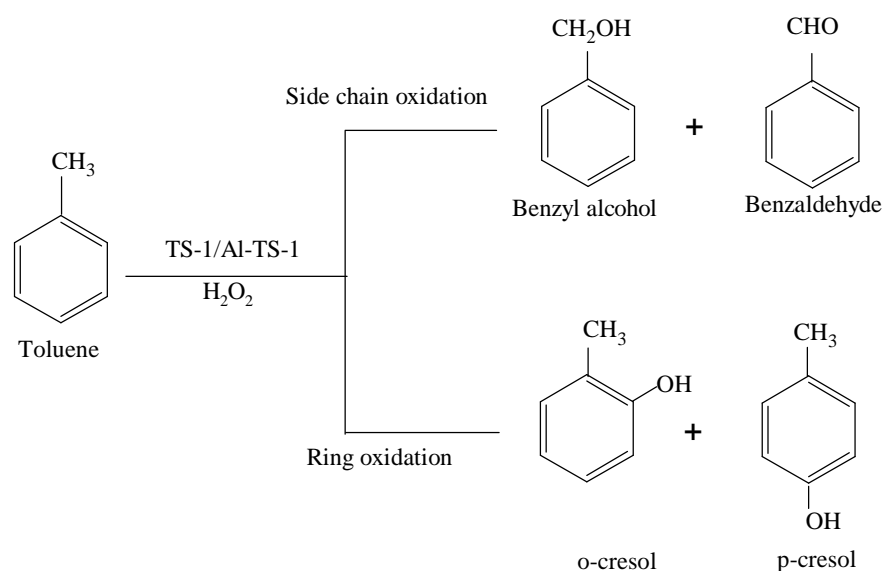


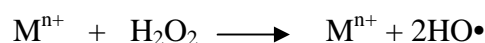
Figure 2.3 The partial oxidation of toluene over TS-1 catalyst.

Previous research, studied the direct synthesis of benzaldehyde between toluene and hydrogen peroxide over TS-1 and TS-1 modified with aluminium cation (Al-TS-1). The reaction was carried out at 70°C and 90°C in a three-necked glass flask fitted with a condenser. The experimental results revealed that the oxidation reaction of toluene could be occurred into two routes as shown Figure 2.3. The TS-1 modified with aluminium cation gave benzaldehyde as main product together with o-cresol and p-cresol as by product. Besides, the selectivity of benzaldehyde was also increase with the increasing of temperature [2].

2.2.2 Proposed mechanism for the formation of benzaldehyde

Previously proposal mechanism for the formation of benzaldehyde is shown in Figure 2.4. The initial step is the breaking of single bond of oxygen atom of the hydrogen peroxide into two hydroxyl free radicals which the oxygen atom of the hydroxyl free radical is very reactive because it has an incomplete valance shell. Next, the hydroxyl free radical collides with the methyl group of toluene molecule result in hydrogen atom insert in the methyl group lead to the formation of benzyl alcohol. Since the nature of primary alcohol which can be easily oxidized, benzyl alcohol form is rapidly oxidized by hydrogen peroxide to benzaldehyde.

Step 1 Decomposition of H₂O₂



Step 2 The oxidation by HO•

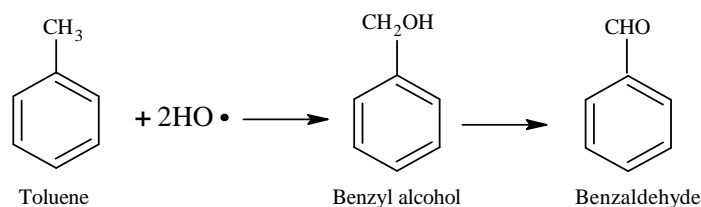


Figure 2.4 Mechanisms of benzaldehyde formation by hydroxyl free radical.

2.3 The decomposition of hydrogen peroxide

Hydrogen peroxide (H₂O₂) is a compound with an oxygen-oxygen single bond. In dilute solution, it appears colorless and slightly more viscous than water. The properties of hydrogen peroxide is oxidizer, it is often used as a bleach or cleaning agent. It is used as a disinfectant, antiseptic, propellant in rocketry and also in chemical syntheses. It is most commonly available as a solution in water. The concentrations of hydrogen peroxide use in pharmacies are 3 and 6 wt% concentration

but in case of laboratory use 30 wt% solutions are most common. It is stabilized against decomposition, which occurs in the presence of traces of iron, copper, aluminium, platinum, and other transition metals. The 30 wt% hydrogen peroxide does not mix with nonpolar organic compounds.

Decomposition of hydrogen peroxide occurs with disproportionate: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ while rate of decomposition is depend on temperature and concentration of the peroxide together with the presence of impurities and stabilizers. The decomposition occurs more rapidly in alkali. Therefore, acid is often added as a stabilizer. In the absence of catalyst, it occurs only gas phase at high temperature. Decomposition can be catalyzed both homogeneously by dissolved ions (especially of the metals iron, copper, manganese, and chromium) and heterogeneously by suspended oxides and hydroxides (e.g., those of manganese, iron, copper, palladium, or mercury) and by metals such as platinum, osmium, and silver. Common catalysts include manganese dioxide, and silver. In the presence of certain catalysts, such as Fe^{2+} or Ti^{3+} , the decomposition may take a different path, with free radicals such as $\text{HO}\cdot$ and $\text{HOO}\cdot$ being formed.

However, the previous research also had the disadvantage that is low conversion owing to decomposition of H_2O_2 before reacting with toluene. Subsequently, the effect of acidity of solution on reaction between toluene and hydrogen peroxide over TS-1 modified with Co was studied. The experimental results were reported that alteration the pH of aqueous in range of acidity could enhance the formation of benzaldehyde [3].

2.4 Bi-phase and tri-phase catalysis

The reaction between toluene, aqueous of hydrogen peroxide and TS-1 catalyst is tri-phase reaction as shown in Figure 2.5. The TS-1 catalyst is solid phase to sink in aqueous of hydrogen peroxide (polar phase) while toluene (non-polar phase) floating on the surface of aqueous of hydrogen peroxide. The reaction will occur when toluene and hydrogen peroxide must exist on the surface of TS-1 catalyst. In the

past, commonly two methods to help toluene and hydrogen peroxide exist on the catalyst surface are:

- I. The use of solvent to combine aqueous hydrogen peroxide and toluene phase to become a homogeneous liquid phase. But this method cause the following problems
 - (a) Solvent are not inert enough which may react with hydrogen peroxide especially at high temperature.
 - (b) Phase arise from the use of solvent harmonize may have low density that make stirring suspended catalyst harder.
 - (c) Bring about the problem in the separation of product, solvent and the reactant.

- II. The vigorous stirring. This method has efficiency when the layer of aqueous hydrogen peroxide is not excessive high due to if layer of aqueous hydrogen peroxide is excessive high, the stirring to make the catalyst encounters toluene phase will be more difficult.

In addition, a factor must be taken into account is the nature of the surface of TS-1. In fact, the nature of TS-1 surface is hydrophobic thus the surface of the TS-1 prefers to adsorb hydrophobic molecule such as toluene. Therefore, if the catalyst excessively contact with toluene, the reaction will be less occurred because almost all the surface of TS-1 is covered by toluene.

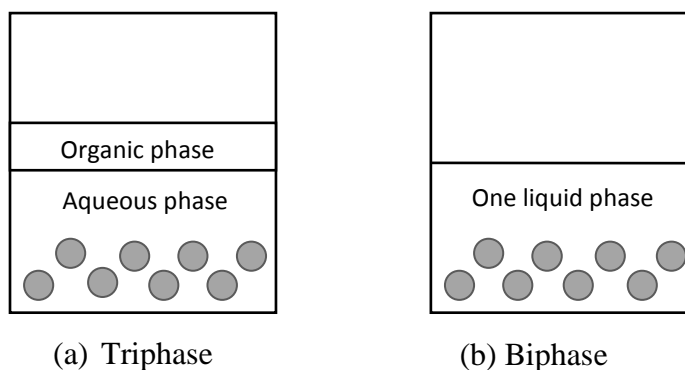


Figure 2.5 Tri-phase and bi-phase system.

2.5 Literature reviewed

The conventional of synthesis titanium silicalite (TS-1) used tetrapropylazanium hydroxide (TPAOH) as the template. In last decade, some researcher tried to decrease the cost of synthesis titanium silicalite (TS-1) by using tetrapropyl Ammonium Bromide (TPABr) replaced TPAOH as the template. The result indicated that the synthesis TS-1 using TPABr as the template revealed a characteristic peak at about 960 cm^{-1} which indicated that titanium incorporated into the framework. Therefore, TPABr could be used to replace TPAOH as the template in the hydrothermal crystallization synthesis method of TS-1[9]. In 2002, synthesis of titanium silicalite (TS-1) from the TPABr system and its catalytic properties for epoxidation of propylene was studied. The results revealed that TS-1 was synthesized by using tetrapropylammonium bromide (TPABr) as the template and n-butylamine as the base had the MFI structure with high crystallinity, large crystal size and with two kinds of titanium species which gave high activity in the epoxidation of propylene [10].

Some researchers try to add another metal to improve catalytic activity of TS-1. Attempt to study the synthesis of TS-1 and TS-1 modified with metal was prepared by hydrothermal method. The second metals (trivalent metal; Al, Fe, Co and V) were added by incorporation in the step of synthesis. All catalysts were found to had the MFI structure and the presence of Ti^{4+} in framework following normal characteristic

of TS-1. The catalytic activity of toluene hydroxylation was evaluated observed at 70°C and 95°C. The reaction at 70°C gave products as p-cresol, o-cresol for all catalysts. Al-TS-1 and Fe-TS-1 also had benzaldehyde. The total conversion of toluene to products follows the order: Fe-TS-1 (10.01%) > Al-TS-1 (5.39%) > TS-1 (1.09%) > Co-TS-1 (0.85%) > V-TS-1 (0.34%) and the selectivity of product observed follows sequence: TS-1 > Co-TS-1 > V-TS-1 > Al-TS-1 > Fe-TS-1 [1].

In addition, some researcher studied the solubility of toluene in various aqueous salt solutions and in distilled water. The experimental of each salt was investigated under three different concentrations and it was carried out at 23°C. Toluene concentration in salt solution was measured by UV-visible spectrometry. The result of the solubility of toluene in distilled water was to be 562.9 ± 9.6 mg/l which lay within the range of previous studied. The results of the solubility of toluene in salt solution including NaCl, NaBr, KCl, KBr, KHCO₃, K₂SO₄, CsBr, MgCl₂, MgSO₄, CaCl₂ and BaCl₂ found that the effect of Na > K > Cs since Setschenow constant (K_s), quantity toluene solubility versus salt solution, decreased from 0.180 to 0.150 to 0.050, for NaBr, KBr and CsBr. The results were confirmed by the chloride salts which K_s decreased from 0.202 to 0.188 for NaCl and KCl. In addition, the result of anion demonstrated than the effect of Cl > Br which revealed the decrease K_s of Na salt from 0.202 to 0.180 for NaCl and NaBr [11].

The enhancement in the reaction rates in the hydroxylation of aromatics (benzene, toluene and anisole) over TS-1/H₂O₂ under solvent-free tri-phase conditions and compared with the conventional to use bi-phase condition in the presence of a co-solvent was studied. They found that the conversion and phenol selectivity of hydroxylation reaction of benzene under tri-phase condition was higher than bi-phase condition along with the increase the benzene/ H₂O₂ molar ratio. As a result, the H₂O₂ efficiency, phenol selectivity among products and rate of reaction were also increase. In case of hydroxylation reaction of substituted benzene (anisole and toluene) demonstrated the reaction occurred mainly inside the channels of TS-1 because system used as a dispersion medium (under tri-phase). Furthermore, the increase of catalyst concentration lead to the number of active titanium species and conversion

were increased with more efficient utilization of the oxidant was obtained. In addition, they found that the vigorous stirring was method to help in dispersion of organic phase in aqueous one through micro droplet formation and simplify the transport of the reactant to the catalyst surface [12].

Some research studied the vanadium catalyzed direct hydroxylation of aromatic hydrocarbons using hydrogen peroxide as oxidant. It was carried out at 65°C for 8 h. The results shown that vanadyl tetraphenoxypthalocyanine gave the highest conversion and selectivity of desired product together with acetonitrile as solvent. In addition, it was found that conversion of aromatic increased with increasing the molar ratio of H₂O₂/substrate while the increase of the catalyst concentration resulted in the conversion increased [13].

The partial oxidation of toluene in CH₃COOH by H₂O₂ in the presence of VO(acac)₂ catalyst was studied. They found that the best catalyst amount for toluene oxidation was 0.10 mmol that gave 19.8% conversion. The optimal catalyst amount for benzaldehyde formation was 0.03 mmol that gave 78% conversion. The best catalysis was obtained reaction temperature at 90°C together with the reaction time within 4 h. In addition, the result showed that excessive amount of hydrogen peroxide was not increased conversion of toluene [14].

Recently, the solubility of toluene and ethyl acetate in aqueous electrolyte solution was studied. The experiment was performed in a temperature near 25°C. The cell was filled with unsaturated solution (salt: NaCl, KCl or acid: benzoic acid, boric acid) afterward the pure solute (toluene or ethyl acetate) was injected into the cell as the cell stand on a magnetic stirrer. The liquid mixture was stirred magnetically and it was stopped after 45 min after that the equilibrium cell was left to settle for 30 min, a syringe was used to withdraw sample 1-2 ml of mixture to be analyzed by a spectrophotometer. The result of the solubility of toluene in distilled water was to be (487 to 588)×10⁻³ kg/m³. In addition, the solubility of toluene in unsaturated solution (NaCl, benzoic acid or boric acid) was found that the solubility of benzoic acid is the highest. In case of ethyl acetate, the solubility of ethyl acetate demonstrated the

solubility of ethyl acetate decrease significantly with more concentrated solution of NaCl and KCl [15].

Some researcher tried to study effects of salt of the Hofmeister series on the hydrogen bond network of water. This research study examined the temperature excursion IR spectra of aqueous solution of 30 salts of the Hofmeister series. Two-state hydrogen bonding model for water was used for quantitatively analysis of O-H stretch of aqueous salt solution. The experimental results were exhibited in the value for $\Delta G_{b \rightarrow 1}$ which divided into cation group and anion group for comparison of the order to the Hofmeister order. The comparison of the salt that had the same cation, it was found that an order appears as a function of anion character for all salts. Besides, this order of salt was the same order seen in the Hofmeister order and corresponds to Jones-Dole viscosity B values [16].

2.6 The summary of the previous review

From the studies the previous review, we can summarize that titanium silicalite-1 modified with metallic aluminium promotes the production of benzaldehyde as main product on the oxidation reaction between toluene and hydrogen peroxide. In addition, when the aqueous phase is added with acidity solution, it not only increases the concentration of toluene in aqueous phase but also increases the hydrogen peroxide conversion. Moreover, the reaction temperatures above the boiling point of water and toluene at atmospheric pressure can increase the reaction rate as well. However, we find that aqueous salt solutions tend to increase the solubility of toluene and the effect of aqueous salt solutions on the aqueous phase oxidation of toluene by H_2O_2 has never been investigated before.

