ผลของชนิดและความเข้มข้นไอออนต่อการออกซิไดซ์โทลูอีนไปเป็นเบนซัลดีไฮด์บนตัวเร่งปฏิกิริยา Al-TS-1

นางสาวปาริฉัตร พงศ์จิรวัฒน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ปีการศึกษา 2556

EFFECT OF ION TYPES AND ION CONCENTRATIONS ON THE OXIDATION REACTION OF TOLUENE TO BENZALDEHYDE OVER AL-TS-1 CATALYST

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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Thesis Title	EFFECT OF ION TYPES AND ION CONCENTRATIONS ON THE OXIDATION REACTION OF TOLUENE TO BENZALDEHYDE OVER AL-TS-1 CATALYST
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ปาริฉัตร พงศ์จิรวัฒน์ : ผลของชนิดและความเข้มข้นไอออนต่อการออกซิไดซ์โทลูอีนไปเป็นเบนซัลดีไฮด์บนตัวเร่งปฏิกิริยา Al-TS-1. (EFFECT OF ION TYPES AND ION CONCENTRATIONS ON THE OXIDATION REACTION OF TOLUENE TO BENZALDEHYDE OVER AL-TS-1 CATALYST) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ธราธร มงคลศรี, 67 หน้า.

งานวิจัยนี้ได้ทำการศึกษาผลของชนิดไอออนและความเข้มข้นไอออนในปฏิกิริยาออกซิเดชันระหว่างระหว่างโทลูอีนและไฮโดรเจนเปอร์ออกไซด์โดยใช้ตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 ที่ได้รับการปรับปรุงด้วยโลหะอะลูมิเนียมเป็นตัวเร่งปฏิกิริยา ตัวเร่งปฏิกิริยาเตรียมโดยวิธีไฮโดรเทอร์มอลและทำการวิเคราะห์คุณลักษณะด้วยเทคนิค XRF, BET, FT-IR, และ XRD ทำปฏิกิริยาที่อุณหภูมิสูงในเครื่องปฏิกรณ์แบบปั่นกวน ผลที่ได้จากการศึกษาพบว่าหากเพิ่มความเข้มข้นไอออนให้สูงมากขึ้นจะเป็นการเพิ่มการละลายของโทลูอีนในเฟสน้ำได้มากขึ้น อีกทั้งอัตราการเกิดปฏิกิริยาจะเพิ่มสูงขึ้นตามแบบจำลองแลงเมียร์-ฮินเชลวูดโดยสารตั้งต้นต้องดูดซับบนพื้นผิวของตัวเร่งปฏิกิริยาในปริมาณที่เหมาะสมกับการเกิดปฏิกิริยา หากมีสารตั้งต้นชนิดหนึ่งมากเกินพอบนพื้นผิวของตัวเร่งปฏิกิริยาจะทำให้ค่าการเกิดผลิตภัณฑ์ที่ลดลง ดังนั้นความเข้มข้นไอออนจึงส่งผลต่อการเกิดปฏิกิริยา นอกจากนี้การพยายามเพิ่มปริมาณไฮโดรเจนเปอร์ออกไซด์ซึ่งเป็นสารตั้งต้นถูกทดสอบโดยการเพิ่มเวลาในการทำปฏิกิริยาและการลดปริมาณไฮโดรเจนเปอร์ออกไซด์ พบว่าได้ปริมาณผลิตภัณฑ์ที่เท่าเดิมหรือเพิ่มสูงเล็กน้อย แสดงว่าอาจมีปัจจัยอื่นที่ส่งผลทำให้ปฏิกิริยาไม่สามารถนำไฮโดรเจนเปอร์ออกไซด์มาใช้ได้สมบูรณ์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

ปีการศึกษา 2556

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PARICHAT PONGJIRAWAT: EFFECT OF ION TYPES AND ION CONCENTRATIONS ON THE OXIDATION REACTION OF TOLUENE TO BENZALDEHYDE OVER AL-TS-1 CATALYST. ADVISOR: ASSOC. PROF. THARATHON MONGKHONSI, Ph.D., 67 pp.

This research studies effects of ion types and ion concentrations 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 XRF, BET, FT-IR, and XRD techniques. The reaction is carried out at elevated temperatures in a pressurized autoclave reactor. It is found that increasing ion concentrations solution not only increases the concentration of toluene in an aqueous phase but also increases the reaction rate following the mechanism of a Langmuir-Hinshelwood. The amount of reactants on the catalyst surface must be appropriately controlled to achieve the highest reaction rate. If most of the catalyst surface is covered by one reactant, this will lead to decreasing of product. Therefore, ion concentrations have affected reaction rate. Moreover, we attempt to increase the consumption of hydrogen peroxide by increasing reaction time and decreasing amount of hydrogen peroxide. The results show that the amount of hydrogen peroxide converted to benzaldehyde is about the same or slightly increase. It may have the significant factors that affect the reaction; hence, hydrogen peroxide does not complete consumption.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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CHAPTER 1

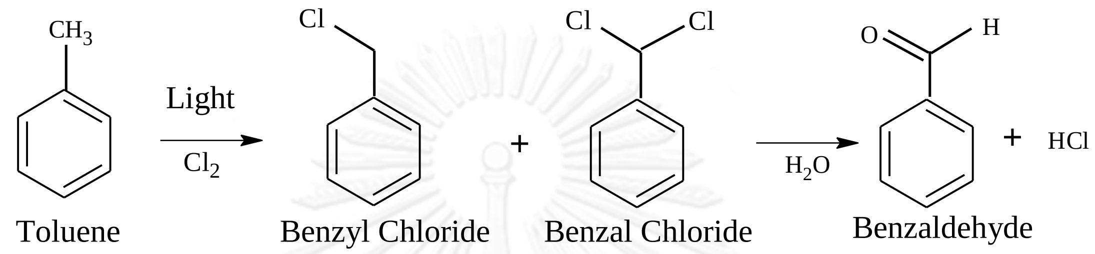
INTRODUCTION

1.1 Rational

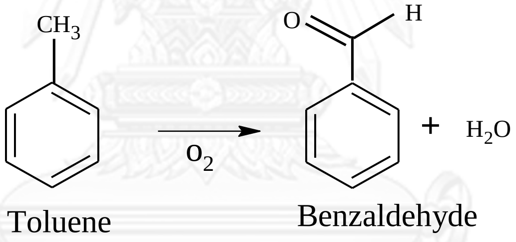
Benzaldehyde (C_6H_5CHO) is an organic compound consisting of a benzene ring which a hydrogen atom is substituted with formyl group (COH). The characteristic chemical property of benzaldehyde is colorless liquid and has almond-like odor. In addition, it can be extracted from a number of natural sources such as apricot, cherry laurel leaves and peach seeds. Benzaldehyde is used as synthetic flavoring material and as a significant chemical intermediate in the manufacture of dyes, flavoring chemicals, perfumes and pharmaceuticals. Furthermore, it is used chiefly as a precursor to other organic compounds such as synthesis of mandelic acid.

Benzaldehyde is mainly produced by the chlorination of toluene and the partial oxidation of toluene. In addition, there are other several manufacturing processes (e.g., the oxidation or dehydrogenation of benzyl alcohol, the hydrolysis of mixtures of benzyl chloride and benzal chloride or the reduction of benzoyl chloride), but these processes have no importance in the industry [1].

Commercially, benzaldehyde is produced mainly through chlorination of toluene, the liquid phase oxidation of toluene and the vapor phase oxidation of toluene. The chlorination of toluene is the major route to produce benzaldehyde. In this process, toluene is reacted with chlorine in presence of light to obtain benzyl chloride followed by hydrolysis. The disadvantages of this method are (i) the reaction in the process has two steps (ii) the use of light to activate the chlorination reaction and (iii) the presence of by-products. Moreover, the process concerning chlorine (Cl_2) causes environmental pollution and equipment corrosion. The oxidation reaction between toluene and oxygen is another reaction to produce benzaldehyde. Besides, the disadvantages of the partial oxidation of toluene are the process must be cautiously operated at high temperature and benzaldehyde produced in this process can be easily oxidized to benzoic acid (low conversion of benzaldehyde). Both benzaldehyde production pathways are shown in Figure 1.1.



(a) The Chlorination of toluene



(b) The oxidation of toluene

Figure 1.1 The synthesis pathway of benzaldehyde from toluene [1].

The oxidation reaction of toluene with oxygen can be carried out in either the gas phase or liquid phase. In case of gas phase, toluene vapor flows, together with oxygen such as air in a homogeneous mixture, through a catalyst bed in a fluidized-bed reactor. The reaction temperature is 250-650 °C and is highly exothermic. The oxidation of toluene in the gas phase can produce by products such as maleic anhydride, cresol, benzoic acid, carbon monoxide, carbon dioxide and water. Some research reported that conversion of this process could increase up to 25% using a cobolt catalyst (selectivities of 40-80%). Another process, the benzaldehyde formation was improved by liquid phase oxidation of the toluene with oxygen (oxygen from hydrogen peroxide decomposition) in the presence of the acids [1].

The development of the manufacturing process for benzaldehyde production is the oxidation of toluene in which O_2 is substituted by H_2O_2 as the oxidizing agent, showed in Figure 1.2. The advantages of the newly developed process are the process can be produced in one step at low temperature and it does not produce by-product. Nevertheless, this process has the drawback which should solve is low product yield.

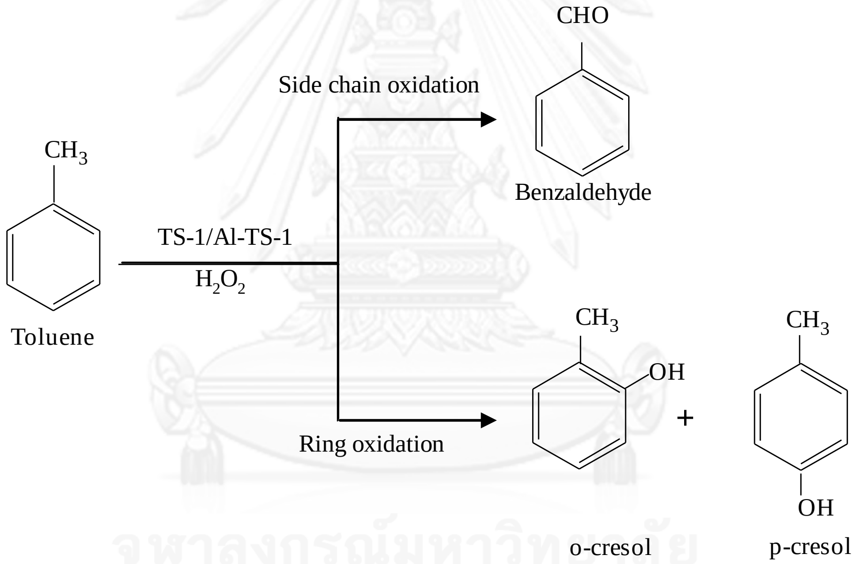


Figure 1.2 Oxidation of toluene over TS-1 catalyst [2].