The present work investigates effect of ions in electrolyte solution such as HCl, HNO_3 , NH_4Cl , NH_4NO_3 , NaCl and $NaNO_3$ which is added into the aqueous phase. The reaction is performed at the reaction temperature higher than the boiling point of water and toluene at atmospheric pressurize autoclave reactor.

CHAPTER III

EXPERIMENTAL

The experimental in this chapter is divided into four major parts: (1) catalyst preparation, (2) catalyst characterization, (3) the solubility of toluene in acidic/salt solutions and (4) reaction study procedures in the oxidation of toluene. The chemicals, instrument and procedures for catalyst preparation are explained in section 3.1. The composition, surface properties, structure, and the functional group of the catalyst measured by various techniques such as XRF, BET, XRD and FT-IR are discussed in section 3.2. The solubility of toluene in acidic/salt solutions is discussed in section 3.3 and the details of the reaction study are explained in section 3.4.

3.1 Catalyst preparation

The incorporation method is used to prepare titanium silicalite-1 modified with aluminium cation (Al-TS-1) catalyst. The identical amount of aluminium nitrate nanohydrate is added in both gel solution and decantation solution. All chemicals use in this preparation procedure of Al-TS-1 catalyst is following 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 Chemicals used in the catalyst preparation.

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

Table 3.2 Reagents used for the preparation of Al-TS-1: Si/Ti = 50, Si/Al = 150.

Solution for the gel preparation	Solution for decant-solution preparation
<p>Solution A1</p> <p>Ti[O(CH₂)₃CH₃]₄ 2.2970 g</p> <p>TPABr 5.72 g</p> <p>NaCl 11.95 g</p> <p>Al(NO₃)₃.9H₂O,Si/Al= 150 0.82 g</p> <p>De-ionized water 60 ml</p> <p>H₂SO₄(conc.) 3.4 ml</p>	<p>Solution A2</p> <p>Ti[O(CH₂)₃CH₃]₄ 2.2970 g</p> <p>TPABr 7.53 g</p> <p>De-ionized water 60 ml</p> <p>Al(NO₃)₃.9H₂O,Si/Al=150 0.82 g</p> <p>H₂SO₄(conc.) 3.4 ml</p>
<p>Solution B1</p> <p>Sodium silicate 69 g</p> <p>De-ionized water 45 ml</p>	<p>Solution B2</p> <p>Sodium silicate 69 g</p> <p>De-ionized water 45 ml</p>
<p>Solution C1</p> <p>TPABr 2.16 g</p> <p>NaCl 40.59 g</p> <p>NaOH 2.39 g</p> <p>De-ionized water 208 ml</p> <p>H₂SO₄ (conc.) 1.55 ml</p>	<p>Solution C2</p> <p>NaCl 26.27 g</p> <p>De-ionized water 104 ml</p>

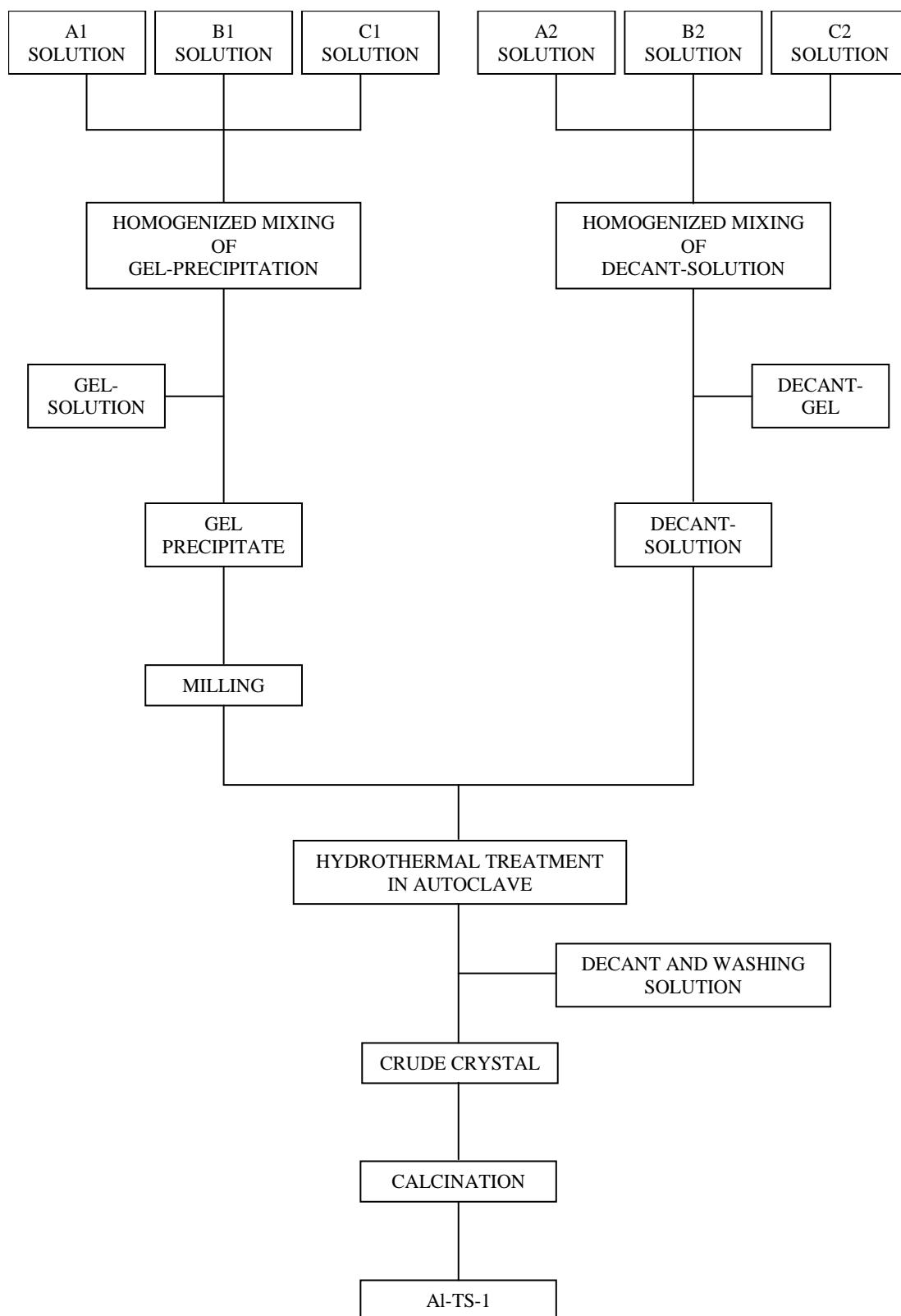


Figure 3.1 Preparation procedure of Al-TS-1 by rapid crystallization method.

The Al-TS-1 catalysts are prepared from the mixture of gel and decant solutions. The Si source and the Ti source is mixed in the atomic ratio of Si/Ti = 50. Tetrapropylammonium bromide (TPABr) was used as organic template and the amount of aluminium nitrate nonahydrate is added both a gel solution and decantation solution in the same ratio. The gel solution is prepared by adding solution A1 and solution B1 into solution C1 in order to adjust the pH of gel mixture with vigorous stirring using a magnetic stirrer at room temperature. The pH of gel mixture is manipulated within the range 9-11. After that, the gel mixture is centrifuged for 15 minutes to separate the formed gel from the supernatant liquid. The precipitated gel mixture is milled for totally 1 hour. The milling time is 15 minutes, alternating with centrifugal separation for 20 minutes in order to separate the supernatant solution. Secondly, a decantation solution is prepared by adding solution A2 and solution B2 into solution C2. The decantation solution are adjusted the pH same as previously. The colorless supernatant liquid is separated from the mixture by centrifugation.

In the step of crystallization, the mixture of gel in supernatant liquid is filled in a 500 ml Pyrex glass. The glass container is placed in a stainless steel autoclave. The autoclave is pressurized to 3 barg by nitrogen gas. The autoclave is heated from room to temperature to 180°C and held at this temperature for 3 days. The product crystals are washed with de-ionized water decreased pH from about 12 to 7 by centrifugation. Then the crystals are dried in an oven at 110°C for at least 24 h and held at that temperature for 7 hr, by heating them from room temperature to 550°C at a heating rate at 8.60°C/min.

The Al-TS-1 is placed into a round bottom flask and then 150 ml of 5 M of HNO₃ aqueous solution is added. After reflux at 80°C for 3 hr, the pretreated catalyst is filtered, washed with distilled water until all residual acid is removed, dried at 110°C for at least 24 h. The dry crystals are calcined at 550°C for 7 h in static air in order to burn off the organic template leave the cavities and channels in the crystals. The final product is obtained as white powder.

3.2 Catalyst characterization

3.2.1 X-Ray Fluorescence Spectrometer (XRF)

The chemical composition analysis of elements of the catalyst is performed by wavelength dispersive X-ray fluorescence spectrometer (WDXRF) BRUKER AXS, Germany: Model S4 PIONEER analysis at Chulalongkorn University.

3.2.2 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 0.1 g of sample is placed into BET Micromeritics ASAP 2020. After degassing step, the surface area and pore volume of catalyst are measured.

3.2.3 X-Ray Diffraction (XRD)

The crystal structure identified using x-ray diffraction technique. The analysis is performed with a SIEMENS D5000. The experiments are carried out by using $\text{CuK}\alpha$ radiation with Ni filter. Scans are performed over the 2θ ranges from 6° to 30° with step size $0.04^\circ/\text{sec}$.

3.2.4 Fourier transform infrared (FT-IR)

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

3.3 The solubility of toluene in acidic/salt solutions

The solubility of toluene in acidic/salt solution is measured by mixing of water or aqueous solution of acid/salts. For example hydrochloric acid, nitric acid, ammonium chloride, ammonium nitrate, sodium chloride and sodium nitrate. The concentration of acidic/salt solution in the solubility test is 0.1 M.

The solubility test of toluene is carried out in a 250 ml beaker which a 1/4" tube is vertically placed in the beaker. The water or aqueous solutions of acid/salts 120 ml are added into the beaker with a volume of toluene sufficiently cover the total surface area of the aqueous phase. At specific intervals, the stirring is stopped and a small volume of the aqueous phase is removed to measure the concentration of dissolved toluene. The collected samples are analyzed by a gas chromatograph (Shimadzu GC9A) equipped with a FID and a GP10% SP-2100 packed column to determine the concentration of toluene.

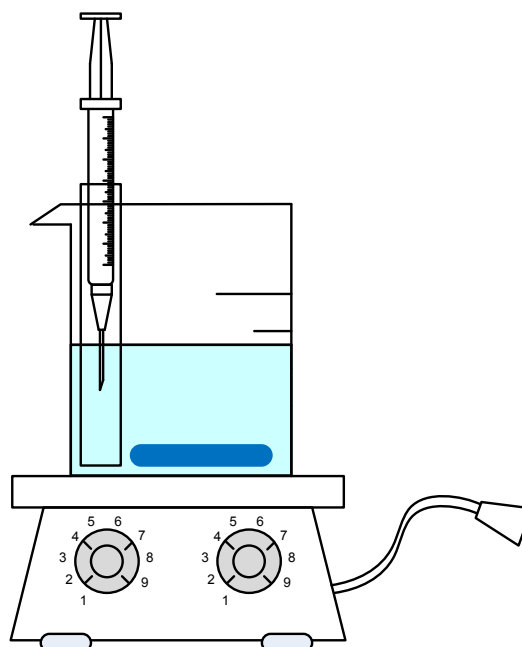


Figure 3.2 The preparation procedure of the solubility of toluene in water/acidic solution.

3.4 Reaction study in oxidation of toluene

3.4.1 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
Toluene	Analytical	Merck
Hydrogen peroxide 30%	Analytical	Merck
Ethanol	Analytical	Merck
Hydrochloric acid	AR	QRëC
Nitric acid	AR	QRëC
Ammonium chloride	Analytical	Univar
Ammonium nitrate	Analytical	Univar
Sodium chloride	Analytical	Univar
Sodium nitrate	Analytical	Univar

3.4.2 Reaction procedure

The oxidation of toluene with molar ratio of reactant (toluene: H₂O₂) are 1:1 using Al-TS-1 as a catalyst is carried out in a pressurized autoclave reactor. The procedures are described in the detail below.

1) Catalyst 1 g, magnetic bar, acidic/salt solutions 120 ml (for dispersion of the catalyst) and toluene 1.1 ml (for toluene to H₂O₂ molar ratio equals to 1:1) 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 90°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) Hydrogen peroxide 30 wt% 1 ml is injected into the reactor.

5) After 2 h, the mixture is immediately cooled down into an ice bath in order to stop the reaction. Ethanol 80 ml is used to homogenize the mixture.

6) The catalyst particle is separated from the homogeneous mixture by using a 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.

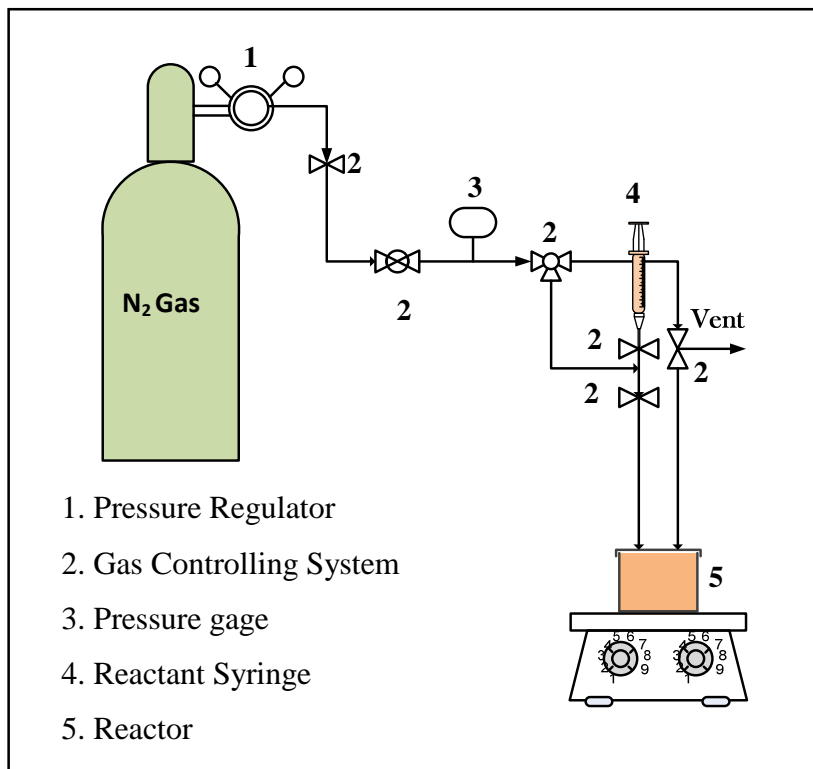


Figure 3.3 The oxidation reaction of toluene system.

Table 3.4 The conditions of the GC.

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N ₂ (99.999%)
Carrier gas flow rate (ml/min)	30
Injector temperature (°C)	250
Detector temperature (°C)	250
Initial column temperature (°C)	80
Initial hold time (min)	5
Program rate (°C /min)	2
Final column temperature (°C)	230
Final hold time (min)	15
Analyzed chemicals	Toluene, Benzaldehyde and Cresol

CHAPTER IV

RESULTS AND DISCUSSION

The result and discussion in this chapter are divided into three parts. The first of all, section 4.1 is the summary of characterization of Al-TS-1 catalyst. This part consist the result of the catalyst composition by using XRF technique, the result of the surface area and pore volume of the catalyst by using BET technique, the result of crystal structure by using XRD technique, the result of the location of titanium cation by using FT-IR technique. The second part, section 4.2 is the solubility of toluene in acidic/salt solutions. In the end, section 4.3 is the results and explanation of catalytic activity of Al-TS-1 catalyst in the oxidation reaction between toluene and hydrogen peroxide to benzaldehyde and cresol are given.

4.1 Catalyst characterization

4.1.1 Chemical compositions (XRF)

The chemical compositions of Al-TS-1, measured by Semi-quantitative X-ray fluorescence spectrometry technique using wavelength dispersive X-ray fluorescence Spectrometer (WDXRF) BRUKER AXS, Germany: Model S4 PIONEER. The results are exhibited in Table 4.1.

Table 4.1 Chemical compositions and surface area of Al-TS-1.

Catalyst sample	%Si	%Ti	%Al	Si/Ti
Al-TS-1	96.56	1.78	0.77	54.17

4.1.2 Surface area measurement (BET)

Surface area and pore volume of Al-TS-1 catalyst, measure by BET technique using Micromeritics ASAP 2020, are found to be 379.20 m²/g and 0.1196 cm³/g respectively.

4.1.3 Crystal structure (XRD)

The crystal structure of Al-TS-1 catalyst is identified using x-ray diffraction technique. The X-ray diffraction result in Figure 4.1 shows six main characteristic peaks at $2\theta \approx 8, 8.8, 14.8, 23.1, 24$ and 26.7 which are typical for MFI structure. This indicates the incorporation of aluminium into TS-1 catalyst does not affect the MFI structure.

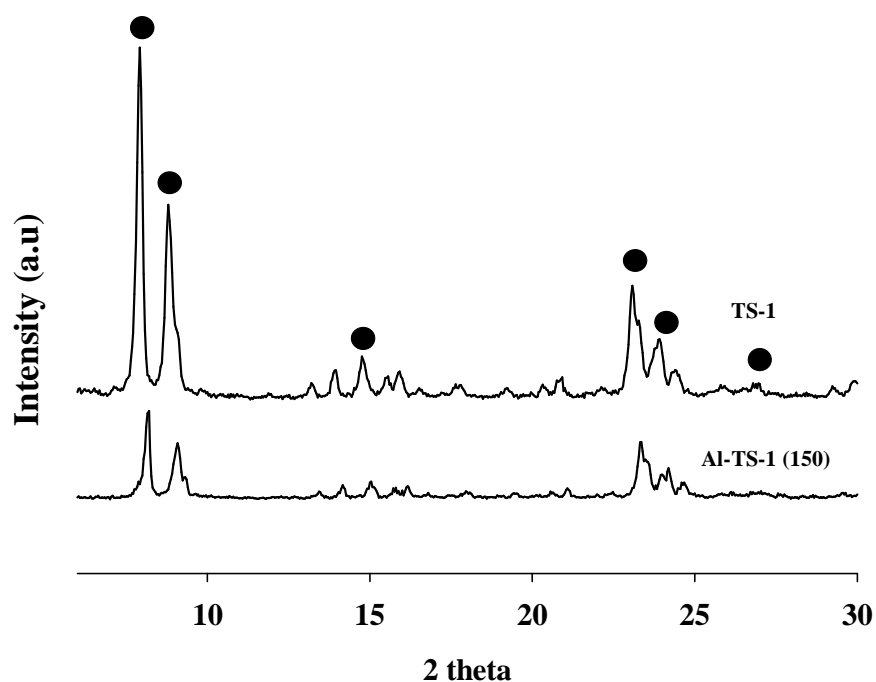


Figure 4.1 The XRD patterns of TS-1 and Al-TS-1.

4.1.4 Fourier transform infrared (FT-IR)

The functional group on the catalyst surface is determined by FT-IR in order to confirm the incorporation of titanium cation into the MFI framework in the tetrahedral group $\text{Ti}(\text{SiO})_4$. The substitution of Si^{4+} by Ti^{4+} produces absorption band around 960 cm^{-1} . The IR spectra of TS-1 and Al-TS-1 in Figure 4.2 reveal the adsorption bands around 960 cm^{-1} which indicate that Al-TS-1 also have Ti^{4+} in the framework of MFI.

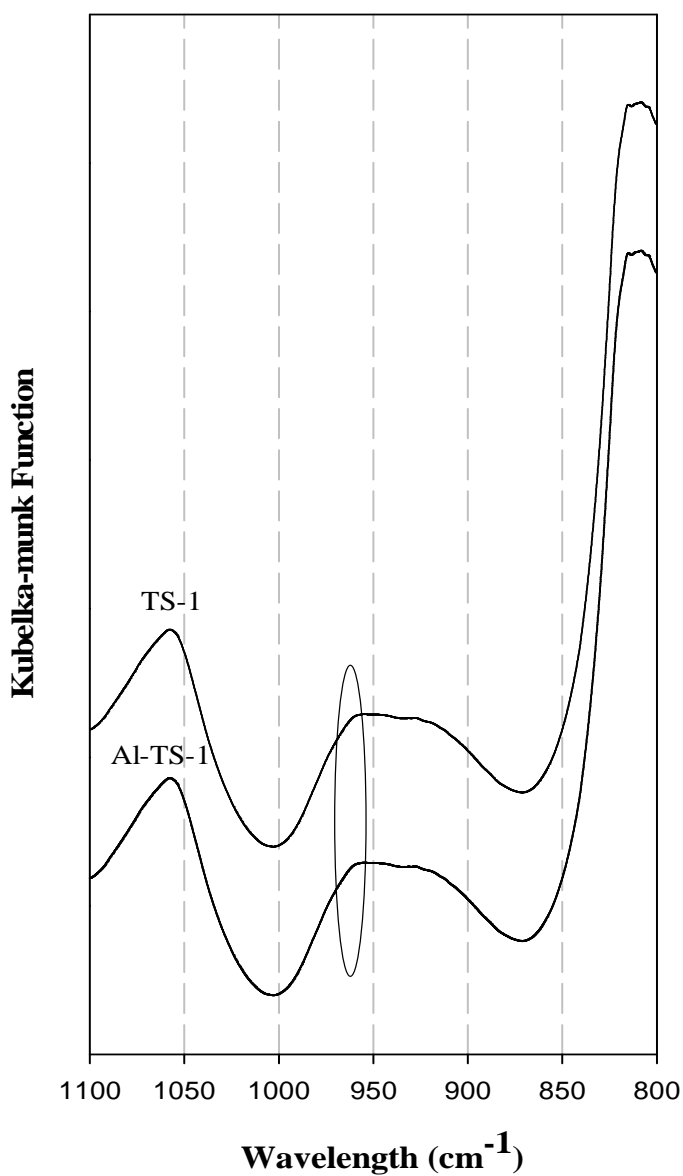


Figure 4.2 The FT-IR pattern of TS-1 and Al-TS-1(150).

4.2 The catalytic performance of reaction

The oxidation reaction between toluene and hydrogen peroxide over Al-TS-1 catalyst is carried out in a pressurized autoclave reactor. The reaction occurs when toluene and hydrogen peroxide exist on the catalyst surface. But the problem is hydrogen peroxide and hydrocarbons are immiscible liquid. In the past, the method to help toluene and hydrogen peroxide exist on the catalyst surface is the use of solvent to homogenize aqueous hydrogen peroxide and toluene phases. But this method cause the other problems already mentioned before. Therefore, this research insists on using a reaction media which results in a tri-phase system as shown in Figure 4.3.

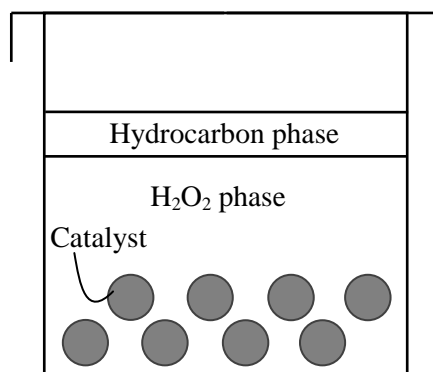


Figure 4.3 System of the oxidation reaction (Tri phase).

Using water as reaction media makes the catalyst surface can be easily accessed by hydrogen peroxide because hydrogen peroxide is polar molecules that can dissolve into water. This method, however, causes hydrocarbon depletion on the catalyst surface. As a result, the reaction occurs not well enough but we use this method because hydrocarbon can bind tightly to the catalyst surface. Therefore, the replacement of hydrogen peroxide on the catalyst surface by hydrocarbon is easier than the replacement of hydrocarbon on the catalyst surface by hydrogen peroxide.

A previous research on the subject suggested that the hydrocarbon in the oxidation reaction may be hydrocarbon dissolved into aqueous phase, not hydrocarbon on the top surface of aqueous phase. Therefore, if quantity of

hydrocarbon (quantity = volume of water \times concentration) increases, the reaction will more proceed in the forward direction. The increase volume of water as a medium is a way to raise quantity of hydrocarbon dissolve in the aqueous phase, which the concentration of hydrocarbon is constant. Beside, the increasing reaction temperature is another way to raise quantity of hydrocarbon. In the latter, the concentration of hydrocarbon increases [5].

Subsequently, the adding acid into the reaction is found that have effect on the reaction in a positive way. It has been observed that equilibrium concentration and the solubility rate of hydrocarbon will be raised [3, 6]. At present, we find that not only acid but also some of ionic compound affect the solubility rate of hydrocarbon into the aqueous phase and the equilibrium concentration of hydrocarbon in the aqueous phase is changed. From this point of view, effect of ions on oxidation reaction is the subject of our.

4.2.1 Effect of ions on the solubility of toluene in acidic/salt solutions

The solubility is ability of one liquid dissolve into another liquid. A liquid (**A**) will dissolve into another liquid (**B**) when liquid (**A**) can penetrate between molecules of liquid (**B**). If intermolecular forces of liquid (**B**) is very high and higher than intermolecular forces of liquid **A** and **B**, a liquid (**A**) cannot penetrate into a liquid (**B**) or less penetrate into a liquid (**B**). In case of aromatic hydrocarbon with water such as toluene, the molecules of aromatic hydrocarbon are bonded by Van der Waals while water molecules are bonded by hydrogen bond with respect to hydrogen bond is stronger than Van der Waals force. Therefore, water molecules like to bond together and not rather allow hydrocarbon to penetrate into water molecules.

The solubility of toluene in acidic/salt solution is measured by mixing of acid or salt. For example, hydrochloric acid, nitric acid, ammonium nitrate, ammonium chloride, sodium nitrate and sodium chloride solutions. The concentration of acidic/salt solution is 0.1 M. The acidic/salt solution is added into a 250 ml beaker with a volume of toluene sufficiently cover the total surface area of the aqueous phase

which a 1/4" tube is vertically placed in the beaker. At a specific interval, the stirring is stopped and a small volume of the aqueous phase is removed to measure the concentration of dissolved toluene. The collected samples are analyzed by a gas chromatograph (Shimadzu GC9A) equipped with a FID and a GP10% SP-2100 packed column to determine the concentration of toluene.



Figure 4.4 The preparation procedure of the solubility of toluene in acidic/salt solution.

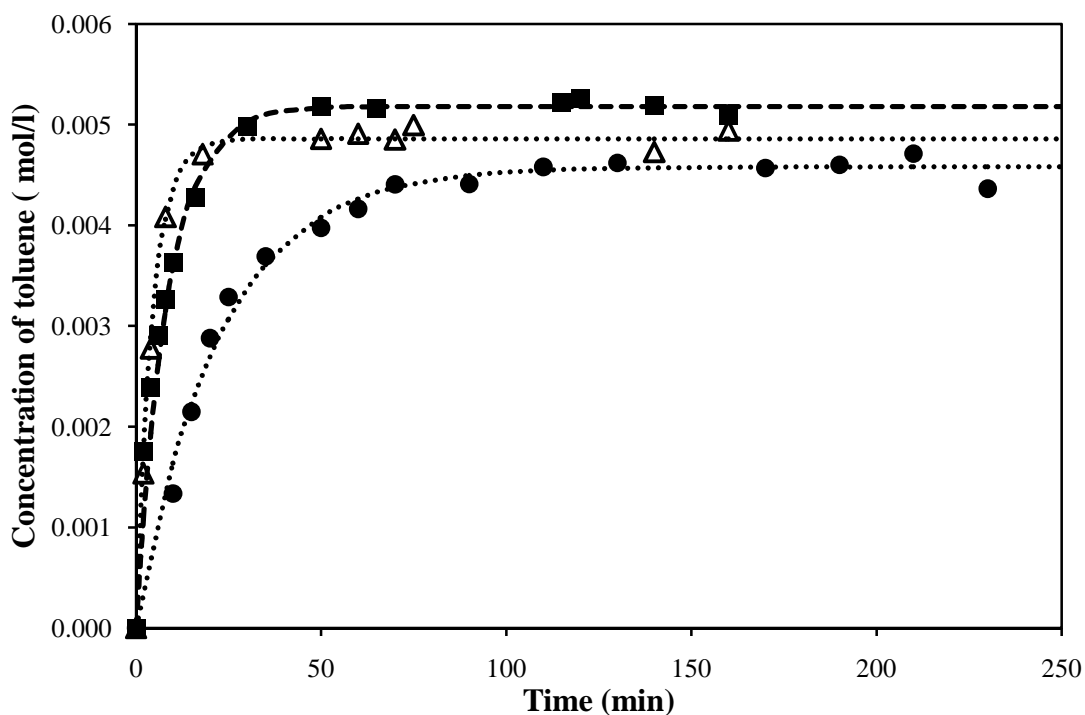


Figure 4.5 The solubility of toluene in deionized water/acidic solution 0.1 M at room temperature, (■) Nitric acid, (▲) Hydrochloric acid, (●) Deionized water.

Figure 4.5 shows the solubility of toluene in aqueous solutions acidified by hydrochloric and nitric acid. Both solutions have the same cation: H^+ . It is clear that the equilibrium concentration of toluene in acidic solution is higher than in the de-ionized water. The equilibrium concentration of toluene in different aqueous phases can be arranged in the following order: nitric acid \gg hydrochloric acid \gg deionized water. Besides, the solubility rates of toluene in the aqueous phase acidified by nitric acid and hydrochloric acid are also higher than the de-ionized water which can be arranged in the following order: hydrochloric acid $>$ nitric acid \gg deionized water.