The early studies of the direct oxidation reaction between toluene and hydrogen peroxide used TS-1 and TS-1 modified with aluminium cation (Al-TS-1). The experimental results reported that the oxidation reaction of toluene could be reacted into two pathways as shown in Figure 1.2. The first way was the side chain oxidation to produce mainly benzaldehyde and the other one was the ring oxidation to give cresol (both o-cresol and p-cresol). Selectivity toward benzaldehyde increased with the increase in reaction temperature [2].

Titanium silicalite-1 (TS-1) is mainly agreed to be the best catalyst for the hydroxylation reactions with H_2O_2 as the oxidant. The best catalyst is defined in terms of total performance, evaluated in terms of activity and selectivity [3]. Taramasso and others first revealed TS-1 in 1983, using two different methods for the preparation of the crystallization gel [4]. Several researchers have studied oxidation reactions using TS-1. Besides, the addition of the second metal is also investigated in order to improve the activity of TS-1 on the oxidation of toluene using hydrogen peroxide as oxidant.

Generally, some organic solvents are used for promoting the miscibility between the organic phase (toluene) and aqueous phase (hydrogen peroxide), this method is called two-phase system. Nevertheless, the solvents which were used in those processes have many disadvantages including (i) solvent may react with hydrogen peroxide especially at high temperature and the competitive absorption of solvent with H_2O_2 to adsorb on TS-1 catalyst which restrains the reaction (ii) the separation of product from solvent is difficult and (iii) homogeneous phase arise from the use of solvent may have density that so low that make catalyst suspended by stirring difficult. Thus, the tri-phase process is selected in order to get rid of those problems. The tri-phase system is composed of TS-1 as solid catalyst, hydrogen peroxide solution (polar-phase) and toluene (non-polar phase). The contact of toluene, hydrogen peroxide and catalyst is performed by vigorous stirring.

A research in our group studying toluene oxidation by hydrogen peroxide elevated temperature over modified TS-1 that was carried out at high temperature which was higher than the boiling point of water and toluene under pressure. The result was shown that raising the reaction temperature could be significantly increased the H_2O_2 conversion [5]. In other research, effect of acidity of solution on reaction between toluene and H_2O_2 over TS-1 catalyst, added HCl to improve conversion in reaction because using acid can help the solubility of toluene in an aqueous phase [6, 7]. However, using acid has the problem due to equipment corrosion. In order to solve this problem, the effect of ion in electrolyte solution was studied [8]. This is the subject of applying this technique to develop conversion in the oxidation of toluene to benzaldehyde.

In the present work, effects of ion types and ion concentrations in acidic/salt solutions on the oxidation reaction of toluene to benzaldehyde over Al-TS-1 by using hydrogen peroxide as oxidant are investigated. Some of the operating parameters are varied such as concentrations, reaction time, solubility of toluene in water at room temperature, etc. Moreover, the oxidation reaction is carried out in a pressurized autoclave stirred reactor under tri-phase condition at temperature higher than the boiling point of reactants.

1.2 Objective

This research studies effects of ion types and ion concentrations 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) Preparation of TS-1 promoted with aluminum ion by using hydrothermal technique synthesis.

2) The synthesize catalyst will be 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 (BET) method to determine surface area and pores volume.

3) Evaluate the solubility of toluene of in aqueous solutions contain 0.05M, 0.10M and 0.15M acidic/salt solutions. The acids and salts used are HNO_3, NH_4NO_3, NH_4Cl, and NaCl.

4) Investigate the influence of ion concentrations (0.05M, 0.10M and 0.15M) in acidic/salt solutions especially the solution(s) that yield(s) benzaldehyde as product.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Titanium silicalite – 1

Titanium slicalite is arranged in a MFI structure that this catalyst is selected in several oxidation reactions with H_2O_2. The properties of TS-1 catalyst are famous in several research and industry. The advantages of catalyst are high activity, selectivity and environmental friendly (by-product is H_2O) [9].

In the first time, titanium slicalite-1 (TS-1) was revealed in 1983 by Taramasso et al. [4]. TS-1 is a catalyst that is developed from silicalite-1 (ZSM-5) by substituting titanium atoms (Ti^{4+}) for silicon atoms (Si^{4+}) in lattice positions. They are arranged in a MFI structure which is a common pattern of crystalline zeolite that it 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). The multiple units are connected together to form chain which leads to the formation of the channel system in the structure. The MFI structure has a three dimensional pore system including sinusoidal 10-ring channels (5.1 × 5.5 Å) and intersecting straight 10-ring channels (5.3 × 5.6 Å) [10]. The MFI structure is showed in Figure 2.1.

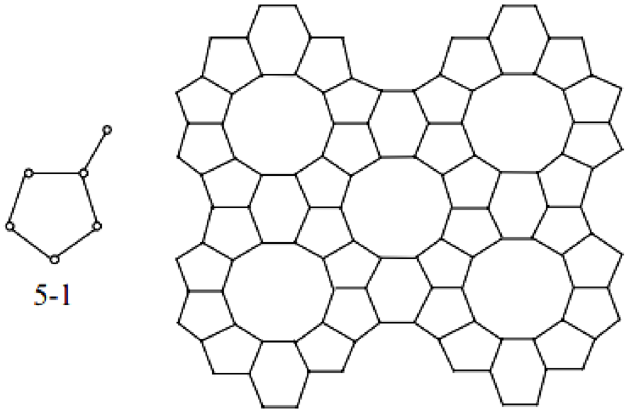


Figure 2.1 MFI structure [10].

TS-1 catalyst can be applied in various oxidation processes with H_2O_2 as oxidant as showed in Figure 2.2, such as hydroxylation of aromatics, oxidation of alcohols, the epoxidation of alkenes, cyclization reactions, and ammoximation of ketones. The properties of TS-1 include of (i) catalyst has the shape-selectivity, (ii) the nature of catalyst is hydrophobic surface and (iii) its isolated, tetrahedrally coordinated Ti sites, preventing the undesired decomposition of H_2O_2 [11].

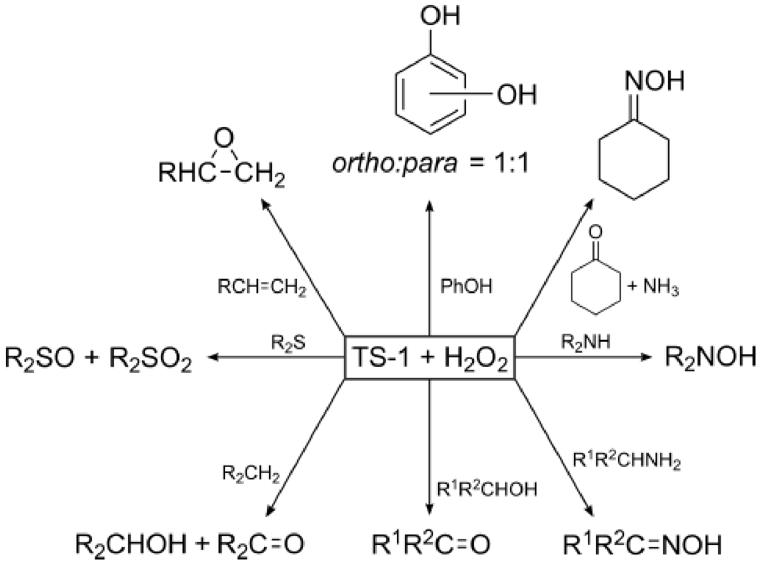


Figure 2.2 Schematic of the versatility of TS-1 [12].

2.2 Mechanism for the formation of benzaldehyde

A proposed reaction mechanism of benzaldehyde formation from the reaction between H_2O_2 and toluene was proposed and shown in Figure 2.5. The first step is the decomposition of H_2O_2 that is the breaking of the single bond of oxygen atom (O-O bond) into two hydroxyl free radicals. The oxygen atom of hydroxyl free radical is not stable because it has an incomplete valance shell. The next step is the oxidation of toluene that hydroxyl free radical attack at the methyl group of toluene molecule results in the construction of benzyl alcohol. However, the formed benzyl alcohol can be easily oxidized hydrogen peroxide to benzaldehyde [13].

Step 1

$$M^{n+} + H_2O_2 \longrightarrow M^{n+} + 2HO\bullet$$

Step 2

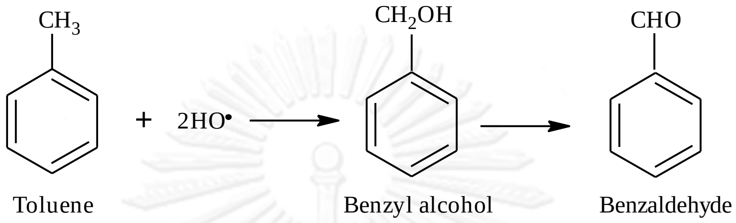


Figure 2.3 The mechanisms of benzaldehyde formation by hydroxyl free radical [13].

2.3 The decomposition of hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a chemical compound with an oxygen-oxygen single bond (H-O-O-H). Physically, it is a colorless and odorless liquid in dilute solution and is weakly acid [14]. Therefore, it is used as oxidizer in wide oxidation reaction and cleanser. Moreover, it is frequently utilized such as bleaching processes in pulp, paper and textile industries, waste water treatment, exhaust air treatment, chemical syntheses and for various disinfection applications. The concentration of hydrogen peroxide available in pharmacies is about 3 to 6 wt%, but the 30 wt% concentration is used in general laboratory. The property of H_2O_2 to decompose exothermally in the presence of catalytically acting impurities with the formation of water and oxygen ($2H_2O_2 \longrightarrow 2H_2O + O_2$), is very important for keeping during storages and during chemical reaction. In addition, the rate of decomposition is influenced by increased temperature, the pH value and the presence of impurities. The decomposition of H_2O_2 can be affected by dissolved ions in the H_2O_2 solution (the heavy metals like chromium, copper, iron, manganese and nickel are especially effective) and a heterogeneous solution by suspended oxides and hydroxide (e.g., those of manganese, iron, copper, palladium, and mercury). The various of catalysts, such as Fe^{2+} or Ti^{3+}, lead to decomposition having different pathway with free radicals such as HO· and HOO· being formed.