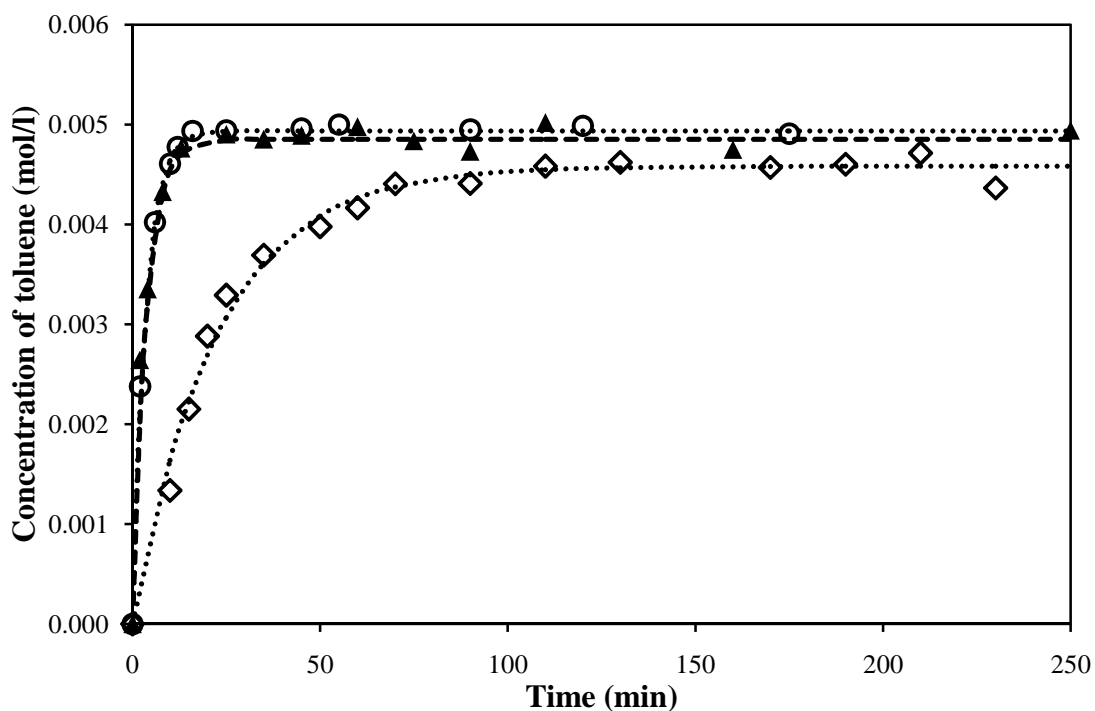


Figure 4.6 The solubility of toluene in deionized water /salt solution 0.1 M at room temperature, (▲) Ammonium chloride, (○) Ammonium nitrate, (◇) Deionized water.

Figure 4.6 shows the solubility of toluene in the aqueous phase having by ammonium chloride and ammonium nitrate dissolved into. Both solutions have the same cation: NH_4^+ . It is clear that the equilibrium concentration of toluene in ammonium nitrate solution is marginally higher than ammonium chloride solution and equilibrium concentrations of both salt solutions is higher than in deionized water. Besides, the solubility rates of toluene in the salt solution are also higher than in deionized water. The solubility rate can be arranged in the following order: ammonium nitrate ~ ammonium chloride \gg deionized water.

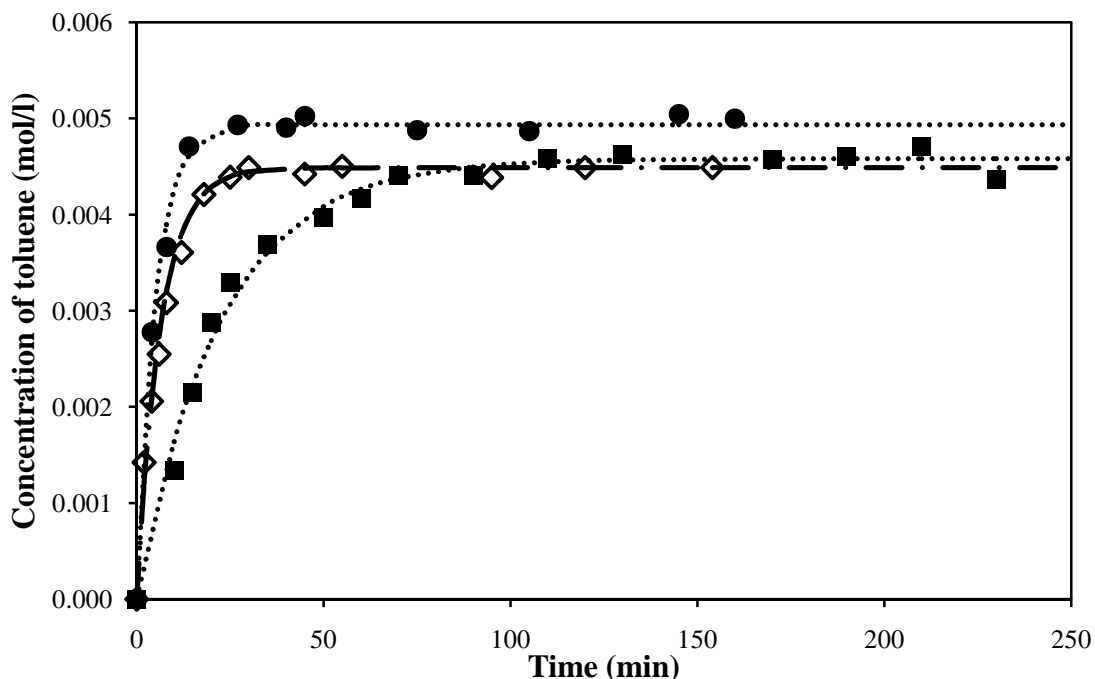


Figure 4.7 The solubility of toluene in deionized water /salt solution 0.1 M at room temperature, (\diamond) Sodium chloride, (\bullet) Sodium nitrate, (\blacksquare) Deionized water.

Figure 4.7 shows the solubility of toluene in the aqueous phase having by sodium chloride and sodium nitrate dissolved into. Both solutions have the same cation: Na^+ . It is clear that the equilibrium concentration of toluene in the sodium nitrate solution is also higher than in sodium chloride and in the de-ionized water. The equilibrium concentrations of toluene in different aqueous phases can be arranged in the following order: sodium nitrate \gg sodium chloride \sim deionized water. Furthermore, the solubility rates of toluene in the aqueous phases, sodium chloride and sodium nitrate solution are also higher than in the deionized water. But the solubility rate of toluene in sodium chloride solution is approximately to the same as of sodium nitrate solution.

The experimental results in Figures 4.5-4.7 exhibit the solubility of toluene in various acidic/salt solutions can be categorized into three groups: H^+ , NH_4^+ and Na^+ . Each category has the same anions: Cl^- and NO_3^- . It is clear that an order emerge as a function of anion character for all salt which NO_3^- ion has stronger effects on the equilibrium concentration and the solubility rate more than Cl^- ion with H^+ ion has the stronger effect on the equilibrium concentration and the solubility rate more than the other cation ion. The explanation of those can be described in term of the chaotropicity or kosmotropicity of the solute which the properties of aqueous ionic solution relative to charge density of ions and the strength of water-water interactions in bulk solution. The best description of the chaotrope or kosmotrope designation is offered by Collins [17].

The “**chaotropes**” are monovalent ions of low charge density which bind the immediately adjacent water molecules weaker than water binds itself thus they interfere little in the hydrogen bonding of the surrounding water whereas “**kosmotropes**” are small or multiply-charged ions of high charge density which bind the immediately adjacent water molecules tightly stronger than water binds itself. As a result, kosmotropes can interfere strongly with the hydrogen bonding of the surrounding water [16, 17].

When comparing the solubility test of salt that have the same cation in Figures 4.5-4.7, the equilibrium concentrations and the solubility rates of toluene in all acid/salt solutions are higher than in the deionized water except sodium chloride solution. The equilibrium concentration of toluene in sodium chloride solution is approximately the same as the deionized water. It is clear that an order emerge as a function of anion character for all salt: $NO_3^- > Cl^-$ which the experimental result conform to the **Hofmeister series***. When comparing with order of the Hofmeister series found that the NO_3^- and Cl^- are chaotropes ion but NO_3^- ion has stronger effects on the equilibrium concentration and the solubility rate of toluene in the ionic salt solution more than the ionic salt solution as Cl^- anion. However, when consider

the breaking strength of the hydrogen bond of water molecules, it is observed that H^+ ion has influence more than the other cation because H^+ ion has the smallest ion and highest charge density affect binding the adjacent water molecules tightly stronger than hydrogen bonding of water molecules with itself. (*Remark: Hofmeister series is a classification of ions in order of their ability on the solubility)

In case of sodium chloride solution, we found that the equilibrium concentration of toluene is approximately the same as the deionized water because Na^+ ion is only marginally a kosmotrope and Cl^- ion is only marginally a chaotrope which both of these ions are nearly neutral in the Hofmesiter sense thus we will see that equilibrium concentration of toluene in sodium chloride solution is approximately to deionized water.

The previous paragraph has explained how the adding of ions in aqueous phase affects solubility of toluene. The equilibrium concentrations and the solubility rates of toluene in aqueous phase increase due to the decrease of viscosity and surface tension of water. It has been reported that cations had only a small influence on the surface tension while anions affected surface tension somewhat significantly. Besides, the dimension of the alteration of the surface tension followed the same sequence of Hofmesiter series [18].

This hypothesis is proven by ordering of ions in Hofmeister series which correlate with the Jones-Dole viscosity B coefficient. The Jones-Dole viscosity B coefficient is determined by

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \quad (4.1)$$

Where η is the viscosity of an aqueous solution of ion, η_0 is the viscosity of pure water at the same temperature, c is the salt concentration (molarity), A is an electrostatic term that is close to one, as long as the salt concentrations are not significantly higher than 0.1 M, The viscosity of neutral solutes would best be

described with $A = 0$ and B is a measure of ion-water interactions. The viscosity B coefficient of relevant ions is shown Table 4.2.

Table 4.2 The Jones-Dole viscosity B coefficient [17].

Cation	B	Anions	B
Mg^{2+}	0.385	PO_4^{3-}	0.059
Ca^{2+}	0.285	CH_3CO^{2-}	0.025
Ba^{2+}	0.22	SO_4^{2-}	0.028
Li^+	0.15	F	0.1
H^+	0.068	HCO^{2-}	0.052
Na^+	0.086	Cl^-	-0.007
K^+	-0.007	Br^-	-0.032
NH_4^+	-0.007	NO_3^-	-0.046
Rb^+	-0.03	ClO_4^-	-0.061
Cs^+	-0.045	I	-0.068
		SCN^-	-0.103

The Jones-Dole viscosity B coefficient can be divided into negative values and positive values. According to Collins, ions that are weakly hydrated with low charge density, exhibit negative B coefficients whereas ions that strongly hydrated with high charge density exhibit positive B coefficients.

When substitute the value of the Jones-Dole viscosity B coefficient from table 4.2 into equation (4.1) with constant η_0 and c for NO_3^- ion and Cl^- ion found that η/η_0 value of NO_3^- ion is less than Cl^- ion. Consequently, the viscosity (η) of NO_3^- ion solution is lower than Cl^- ion solution. These correlate with the equilibrium concentrations of toluene in the ionic salt solution that have NO_3^- as anion which the

equilibrium concentration of toluene is higher than the ionic salt solution that have Cl^- as anion.

4.2.2 Effect of ions on the oxidation reaction

Accounting to effect of ions on the solubility of toluene in acidic/salt solutions, the results show that adding acid/salt into the water help increasing the solubility of toluene. But the nature of surface of the TS-1 is the hydrophobic thus the surface of the TS-1 prefers to adsorb hydrophobic molecule such as toluene. Consequently, if the surface of the TS-1 is full of toluene, the reaction will less occur because H_2O_2 cannot reach the surface of TS-1. In this section, we investigate the effect of ions on the oxidation reaction by carried out at 110°C

The oxidation reaction between toluene and H_2O_2 over Al-TS-1 catalyst can produce three products: benzaldehyde, ortho-cresol and para-cresol. The experimental results are reported in the form of the total percentage of hydrogen peroxide converted to products and moles of each product formed.

I. The percentage of H_2O_2 conversion

$$\text{The \%H}_2\text{O}_2 \text{ converts to product} = \frac{(2 \times N_B) + (N_o + N_p)}{N_{\text{H}_2\text{O}_2}} \times 100 \quad (4.2)$$

Where;

N_B	=	the overall mole of benzaldehyde formed
N_o	=	the overall mole of o-cresol formed
N_p	=	the overall mole of p-cresol formed
$N_{\text{H}_2\text{O}_2}$	=	the overall mole of H_2O_2 introduced

II. The percentage of product selectivity

The selectivity of products: benzaldehyde, o-cresol and p-cresol of the reaction can be calculated as following:

$$\% \text{Selectivity of benzaldehyde} = \frac{N_B}{N_B + N_o + N_p} \times 100 \quad (4.3)$$

$$\% \text{Selectivity of o-cresol} = \frac{N_o}{N_B + N_o + N_p} \times 100 \quad (4.4)$$

$$\% \text{Selectivity of p-cresol} = \frac{N_p}{N_B + N_o + N_p} \times 100 \quad (4.5)$$

III. The productivity of products

The productivity of products: benzaldehyde, o-cresol and p-cresol of the reaction can be calculated as following:

$$\text{Productivity of benzaldehyde} = \frac{N_B}{W_{cat} \times 120 \text{ min} \times 10^{-6}} \quad (4.6)$$

$$\text{Productivity of o-cresol} = \frac{N_o}{W_{cat} \times 120 \text{ min} \times 10^{-6}} \quad (4.7)$$

$$\text{Productivity of p-cresol} = \frac{N_p}{W_{cat} \times 120 \text{ min} \times 10^{-6}} \quad (4.8)$$

Where;

W_{cat} = weight of catalyst (gram) is used in the reaction

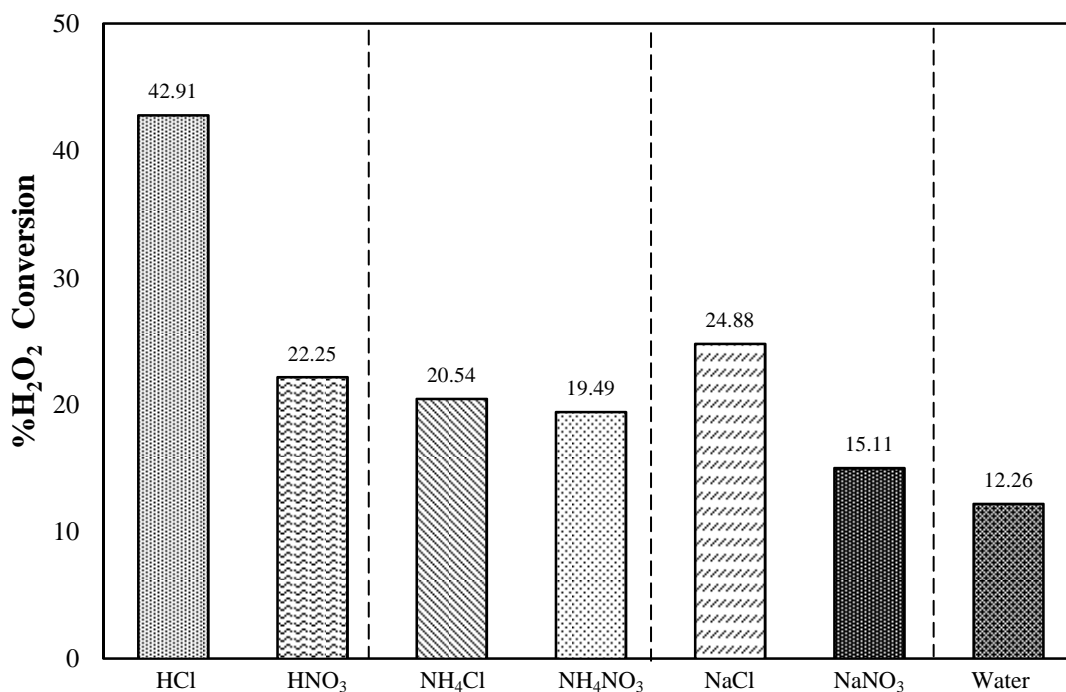


Figure 4.8 %H₂O₂ convert to product at 110°C.