2.4 Literature reviewed

Some researchers tried to improved catalytic activity of TS-1 by adding another metal. It was reported that TS-1 samples modified by Al, V Cr, Fe, Co and Ru as another metal in the oxidation of benzene to phenol. The results illustrated that all samples remained same structure with TS-1 and Fe-TS-1 which had high activity and selectivity [15]. At the same time, the hydroxylation alkyl benzene (toluene and ethyl benzene) and TS-1 modified with second metals (Al, V, Fe and Co) were investigated. The catalytic activity of toluene hydroxylation was operated at 70 °C and 95 °C. The second metals affected the products production of reaction Co and V restricted benzaldehyde production while Al and Fe promoted the formation of benzaldehyde as main product [13].

Attempt to study direct synthesis of benzaldehyde from toluene and hydrogen peroxide using titanium silicalite-1 catalysts modified with different amount of Al. The reaction was carried out at reaction temperature 70 °C and 90 °C, and toluene per hydrogen peroxide molar ratios 1:1 and 2:1. The experimental results also showed that Al added into TS-1 promote the formation of benzaldehyde and suppressed the formation of cresols. Too much Al added, however, would decrease the catalytic activity of the modified catalysts. Selectivity toward benzaldehyde increased with the increase in reaction temperature. On the other hand, benzaldehyde selectivity decreased if toluene per hydrogen peroxide malar ratio was increased from 1:1 to 2:1, ascribed that toluene may cover the catalyst surface leading to decrease the amount of hydrogen peroxide on the catalyst surface [2].

The effect of vast reaction parameters such as H_2O_2/substrate molar ratio and reaction temperature was investigated in the direct hydroxylation of aromatic hydrocarbons on vanadium catalyzed using hydrogen peroxide as oxidant. It was reacted at 65 °C for 8 h. The results summarized that all cases the conversion of the aromatics to hydroxyl aromatic increased with raising the molar ratio of H_2O_2/substrate from 1 to 5. The products of hydroxylation of toluene were o-cresol and m/p-cresol with m/p-cresol being formed predominantly. In case of higher reaction temperature that was 25 °C to 80 °C, although the conversion were concluded to increase but selectivity decreased with the increased formation of unidentified products [16]. Furthermore, solvent-free oxidation of toluene in an ionic liquid with H_2O_2 as oxidant was studied. It was examined in the range of 70-110 °C for 6 h. The result showed that the selectivity and conversion to benzaldehyde and benzyl alcohol were dependent on the temperature. However, high temperature led to a low conversion because H_2O_2 was rapidly decomposed. Benzyl alcohol was converted into benzaldehyde in the oxidation of toluene. According to stoichiometry, one mole of H_2O_2 was required for one mole of toluene in reaction into benzaldehyde [17]. Moreover, some research used the reaction temperature higher than the boiling point of the reactant or the solvent by increasing the pressure. The research asserted that the increasing of temperature in the reaction beyond the normal boiling increased the reaction rate [5].

Benzene hydroxylation by hydrogen peroxide at elevated temperature over titanium silicalite-1 catalyst was studied. They found an important factor that increasing the volume of water as a solvent could increase the conversion of H_2O_2 because the benzene might dissolve into the aqueous phase before it reacted with H_2O_2. It could higher chance to contract between catalyst and reactant. Therefore, it concluded that increasing the volume of water relating to increasing quantity of toluene in water phase expressed by: quantity = volume of water x concentration. However, the increase of water is limited by the reactor size [18].

Some research added acid to improve conversion of the reaction between toluene and hydrogen peroxide at 70 °C and 90 °C over TS-1 modified with Co. The results revealed that benzaldehyde yield could be increased by adding hydrochloric acid, thus acid was added as a stabilizer [6]. In addition, the research studied the effect of acidity on the oxidation of toluene by hydrogen peroxide by TS-1 catalyst modified with Al. The reaction carried out at 100 °C and 120 °C which are equal or higher than the normal boiling point of water and toluene. The result revealed that the suitable volume of hydrochloric acid can increase the conversion of H_2O_2. Besides, it could improve the productivity of benzaldehyde and suppressed the productivity of o-cresol and p-cresol. The hydrochloric acid could increase the toluene solubility in water due to the effect of photon (H^+) [7].

Recently, the report studied the effort ions in electrolyte solution on the oxidation reaction of toluene to benzaldehyde over Al-TS-1 catalyst. The solutions were studied which include HCl, HNO_3, NH_4Cl, NH_4NO_3, NaCl, and $NaNO_3$. These electrolyte solutions were added in aqueous phase. The reaction temperature was maintained higher than the normal boiling point of water and toluene. The type of acid/salt solution had an influence upon the solubility of toluene in water phase and H_2O_2 convert to product. The result found that the highest productivity of organic products (benzaldehyde plus cresols) was obtained in HCl solution and $NaNO_3$ solution would produce both benzaldehyde and cresol. The higher productivity of benzaldehyde, however, was obtained when HNO_3 is used. Moreover, the presence of ions (NH_4Cl, NH_4NO_3 and NaCl) in aqueous solution could produce only one product forms, benzaldehyde. In case of cation, H^+ ion had affected more than the other cation. Moreover, anion, the nitrate ion had the effect on the equilibrium concentration and the solubility rate of toluene more than chloride ion [8].

2.5 The summary of the previous review

From the previous studies, we can see that many researchers try to improve the conversion in the oxidation reaction of toluene. The normal methods are using catalyst modification by second metal, solvent, reactant ratio, and temperature at lower than normal boiling point of toluene and water. Researchers find that the operating temperature above the boiling point of toluene and water at atmospheric pressure can improve the percentage of hydrogen peroxide converted to organic product; therefore, temperature is an important factor [5]. In another interesting factor, many researchers try to add the chemical such as acidic/salt solutions which not only increases the concentration of toluene in an aqueous phase but also improve the H_2O_2 conversion [6-8].