Figure 4.8 demonstrates effects of ions on the oxidation reaction between toluene and H₂O₂. The results are grouped into three groups: proton group, ammonium group and sodium group. The experimental results in the presence of ions give the H₂O₂ conversion higher than in the absence ions since ions affect the equilibrium concentration and the solubility rate of toluene. When considering each group found that the acidic solution/ionic salt solution that have chloride ion, give the H₂O₂ conversion higher than in acidic solution/ionic salt solution that have nitrate ion.

In case of proton group, the experimental results show that hydrochloric acid give the H₂O₂ conversion higher than nitric acid with respect to the solubility rate of hydrochloric acid more than nitric acid although nitric acid have the equilibrium concentration of toluene more than hydrochloric acid. These may be occurred because the equilibrium concentration of toluene at beginning the reaction determines the progress of the reaction. In this study, we make the water saturated with toluene before reacts with hydrogen peroxide. When the reaction is begun, saturated toluene in water is used in the reaction hence the solubility rate of toluene into water phase

help compensated consume toluene. It can be said that the solubility rate is an important factor in determining the forward reaction.

In case of ammonium group, the experimental result demonstrates that ammonium chloride gives the H_2O_2 conversion approximately the same as ammonium nitrate with respect to the equilibrium concentration and the solubility rate of toluene in ammonium chloride have nearby value of ammonium nitrate.

In case of sodium group, the experimental results reveal that sodium chloride solution give the H_2O_2 conversion higher than in the sodium nitrate solution. With respect to sodium chloride solution has the value of the solubility rate approximately the same as sodium nitrate solution result in the compensation rate of toluene as dissolve into aqueous phase of sodium chloride and sodium nitrate solution have the value approximately the same. But the equilibrium concentration of toluene in sodium nitrate solution is higher than sodium chloride solution. These may affect the catalyst surface in sodium nitrate solution that makes the catalyst surface is excessive covered by toluene molecules hence the H_2O_2 conversion is lower than sodium chloride.

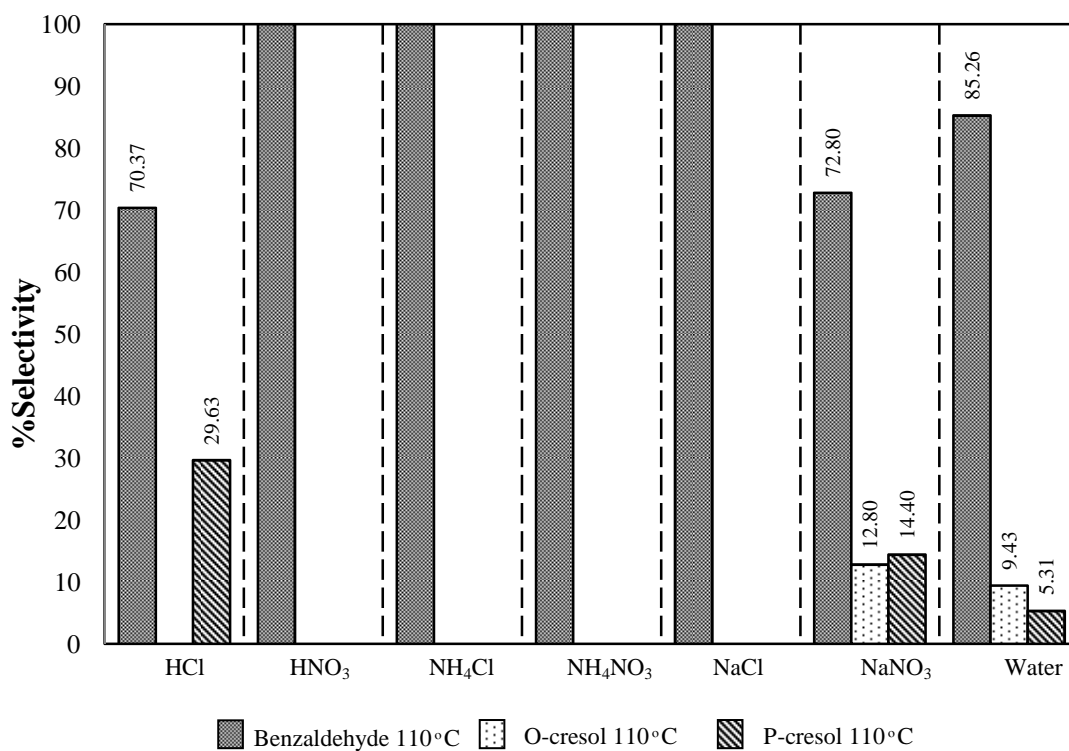


Figure 4.9 %Selectivity of product at 110°C.

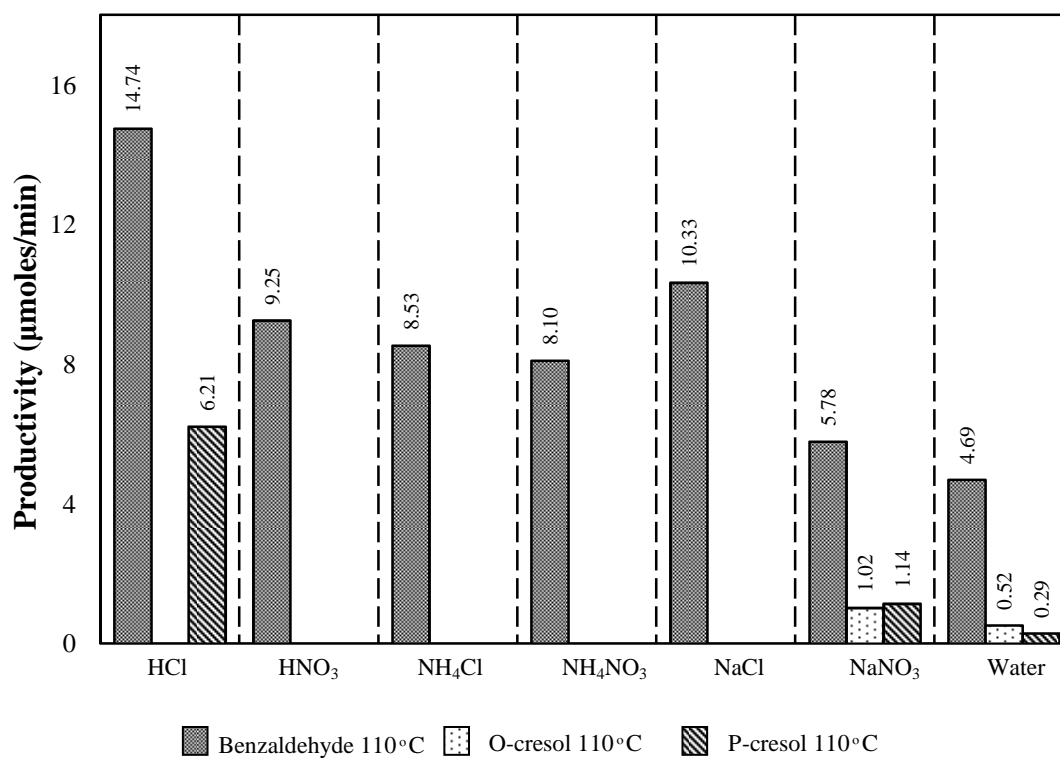


Figure 4.10 Productivity of product (μmoles/min) at 110°C.

Figure 4.9 illustrates the selectivities of products on the oxidation reaction at 110°C. It is found that the presence of ions (HNO_3 , NH_4Cl , NH_4NO_3 and NaCl) in the aqueous phase can increase the selectivity of benzaldehyde more than in the absence ions. On the contrary, the presence of hydrochloric acid and sodium nitrate will decrease the selectivity of benzaldehyde and increase the selectivity of o-cresol and p-cresol. But when comparing with nitric acid and sodium chloride will see that the selectivity of benzaldehyde increase but the selectivity of o-cresol and p-cresol decrease. In case of ammonium group, the experimental result show that ammonium chloride and ammonium nitrate can increase the selectivity of benzaldehyde and decrease the selectivity of o-cresol and p-cresol.

Figure 4.10 illustrates the productivities of products at 110°C. The experimental result reveals that the presence of ions in the aqueous phase promotes the production of benzaldehyde. When comparing the production of benzaldehyde in hydrochloric acid solution and nitric acid solution, it is observed that hydrochloric acid solution promote the production of benzaldehyde more than in nitric acid solution. Also, hydrochloric acid solution can produce p-cresol whereas nitric acid solution inhibits the production of cresol. In case of ammonium salts, it is found that the production of benzaldehyde in ammonium chloride solution has the value approximately the same as ammonium nitrate solution. Furthermore, sodium chloride solution can produce only benzaldehyde while sodium nitrate can produce benzaldehyde, o-cresol and p-cresol.

From the experimental result above, if acids/salts solution added into aqueous phase affects only the solubility of toluene, the products of the reaction would be the same. It can be said that the reaction may relate to occurrence of the reaction on the catalyst surface. For the detail of the reaction on the surface of catalyst will be explained later.

4.2.3 Effect of reaction temperature

Data of the solubility of toluene at room temperature of acidic/salt solution and the volume of acidic/salt solution for use in the reaction can be used to estimate amount of toluene dissolve into the aqueous phase. When comparing amount of toluene dissolve into the aqueous phase with amount of H_2O_2 that use in the reaction, it is found that amount of toluene in aqueous is less than the aqueous of H_2O_2 . Therefore, if amount of toluene dissolve into the aqueous phase increases, the H_2O_2 conversion should increase.

This research further increases the concentration of toluene in aqueous phase by increasing the reaction temperature. The reaction temperature used in this research is 110°C and 120°C .

Figure 4.13 illustrates the increase of the H_2O_2 conversion convert to product when the reaction temperature is increased. This phenomenon is due to the following reasons.

a) Toluene will dissolve into the acidic/salt solution which the concentration of toluene depend on the solubility of toluene in acidic/salt solution.

b) The surfaces of Al-TS-1 prefer to adsorb hydrophobic molecule, so toluene can be adsorbed on the surface of Al-TS-1 while catalyst is stirred in aqueous phase. The reaction will occur when toluene and H_2O_2 exist on the catalyst surface as shows in Figure 4.11. But the best reaction will occur when they present on the catalyst surface in the equal mole ratio because the reaction proceed following Langmuir-Hinshelwood model as shown in Figure 4.12.

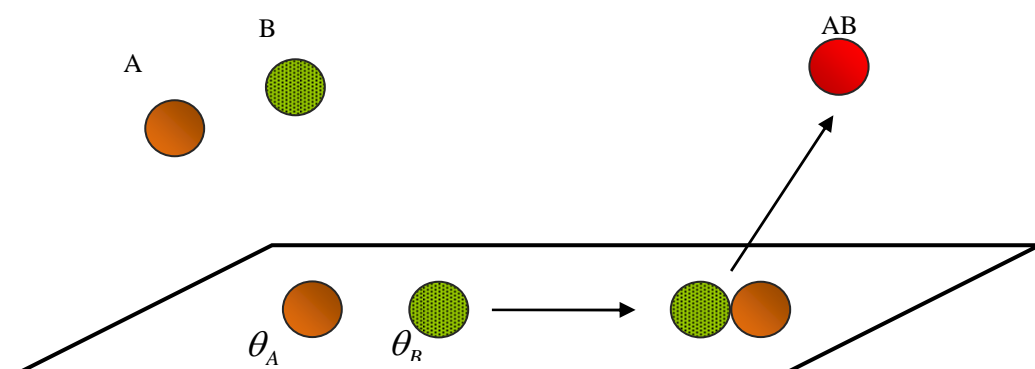


Figure 4.11 Adsorption of toluene and H_2O_2 on the surface of Al-TS-1 catalyst.

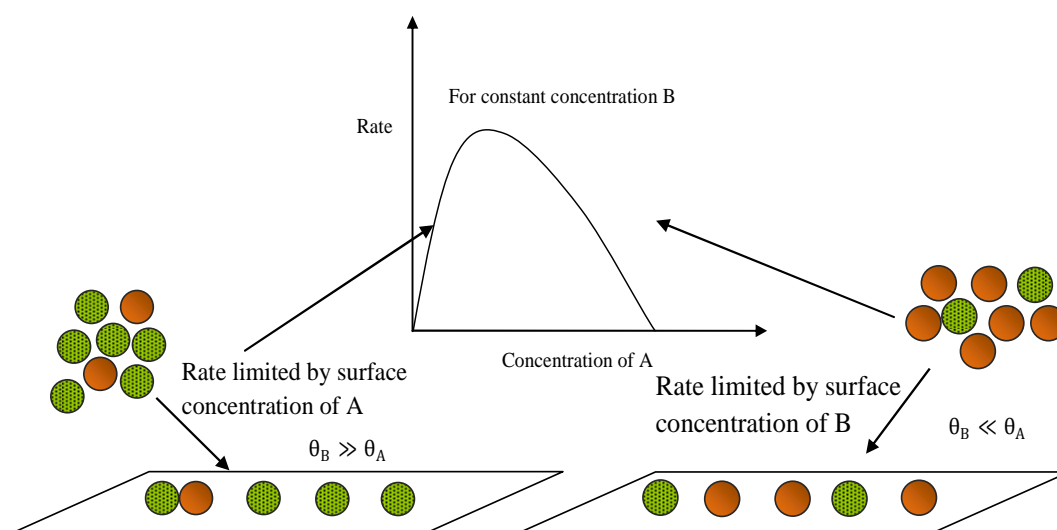


Figure 4.12 Relationship between concentration of reactant (toluene and H_2O_2) and rate of reaction follow Langmuir-Hinshelwood model.

Figure 4.12 demonstrates that the rate of reaction is low when the amount of toluene on the Al-TS-1 surface is less than the amount of H_2O_2 . If concentration of toluene on the catalyst surface increases, rate of reaction will increase until reaching a highest point, the equal mole ratio of toluene and H_2O_2 . Next, if the concentration of toluene is further increased continuously, the amount of H_2O_2 on the catalyst surface of Al-TS-1 will decrease which will result in a drop in the rate of reaction.

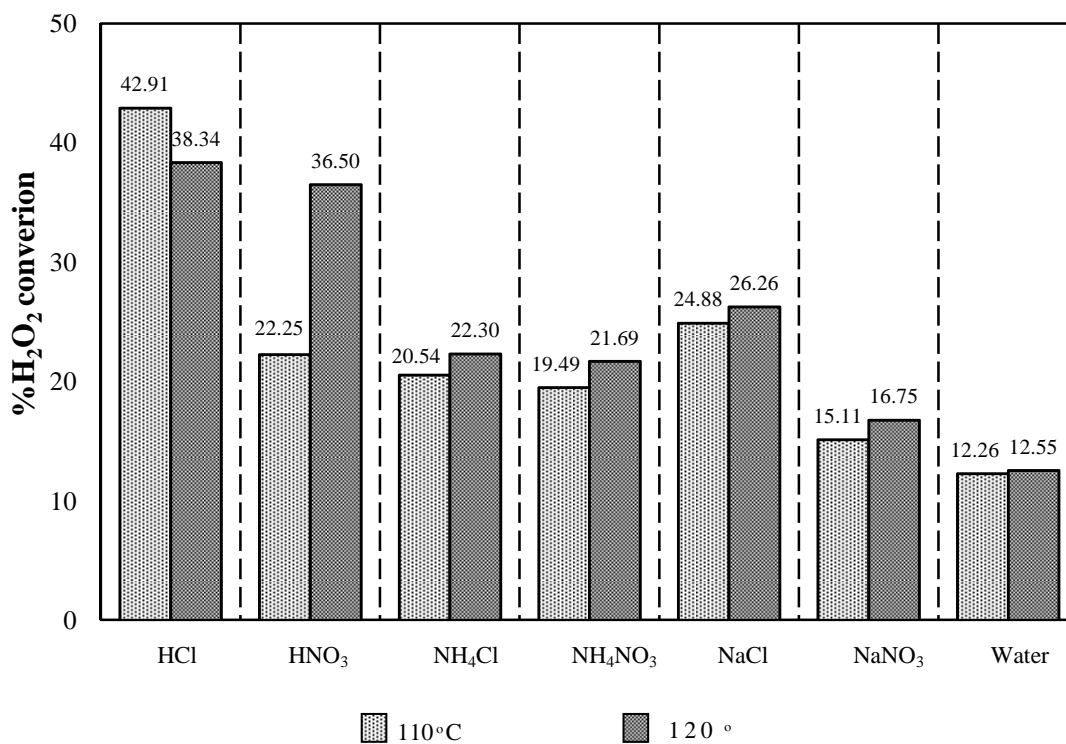


Figure 4.13 %H₂O₂ conversion at the reaction temperature 110°C and 120°C.

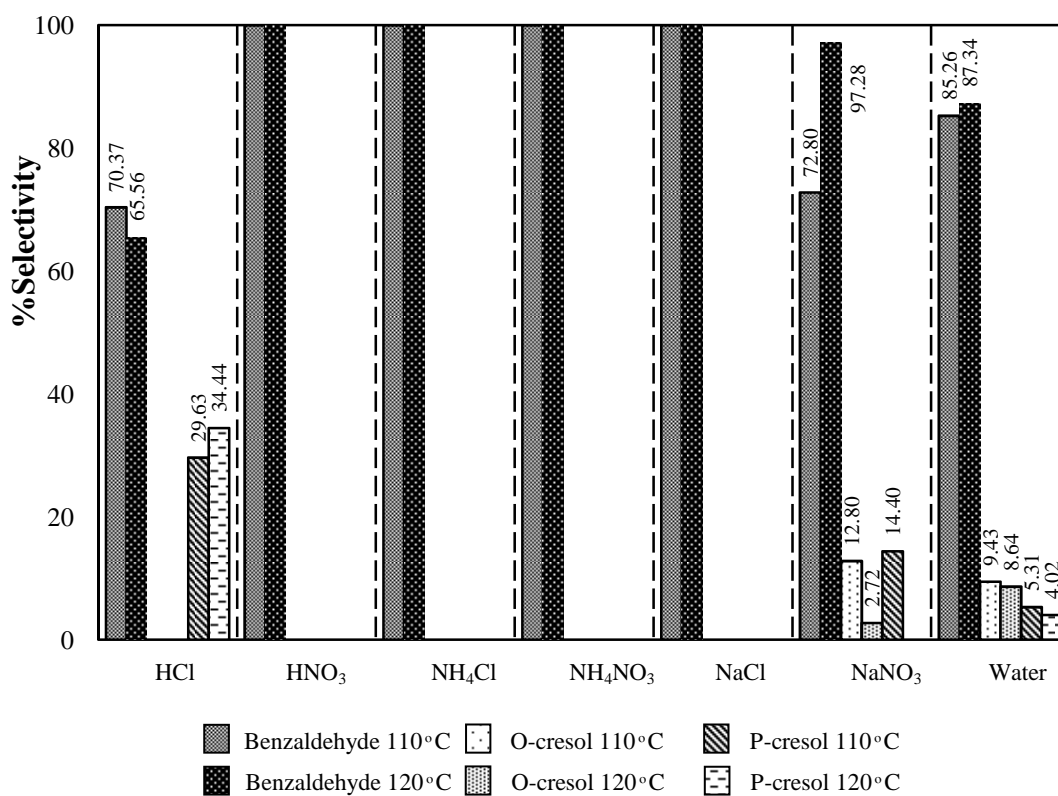


Figure 4.14 %Selectivity of product at the reaction temperature 110°C and 120°C.

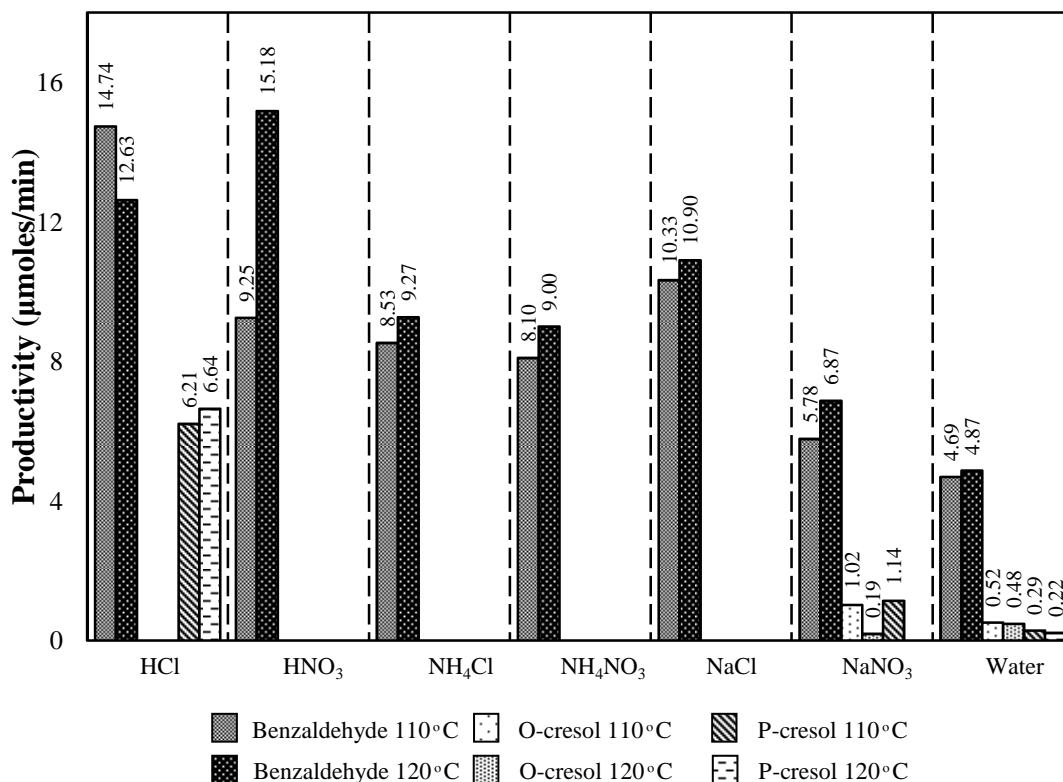


Figure 4.15 Productivity of product ($\mu\text{moles}/\text{min}$) at the reaction temperature 110°C and 120°C .

The comparison of the results of the H_2O_2 conversion between the reaction temperature 110°C and 120°C is shown in the Figure 4.13. In part of deionized water, it is observed that the H_2O_2 conversion increase with the increasing reaction temperature. Besides, the selectivity of benzaldehyde in the deionized water increases with the increasing of the reaction temperature. But the increase in reaction temperature decreases the selectivity of o-cresol and p-cresol as shown in Figure 4.14. These conform to the productivity of benzaldehyde and cresol as shown in Figure 4.15.

In case of the ammonium salt solutions, the experimental results of the H_2O_2 conversion shown in Figure 4.13 exhibit that both ammonium salt solutions give the H_2O_2 conversion increase with the increasing reaction temperature. Besides, it is found that ammonium chloride solution gives the H_2O_2 conversion approximately the same as ammonium nitrate solution. Also, the both ammonium salt solutions promote

the production benzaldehyde as shown in Figure 4.14. When consider the productivity of benzaldehyde in Figure 4.15, it is found that ammonium chloride solution is slightly higher than in the ammonium nitrate solution at 110°C and 120°C.

In part of the sodium salt solutions, the experimental results of the H_2O_2 conversion in Figure 4.13 reveal that both of the sodium salt solutions give the H_2O_2 conversion increases with the increasing of the reaction temperature. It can be observed that the H_2O_2 conversion of sodium chloride solution is higher than sodium nitrate solution. When consider the selectivity and productivity in Figures 4.14 and 4.15, it indicates that sodium chloride solution promote the production of benzaldehyde because it can produce more amount of benzaldehyde with the increasing reaction temperature. On the contrary, sodium nitrate solution promotes the production of benzaldehyde with the increasing reaction temperature. Also, it can be inhibited the production of o-cresol and p-cresol. From the effect of solubility of toluene in sodium salt, it can be recalled that the equilibrium concentration of toluene in sodium nitrate solution is higher than sodium chloride solution whereas the solubility rate of both sodium salt solution have the value approximately the same. With respect to the equilibrium concentration of toluene in sodium nitrate solution is higher than sodium chloride, it cause the opportunity of occurrence cresol more than benzaldehyde because toluene binds to the catalyst surface as more. In other words, it should be noted that two H_2O_2 molecules are required to oxidize toluene to benzaldehyde but only one molecule H_2O_2 in required producing cresol.

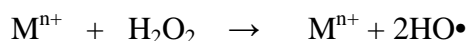
In part of the proton salt solutions, the experimental results show that the H_2O_2 conversion in Figure 4.13 of solution acidified by nitric acid increases with the increasing reaction temperature but the solution acidified by hydrochloric acid decrease with the increasing reaction temperature. When comparing the H_2O_2 conversion of solution acidified by hydrochloric acid and nitric acid, it is found that the solution acidified by hydrochloric acid gives the H_2O_2 conversion higher than the solution acidified by nitric acid at 110°C and 120°C. But when consider the selectivity of products in Figure 4.14, it is observed that the selectivity of benzaldehyde in the solution acidified by nitric acid is higher than the solution acidified by hydrochloric

acid since the solution acidified by hydrochloric acid has also produce p-cresol. However, the productivity of products in the solution acidified by hydrochloric acid at 110°C and 120°C is higher than in the solution acidified by nitric acid as shown in Figure 4.15. From the results of the oxidation reaction of toluene in the solution acidified by hydrochloric, it can be observed that behaviors of reaction differ from other solutions. Thus, it may be possible that the mechanism of reaction for the solution acidified by hydrochloric differ from the other acidic/salt solutions.

4.3 Proposed mechanism for the reaction occurs in aqueous phase additional by hydrochloric acid

In general, the oxidation reaction between toluene and H₂O₂ gives three products: benzaldehyde, o-cresol and p-cresol for the reaction in de-ionized water. However, the experimental results of acid/salt solution not only affect the solubility of toluene but also effect of the oxidation reaction. Especially, the experimental of the oxidation reaction of toluene in hydrochloric acid solution has different product distribution. The products in the reaction are benzaldehyde and p-cresol. No o-cresol is observed. It can be said the reaction may relate to occurrence of the reaction on the surface of catalyst.

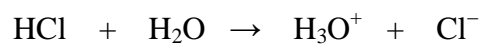
In fact, the oxidation reaction of toluene is occurred from toluene react with free radicals which free radicals are generated from the decomposition of hydrogen peroxide by the presence of some cations.



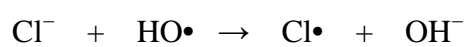
The experimental result in case of hydrochloric acid found that the reaction do not produce o-cresol in spite of the chance to occur at o-cresol is more than the para site since there is only one para site but two ortho sites and methyl group is not a large group. Therefore, if oxidant occurred in bulk fluid, the oxidant should react at the ortho site more than the para site. Because of this, it is hypothesized that the oxidant is probably not free radicals in fluid phase but it is probable the substance as occurred

and hold on the catalyst surface. In addition, the oxidant will react with toluene when toluene must be turned the para site to the oxidant. The mechanism for the formation oxidant is proposed:

Step I



Step II



Step III



Moreover, they may not only have the ability to oxidize different from H_2O_2 , but also has the ability to seize the surface of the catalyst with H_2O_2 .

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The present work investigates effect of ions in electrolyte solution on the oxidation reaction of toluene to benzaldehyde over Al-TS-1 catalyst. The conclusions and recommendations for future study are presented following sections 5.1 and 5.2, respectively.

5.1 Conclusions

1. The oxidation reaction between toluene and hydrogen peroxide give bezaldehyde as main product and cresols as by products.
2. The addition of acid or salt solution into water helps to increase the solubility of toluene.
3. An order emerge as a function of anion character for all salt that nitrate ion affect the equilibrium concentration and the solubility rate of toluene more than chloride ion.
4. The H_2O_2 converts to product depend on type of acid/salt solution adding into aqueous phase and the reaction temperature.

5.2 Recommendations

From the previous conclusions, the following proposed recommendation for the future studies.