Nevertheless, there is no study about combination both ways together with various concentrations of acidic/salt solutions. Thus, we study effect of ion types and ion concentrations on the oxidation reaction of toluene over Al-TS-1 by hydrogen peroxide using HNO_3, NH_4Cl, NH_4NO_3 and NaCl solutions at the reaction temperature above the boiling point of toluene and water. Besides, the appearance of some ions in aqueous solution can produce both benzaldehyde (main product) and cresol (by product), whereas some ions can provide only benzaldehyde [8]. In this research, we focus on study ion solutions that produce specially benzaldehyde product, hence, HNO_3, NH_4Cl, NH_4NO_3 and NaCl solutions are selected to study for various concentrations.

The selection of using acidic/salt solutions, we consider the decomposition of H_2O_2 which H_2O_2 will decompose faster when pH is more than 7 and the presence of some metal ions. Therefore, the property of the solution to determine if it is an acid, hydrochloric acid is chosen to study for decreased pH. The previous research is shown that cation has affected the solubility of hydrocarbon compounds in aqueous phase. Although H^+ ion in HCl solution has the small ion, it has the high charge density that affects stronger interactions with water molecules than water-water hydrogen bonds. In other words, H^+ ion can reduce strength of water's hydrogen bonding and enhance solubility of toluene in water phase; however, using acid has the problem owing to equipment corrosion. Hence, we choose the salt solution instead of acid solution that using NaCl is investigated. The results show that the solubility of toluene in NaCl solution is not better than the solubility of toluene in acid solution. Thus, we select NH_4^+ because it has ion size between H^+ and Na^+. Moreover, the property of NH_4NO_3 solution is less then pH 7 which can decrease the decomposition of H_2O_2 and will not lead to a problem of equipment corrosion. In case of anion, Cl^- ion is used for compared with NO_3^- ion. The results are presented that the nitrate ion has the effect on the equilibrium concentration and the solubility rate of toluene more than chloride ion.

CHAPTER 3

EXPERIMENTAL

The experimental in this chapter is divided into four major parts: (1) catalyst preparation, (2) catalyst characterization (3) the solubility of toluene and (4) reaction study in oxidation of toluene. The chemicals, instrument and procedures for catalyst preparation are explained in section 3.1. The composition, structure, surface properties and acidity 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 illustrated in section 3.4.

3.1 Catalyst preparation

3.1.1 Chemicals

All chemicals use in this preparation procedure of Al-TS-1 catalyst is following in Table 3.1.

Table 3.1 The chemicals use in the catalyst preparation.

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

3.1.2 Preparation procedures

The preparation procedure of Al-TS-1 by hydrothermal method is shown in Figure 3.1. and the reagents are summarized in Table 3.2.

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

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			**Solution A2**		
$Ti[O(CH_2)_3CH_3]_4$	2.2970	g	$Ti[O(CH_2)_3CH_3]_4$	2.2970	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
$Al(NO_3)_3.9H_2O$, Si/Al = 150	0.82	g	$Al(NO_3)_3.9H_2O$, Si/Al = 150	0.82	g
De-ionized water	60	ml	H_2SO_4 (conc.)	3.4	ml
H_2SO_4 (conc.)	3.4	ml			
Solution B1			**Solution B2**		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
Solution C1			**Solution C2**		
TPABr	2.16	g	NaCl	26.27	g
NaCl	40.59	g	De-ionized water	104	ml
NaOH	2.39	g			
De-ionized water	208	ml			
H_2SO_4 (conc.)	1.55	ml			