1. The experimental should carry out at increasing reaction temperature.

2. The catalyst TS-1 should be added the other second metal since ion arises from acidic/salt solution may affect the catalyst surface.
3. The concentration of acidic/salt solution should increase or decrease in order to investigate effect of the hydrogen peroxide converts to product.
4. The future research should investigate the occurrence of the reaction on the catalyst surface.
5. The future research should investigate effect of hypochlorous acid (HOCl) to affects the occurrence of the reaction on the surface of catalyst.

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

The calculation is based on weight of sodium silicalite ($\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) in B1 and B2 solutions.

$$\text{Molecular Weight of Si} = 28.0855$$

$$\text{Molecular Weight of SiO}_2 = 60.0843$$

$$\text{Weight percent of SiO}_2 \text{ in sodium Silicate} = 28.5$$

Using Sodium Silicate 69 g with 45 g of water as B1 solution,

$$\begin{aligned} \text{Mole of Si is used} &= \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W. of Si})}{(\text{M.W. of SiO}_2)} \times \frac{(1 \text{ mole})}{(\text{M.W. of Si})} \\ &= 69 \times (28.5/100) \times (1/60.0843) \\ &= 0.3273 \end{aligned}$$

For example, to prepare Si/Ti atomic ratio of 50 by using $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ for titanium source.

$$\text{Molecular weight of Ti} = 47.88$$

$$\text{Molecular weight of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 = 340.36$$

$$\text{Weight \% purities of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 = 97$$

Si/Ti atomic ratio = 50

$$\begin{aligned} \text{Mole of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 \text{ required} &= 0.3273/50 \\ &= 6.546 \times 10^{-3} \quad \text{mole} \end{aligned}$$

$$\begin{aligned} \text{The amount of Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 &= (6.546 \times 10^{-3}) \times (340.36) \times (100/97) \\ &= 2.2970 \text{ g} \end{aligned}$$

For example, to prepare Si/Al atomic ratio of 150 by using $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ for cobalt source.

$$\text{Molecular weight of Al} = 26.98$$

$$\text{Molecular weight of Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} = 375.13$$

Si/Al atomic ratio = 150

$$\text{Mole of Al(NO}_3)_3 \cdot 9\text{H}_2\text{O required} = 0.3273/150$$

$$= 2.18 \times 10^{-3} \text{ mole}$$

$$\text{The amount of Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} = (2.18 \times 10^{-3}) \times (375.13)$$

$$\text{This is used in A1 and A2 solutions.} = 0.82 \text{ g}$$

APPENDIX B

CALIBRATION CURVES

Appendix B shows the calibration curves for calculation of products in the oxidation reaction between toluene and hydrogen peroxide. The products are benzaldehyde, o-cresol and p-cresol.

The samples are analyzed by a gas chromatograph (Shimadzu GC 9A) equipped with a FID and a GP 10% SP-2100 packed column to determine the concentration of toluene and the products of the reaction.

The concentrations of toluene in y-axis and area reported by gas chromatograph in x-axis are exhibited in the curves. The calibration curve of toluene is illustrated in the following figure.

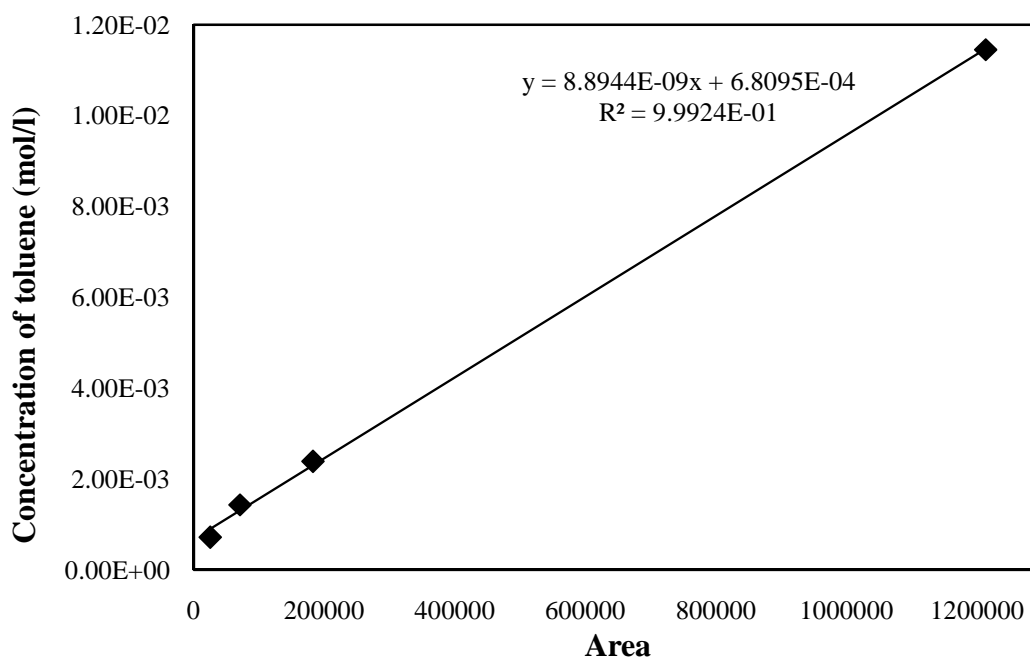


Figure B1 The calibration curve of toluene.

Mole of the products in y-axis and area reported by gas chromatograph in x-axis are exhibited in the curves. The calibration curves of benzaldehyde, o-cresol and p-cresol are illustrated in the following figures.

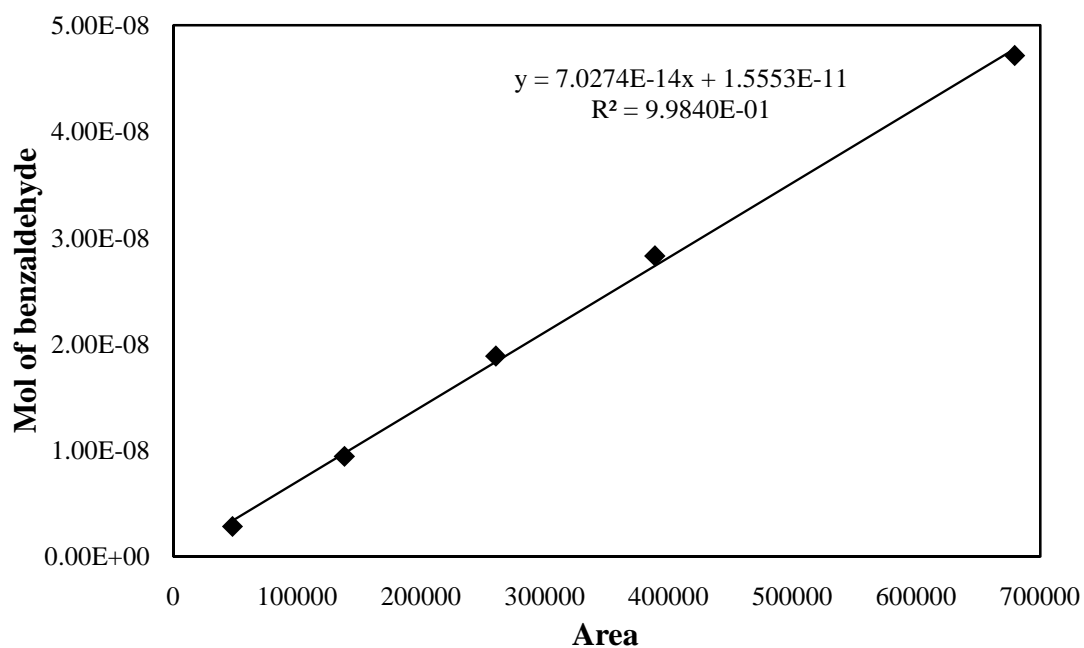


Figure B2 The calibration curve of benzaldehyde.

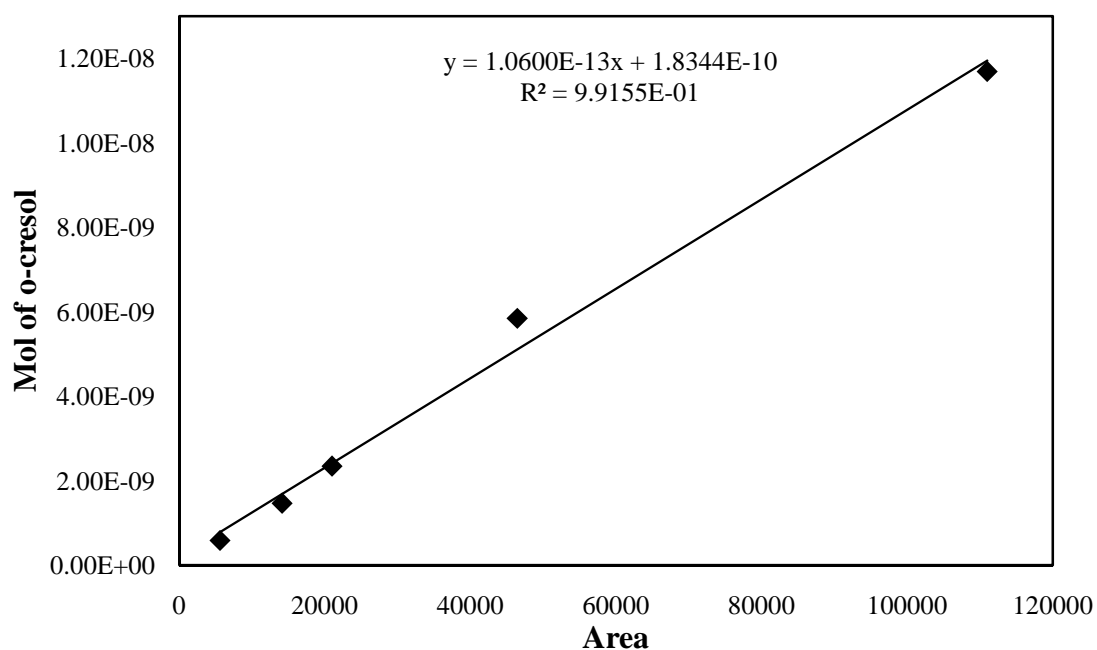


Figure B3 The calibration curve of o-cresol.

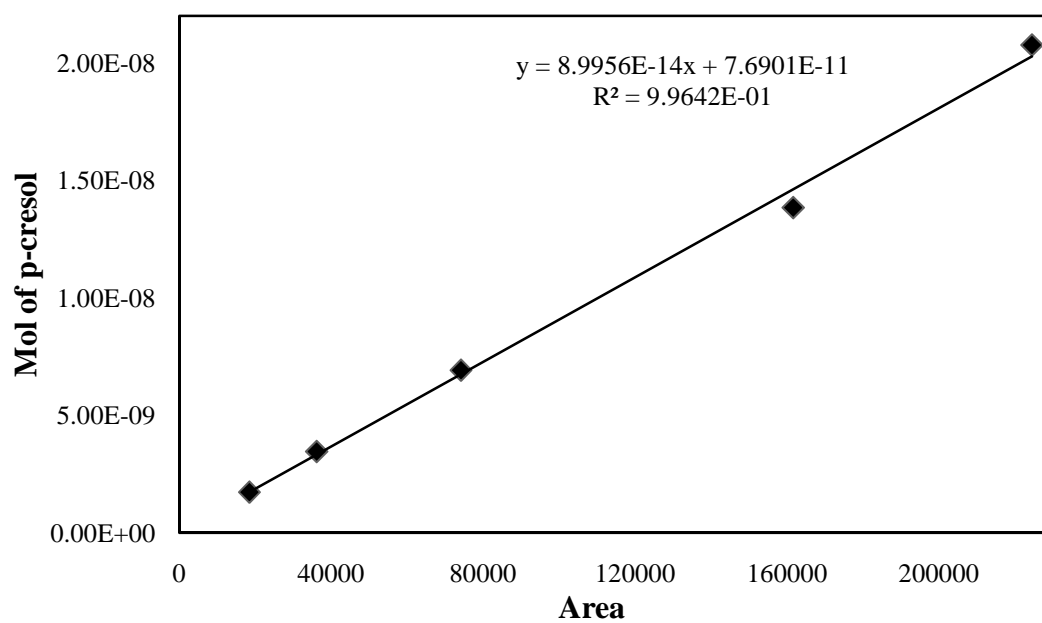


Figure B4 The calibration curve of p-cresol.

APPENDIX C

CALCULATION OF CONVERSION AND PRODUCT SELECTIVITY

The overall mole of H_2O_2 can be calculated as follows:

$$N_{H_2O_2} = \frac{\text{Volume of } H_2O_2 \text{ feeding} \times \text{Density of } H_2O_2}{\text{Molecular weight of } H_2O_2}$$

$$N_{H_2O_2} = \frac{\text{Volume of } H_2O_2 \text{ feeding} \times 1.110}{34.0147} \quad (C1)$$

In addition, the overall mole of products: benzaldehyde, o-cresol and p-cresol in the reaction can be calculated as follows:

$$N_i = \frac{n_i \times V_{all}}{V_{inj}} \quad (C2)$$

Where;

- N_i = the overall mole of product in the solution
 - i,j,k = benzaldehyde, o-cresol and p-cresol respectively
 - n_i = Mole of product of the sample inject into GC
 - V_{all} = Total volume of solution before injection into GC
 - V_{inj} = Volume of the sample inject into GC
- (In this case equal to 5 μ l)

Mole of products of the sample inject into GC can be calculated employing the calibration curves in Figures B2, B3 and B4 reported previously in **Appendix B** as follows:

$$\text{Mole of benzaldehyde } (n_B) = \left[(7.0274 \times 10^{-14}) \times \text{Area} \right] + (1.5553 \times 10^{-11}) \quad (\text{C3})$$

$$\text{Mole of o-cresol } (n_o) = \left[(1.0600 \times 10^{-13}) \times \text{Area} \right] + (1.8344 \times 10^{-10}) \quad (\text{C4})$$

$$\text{Mole of p-cresol } (n_p) = \left[(8.9956 \times 10^{-14}) \times \text{Area} \right] + (7.6901 \times 10^{-11}) \quad (\text{C5})$$

Total volume of solution before injection into GC can be calculated as following:

$$\begin{aligned} \text{Total volume of solution } (V_{\text{all}}) &= \text{vol. of acidic/salt solution} + \text{vol. of toluene} + \\ &\quad \text{vol. of H}_2\text{O}_2 + \text{vol. of water} + \text{vol. of ethanol} \\ &= 120 \text{ ml} + 1.1 \text{ ml} + 1 \text{ ml} + 1 \text{ ml} + 80 \text{ ml} \\ &= 203.1 \text{ ml of solution} \end{aligned}$$

Therefore, the overall mole of product in the solution

$$N_i = \left(n_i \times \left[\frac{(203.1 \text{ ml})}{5 \mu\text{l}} \right] \times \left(\frac{1000 \mu\text{l}}{1 \text{ ml}} \right) \right)$$

APPENDIX D

DATA OF EXPERIMENTS

Table D1 The percentage of hydrogen peroxide conversion.

Solution	%H ₂ O ₂ conversion	
	110 °C	120 °C
HCl	42.91	38.34
HNO ₃	22.25	36.50
NH ₄ Cl	20.54	22.30
NH ₄ NO ₃	19.49	21.69
NaCl	24.88	26.26
NaNO ₃	15.11	16.75
Deionized water	12.26	12.55

Table D2 The percentage of selectivity of product at 110°C and 120°C.

Solution	%Selectivity					
	Benzaldehyde		O-cresol		P-cresol	
	110°C	120°C	110°C	120°C	110°C	120°C
HCl	70.37	65.56	0	0	29.63	34.44
HNO ₃	100	100	0	0	0	0
NH ₄ Cl	100	100	0	0	0	0
NH ₄ NO ₃	100	100	0	0	0	0
NaCl	100	100	0	0	0	0
NaNO ₃	72.80	97.28	12.80	2.72	14.4	0
Deionized water	85.26	87.34	9.43	8.64	5.31	4.02

Table D3 The percentage of productivity of product at 110°C and 120°C.

Solution	%Productivity					
	Benzaldehyde		O-cresol		P-cresol	
	110°C	120°C	110°C	120°C	110°C	120°C
HCl	14.74	12.63	0	0	6.21	6.64
HNO ₃	9.25	15.18	0	0	0	0
NH ₄ Cl	8.53	9.27	0	0	0	0
NH ₄ NO ₃	8.10	9.00	0	0	0	0
NaCl	10.33	10.90	0	0	0	0
NaNO ₃	5.78	6.87	1.02	0.19	1.14	0
Deionized water	4.69	4.87	0.52	0.48	0.29	0.22

APPENDIX E

MATERIAL SAFETY DATA SHEET

Material safety data sheet in the Appendix E consist of material safety data sheet of chemical substance used in the experimental. For example, toluene, hydrogen peroxide, hydrochloric acid, nitric acid, ammonium chloride, ammonium nitrate, sodium chloride and sodium nitrate. The origin of the document: <http://www.sciencelab.com>

I. Toluene

General

Synonyms	: Toluol, Tolu-Sol; Methylbenzene; Methacide; Phenylmethane; Methylbenzol
Molecular formula	: C ₆ H ₅ CH ₃

Physical data

Appearance	: colourless liquid with Sweet, pungent, Benzene-like odour
Molecular Weight	: 92.14 g/mole
Melting Point	: -95°C (-139°F)
Boiling Point	: 110.6°C (231.1°F)
Critical Temperature	: 318.6°C (605.5°F)
Specific Gravity	: 0.8636 (Water = 1)
Vapor Pressure	: 3.8 kPa (at 25°C)
Vapor Density	: 3.1 (Air = 1)
Volatility	: Not available.
Dispersion Properties	: See solubility in water, diethyl ether, acetone

Density (g cm ⁻³)	: 0.903
Flash point	: 54 °C
Explosion limits	: 1.9 - 6.1 %
Solubility in water	: 0.561 g/l at 25 °C

Stability

Stability	: The product is stable.
Instability Temperature	: Not available.
Conditions of Instability	: Heat, ignition sources (flames, sparks, static), incompatible materials
Incompatibility with various substances	: Reactive with oxidizing agents. Corrosivity: Non-corrosive in presence of glass

Toxicology

The routes of entry into body are absorbed through skin, dermal contact, eye contact, inhalation and ingestion.

Acute potential health effects:

Skin	: Causes mild to moderate skin irritation. It can be absorbed to some extent through the skin.
Eyes	: Causes mild to moderate eye irritation with a burning sensation. Splash contact with eyes also causes conjunctivitis, blepharospasm, corneal edema, corneal abrasions
Inhalation	: Inhalation of vapor may cause respiratory tract irritation causing coughing and wheezing, and nasal discharge.
Ingestion	: Aspiration hazard. Aspiration of Toluene into the lungs may cause chemical pneumonitis.

Personal protection

Safety glasses, good ventilation.

II. Hydrogen Peroxide 30%**General**

Synonyms	: Peroxide, 100 volume peroxide, Hydrogen dioxide solution, Hydrogen peroxide, 30%, unstabilized, Hydrogen Peroxide, 30%
Molecular formula	: H_2O_2

Physical data

Appearance	: colour less liquid
Taste	: Slightly acid. Bitter
Molecular Weight	: 34.0147 g/mol
Color	: Clear Colorless.
pH (1% soln/water)	: Not available
Boiling Point	: 108°C (226.4°F)
Melting Point	: -33°C (-27.4°F)
Critical Temperature	: Not available.
Specific Gravity	: 1.1 (Water = 1)
Vapor Pressure	: 3.1 kPa (at 20°C)
Vapor Density	: 1.1 (Air = 1)
Melting point	: -28°C
Boiling point	: 114°C
Specific gravity	: typically near 1.19
Vapour pressure	: 23.3 °C at 30°C
Dispersion Properties	: See solubility in water, diethyl ether.

Solubility : Easily soluble in cold water. Soluble in diethyl ether.

Stability

Stability : The product is stable. It contains a stabilizer.

Instability Temperature : Not available.

Conditions of Instability : Excess heat, incompatible materials

Incompatibility with various substances : Reactive with reducing agents, combustible materials, organic materials, metals, acids, alkalis

Corrosivity : Non-corrosive in presence of glass.

Toxicology

The routes of entry into body are absorbed through skin and eye contact. Acute potential health effects on skin causes severe skin irritation and possible burns. Absorption into skin may affect behavior/central nervous system (tremor, ataxia, and convulsions), respiration (dyspnea, pulmonary emboli) and brain. Furthermore, the effect on eyes causes severe eye irritation, superficial clouding, corneal edema, and may cause burns.

Hazards Identification

Hydrogen peroxide is strong oxidizer when contact with other material may cause a fire.

Personal protection

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

III. Hydrochloric acid

General

Synonyms	: Hydrochloric Acid; Muriatic Acid
Molecular formula	: HCl

Physical data

Physical state	: Colorless to light yellow liquid.
Odor	: Pungent. Irritating (Strong.)
Molecular Weight	: 36.46 g/mol
pH (1% sol/water)	: Acidic.
Boiling Point	: 108.58 °C at 760 mm Hg (for 20.22% HCl in water) 83 °C at 760 mm Hg (for 31% HCl in water) 50.5 °C (for 37% HCl in water)
Melting Point	: -62.25 °C (20.69% HCl in water) -46.2 °C (31.24% HCl in water) -25.4 °C (39.17% HCl in water)
Vapor Pressure	: 16 kPa (at 20 °C) average
Vapor Density	: 1.267 (Air = 1)
Dispersion Properties	: See solubility in water, diethyl ether.
Solubility	: Soluble in cold water, hot water, diethyl ether.

Stability

Stability	: The product is stable.
Instability Temperature	: Not available.
Conditions of Instability	: Incompatible materials, water

Incompatibility with various substances	:Highly reactive with metals. Reactive with oxidizing agents, organic materials, alkalis.
Corrosivity	: Extremely corrosive in presence of aluminum, of copper, of stainless steel(304), of stainless steel(316). Non-corrosive in presence of glass.

Toxicology

The routes of entry into body are absorbed through skin, dermal contact, eye contact and inhalation. Acute potential health effects on skin are corrosive cause severe skin irritation and burns. The effect on eyes corrosive causes severe eye irritation/conjunctivitis, burns, corneal necrosis. In addition, effect on inhalation may be fatal. Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract.

First Aid Measures

Eye Contact:

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin Contact:

In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

IV. Nitric acid

General

Synonyms	: Hydrogen nitrate; Azotic acid; Rfna; Aqua fortis; Fuming nitric acid; Red fuming nitric acid; Nital; Nitryl Hydroxide; Nitric acid red fuming; Nitric acid, other than red fuming;
Molecular formula	: HNO ₃

Physical data

Physical state	: Colorless to light yellow liquid.
Odor	: Acrid. Disagreeable and choking.
Molecular Weight	: 63.01 g/mol
pH (1% soln/water)	: Acidic.
Boiling Point	: 121°C (249.8°F)
Melting Point	: -41.6°C (-42.9°F)
Specific Gravity	: 1.408 (Water = 1)
Vapor Pressure	: 6 kPa (at 20°C)
Vapor Density	: 2.5 (Air = 1)
Dispersion Properties	: See solubility in water, diethyl ether.
Solubility	: Easily soluble in cold water, hot water.

Stability

Stability	: The product is stable.
Instability Temperature	: Not available.
Conditions of Instability	: Incompatible materials

Incompatibility with various substances	:Highly reactive with alkalis. Reactive with reducing agents, combustible materials, organic materials, metals, acids.
Corrosivity	: Extremely corrosive in presence of aluminum, of copper, of brass. Non-corrosive in presence of glass, of stainless steel.

Toxicology

The routes of entry into body are absorbed through skin, dermal contact, eye contact, inhalation and ingestion. Other Toxic Effects on Humans are extremely hazardous in case of inhalation (lung corrosive), very hazardous in case of skin contact (corrosive, irritant, permeator), of eye contact (corrosive), of ingestion.

First Aid Measures

Eye Contact:

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin Contact:

In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

V. Ammonium chloride

General

Synonyms	: Ammonium Chloratum; Ammonium Chloridum; Ammonium Muriate; Sal Ammonia; Salmiac
Molecular formula	: NH_4Cl

Physical data

Physical state	: Solid. (Solid crystalline powder.)
Odor	: Odorless. (Slight.)
Taste	: Cooling, Saline.
Molecular Weight	: 53.49 g/mol
Color	: White.
pH (1% soln/water)	: 5.5 [Acidic.]
Boiling Point	: 520°C (968°F)
Melting Point	: Decomposition temperature: 338°C
Specific Gravity	: 1.53 (Water = 1)
Dispersion Properties	: See solubility in water, methanol.
Solubility	: Soluble in cold water, hot water, methanol. Insoluble in diethyl ether, acetone.

Stability

Stability	: The product is stable.
Instability Temperature	: Not available.
Conditions of Instability	: Incompatible materials, moisture.
Incompatibility with various substances	: Reactive with oxidizing agents, acids, alkalis.

Corrosivity :Extremely corrosive in presence of copper.
Corrosive in presence of steel, of stainless steel.

Toxicology

The routes of entry into body are inhalation and ingestion. Acute potential health effects are skin. It can cause skin irritation which is usually mild. In case of eyes, it causes moderate eye irritation. In case of inhalation, it can cause respiratory tract and mucous membrane irritation which is usually mild. In case of ingestion, it may be harmful if swallowed.

First Aid Measures (<http://www.tps.com.au/msds>)

Swallowed : If conscious wash out mouth with water. Seek medical advice

Eye : Immediately hold eyelids open and flood with water for at least 15 minutes. Obtain medical aid.

Skin : Remove contaminated clothing. Immediately wash skin thoroughly with water and mild soap.

Inhaled : Remove from contaminated air. Maintain breathing with artificial respiration if necessary.

VI. Ammonium nitrate

General

Synonyms	: Ammonium Saltpeter; Nitric acid, ammonium salt
Molecular formula	: NH_4NO_3

Physical data

Physical state and appearance	: Solid. (white granular solid.)
Odor	: Odorless.
Molecular Weight	: 80.05 g/mole
pH (1% soln/water)	: 4.5 - 6.0 at 25 deg.
Boiling Point	: Decomposition temperature: 210 °C
Melting Point	: 169.6 °C
Specific Gravity	: 1.725 (Water = 1)
Dispersion Properties	: See solubility in water, methanol, acetone.
Solubility	: Easily soluble in cold water, hot water. Soluble in acetone. Partially soluble in methanol. Insoluble in diethyl ether.

Stability

Stability	: The product is stable.
Instability Temperature	: Not available.
Conditions of Instability	: Incompatible materials
Corrosivity	: Non-corrosive in presence of glass.

Incompatibility with
various substances

: Reactive with reducing agents, combustible materials, organic materials, metals,alkalis.

Toxicology

Routes of Entry

: Absorbed through skin, inhalation or ingestion.

First Aid Measures

Eye Contact

: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention.

Skin Contact

: In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient.Remove contaminated clothing and shoes. Cold water may be used. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Inhalation

: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen.

VII. 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⁻³) : 2.16

Solubility in water : 35.7 g/100g at °C

Stability

Stability : The product is stable.

Conditions of instability : Incompatible materials, high temperatures.

Incompatibility with various substances : Reactive with oxidizing agents, metals, acids.

Corrosivity : Not considered to be corrosive for metals and glass.

Toxicology (<http://grice.cofc.edu/pdf/MSDS>)

Potential Health Effects

Inhalation : May be harmful if inhaled. May cause respiratory tract irritation.

Skin : May be harmful if absorbed through skin. May cause skin irritation.

Eyes : May cause eye irritation.

Ingestion : May be harmful if swallowed.

First Aid Measures (<http://www.bioeng.nus.edu.sg>)

After inhalation	: Fresh air
After skin contact	: wash off with plenty of water. Remove contaminated clothing.
After eye contact	: rinse out with plenty of water with the eyelid held wide open.
After swallowing	: make victim drink plenty of water. Consult doctor if feeling unwell.

VIII. Sodium nitrate**General**

Synonyms	: Chile saltpeter; soda niter; Sodium saltpeter; Nitric acid, sodium salt; Nitratine
Molecular formula	: NaNO_3

Physical data

Physical state	: Solid. (Granular solid. Powdered solid.)
Taste	: Bitter. Saline.
Molecular Weight	: 84.99 g/mole
Color	: White.
Boiling Point	: Decomposition temperature: 380°C
Melting Point	: 308 °C
Ignition temperature	: 490 °C

Specific Gravity	: 2.26 (Water = 1)
Density	: 2.168 g/cm ³
Water solubility	: 820 g/l at 20 °C

Stability (<http://www.wku.edu/msds/docs/3325.pdf>)

Chemical stability

Stable under recommended storage conditions.

Conditions to avoid

Exposure to moisture.

Materials to avoid

Acids, Powdered metals, Ammonia, Cyanides, Amines, Activated carbon

Toxicology (<http://www.wku.edu/msds/docs/3325.pdf>)

Potential health effects

Inhalation : May be harmful if inhaled. Causes respiratory tract irritation.

Ingestion : Toxic if swallowed.

Skin : May be harmful if absorbed through skin.
Causes skin irritation.

Eyes : Causes eye irritation.

First aid measures (<http://www.wku.edu/msds/docs/3325.pdf>)

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance. Move out of dangerous area.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Wash off with soap and plenty of water. Take victim immediately to hospital. Consult a physician.

In case of eye contact

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed

Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

VITA



Miss Sunantha Kaenthong was born on October 11th, 1988 in Nakhon Si Thammarat, Thailand. She finished high school from Triam Udom Suksa School of the South in 2006, and received the bachelor's degree of Chemical Engineering from Prince of Songkla University in 2009. She continued her master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University on June, 2010. She participated in the 21th Thailand Chemical Engineering and Applied Chemistry Conference (TIChE) in the topic "Effect of acids on the oxidation reaction of toluene to benzaldehyde over Al-TS-1 catalyst" on November, 10-11, 2011 at Hatyai, Songkhla, Thailand.