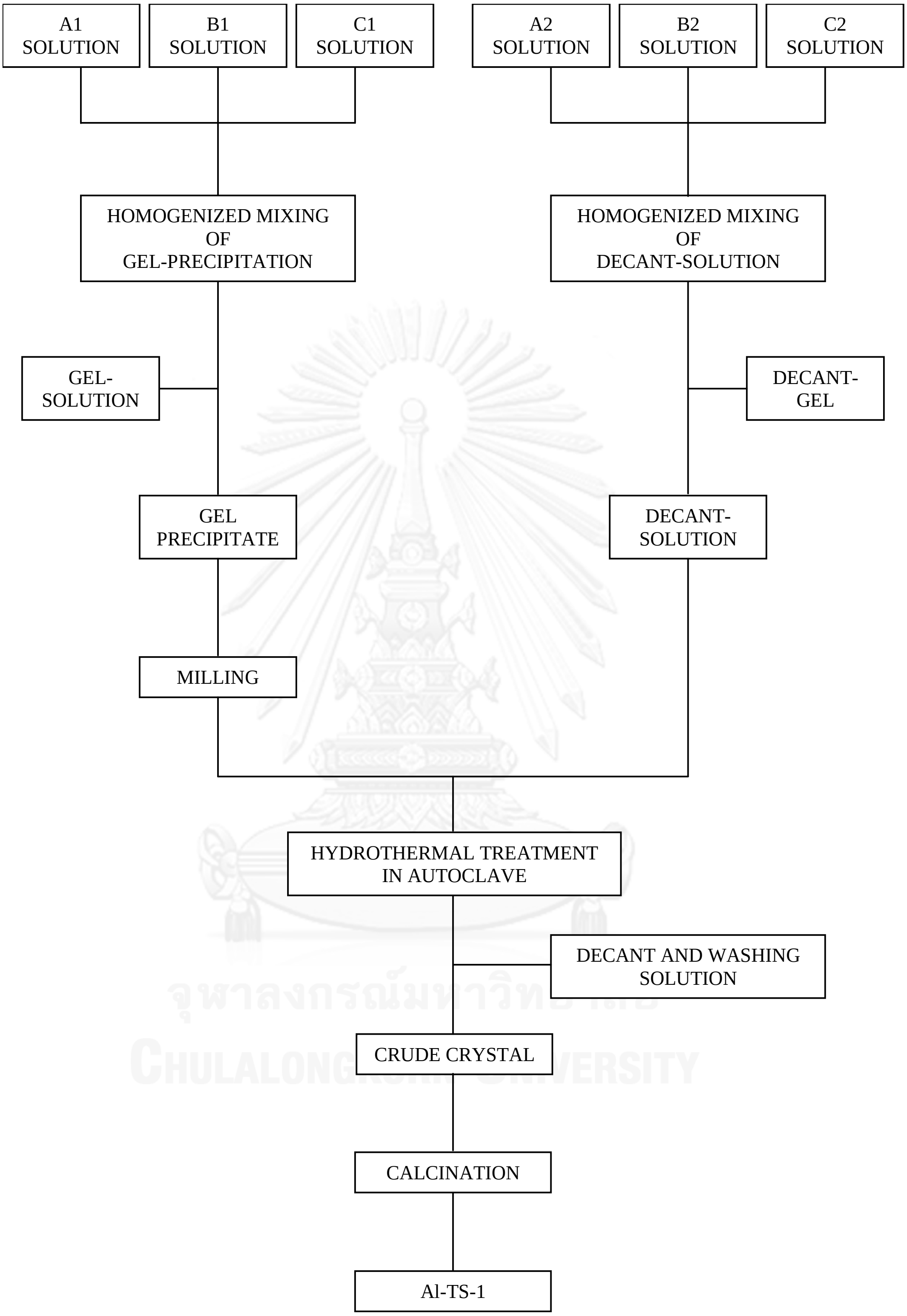


Figure 3.1 The preparation procedure of Al-TS-1 by rapid crystallization method.

A hydrothermal method was used to prepare titanium silicalite-1 modified with aluminium cation (Al-TS-1) catalyst. Firstly, the gel solution was prepared by adding solution A1 and solution B1 into solution C1 with vigorous stirring using a magnetic stirrer at room temperature. The gel mixture was stirred to control the pH within the range 9-11 because this pH range was suitable for precipitation. In case of necessity, H_2SO_4 (conc.) or NaOH solution were used to adjust pH of the gel mixture to an appropriate level. Then, the gel mixture was centrifuged for 15 minutes to separate the formed gel from the supernatant liquid. The precipitated gel mixture was milled for a total of 1 hour. In order to separate the supernatant solution, the gel was milled for 15 minutes, alternating with being centrifuged for 15 minutes. Secondly, the decant solution was prepared by adding solution A2 and solution B2 into solution C2. The supernatant liquid was separated from the mixture by centrifugation for 15 minutes, same as for the preparation of gel mixture.

In the stage of crystallization, the mixture of gel in supernatant liquid was filled in a glass tube and put in an autoclave. The autoclave was pressured up to 3 bars by nitrogen gas and was maintained at 180 °C for 3 days. Afterwards, the crystal products were washed by de-ionized water in order to decrease the pH 7 by centrifugation. Then, the crystals were dried in an oven at 110 °C for at least 24 hours and calcined at 550 °C in air stream for 7 hours by heating rate of 8.60 °C/min.

The Al-TS-1 was boiled at 80 °C in 5 M of HNO_3 solution for 3 hours. After that the crystals were removed from the acid by washing with de-ionized water until the pH was 7 and dried at 110 °C. The dried crystals were calcined in an air stream at 550 °C for 7 hours. Finally, the final product was obtained as white solid powder.

3.2 Catalyst characterization

3.2.1 X-Ray Fluorescence Spectrometer (XRF)

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

3.2.2 BET surface area measurement

The important analysis for the specific surface area, pore volume and pore size of catalyst are determined using Micremeritrics ASAP 2020. The sample cell which contained 0.1-0.3 g of sample is placed into Micromeritrics ASAP 2020.

3.2.3 Fourier transform Infrared (FT-IR)

The functional groups on the catalyst surface are identified by FT-IR technic using Thermo Nicolet model Impact 6700. Infrared spectra are analyzed in the range of 400 and 4000 cm^{-1}. The number of scan is 100 with a resolution of 4 cm^{-1}.

3.2.4 X-Ray Diffraction (XRD)

The crystal structures of catalyst are analyzed by an x-ray diffraction (XRD) technique using a BRUKER D8 ADVANCE. The experiments are carried out by using CuKα radiation with Ni filter. Scans are performed over the 2θ ranges from 6° to 30° with step size 0.04° /sec.

3.3 The solubility of toluene in acidic/salt solutions

The solubility of toluene in various concentration of acidic/salt solution was measured at room temperature. The acids and salts used are HNO_3, NH_4NO_3, NH_4Cl and NaCl. In each experiment 160 ml of acidic/salt aqueous solution (0.05M, 0.1M, or 0.15M of acidic/salt solutions) was added into a 250 ml beaker. Afterwards, a 1/4 inch OD stainless steel tube was vertically placed in the reactor for sampling well. Then a volume of toluene was added to cover all the surface of aqueous phase. At a specify intervals, the stirring was stopped and liquid sample was taken from the vertically placed tube. Then, the concentration of dissolve toluene in the aqueous solution was analyzed by a gas chromatograph (Shimadzu GC8A) equipped with FID and GP10% SP-2100 packed column to determine the concentration of toluene.

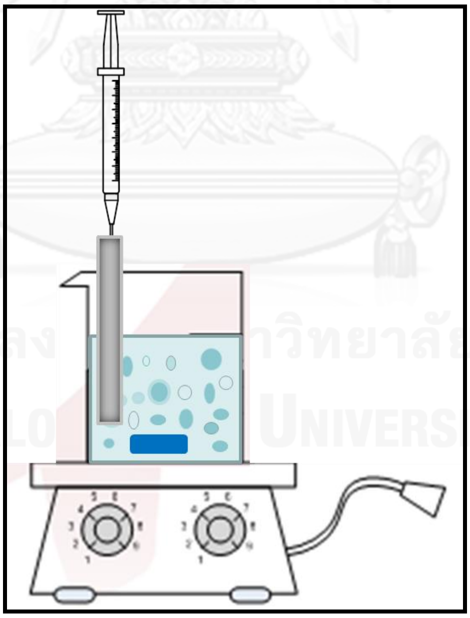


Figure 3.2 The preparation procedure of the solubility of toluene.

Table 3.3 The gas chromatography conditions for toluene analysis.

Gas chromatograph	SHIMADZU GC8A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N_2 (99.999%)
Carrier gas flow rate (ml/min)	30
Injector temperature (°C)	200
Detector temperature (°C)	200
Column temperature (°C)	100
Analyzed chemicals	Toluene

3.4 Reaction study in the oxidation of toluene

3.4.1 Chemicals

The reactants used for the reaction study are shown in Table 3.4.

Table 3.4 The chemicals use for the reaction study.

Chemical	Grade	Supplier
Toluene	Analytical	Fisher Scientific
Hydrogen peroxide 30%	Analytical	Merck
Ethanol	Analytical	Merck

3.4.2 Reaction procedure

The oxidation of toluene using Al-TS-1 as a catalyst was carried out in a stainless steel SS304 reactor. The procedures are described in the detail below.

The hydroxylation of toluene was carried out under vigorous stirring in a reactor. Typically, 1 g of Al-TS-1, 120 ml of water or acid/salts aqueous solution, and 1.1 ml of toluene (for toluene to H_2O_2 molar ratio equals to 1:1) were added into the reactor. The reactor system was pressurized up to 2 barg by nitrogen gas and heated up at 90 °C using an oil bath (Figure 3.3). The initial system remained at this temperature for 1 hour to remove all gas in the pore of the catalyst. After that the reactor temperature was raised to 120°C, the reaction temperature. To start the reaction, 30%wt hydrogen peroxide was injected via an injection port using a 1.0 ml syringe. The reaction was allowed to continue for 2 hours. Afterwards, the reactor was stopped using an ice bath. The two phases (aqueous and organic) were homogenized by adding 80 ml of ethanol. The catalyst was separated from the homogenized liquid phase by centrifugation. The reaction products were analyzed with a gas chromatograph (Shimadzu GC8A) equipped with a FID detector. The condition of the gas chromatography was listed in Table 3.5. The chromatogram data are converted into mole of products using a calibration curve.

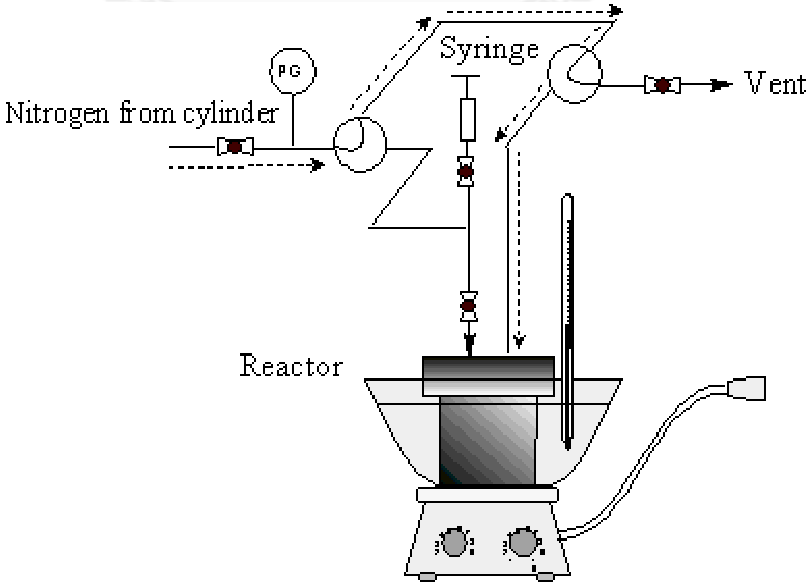


Figure 3.3 The oxidation reaction of toluene system.

Table 3.5 The conditions of the gas chromatography for the reaction study.

Gas chromatograph	**SHIMADZU GC8A**
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N_2 (99.999%)
Carrier gas flow rate (ml/min)	30
Injector temperature (°C)	200
Detector temperature (°C)	200
Initial column temperature (°C)	80
Initial hold time (min)	0.1
Program rate (°C/min)	5
Final column temperature (°C)	230
Final hold time (min)	20
Analyzed chemicals	Toluene, Benzaldehyde

CHAPTER 4

RESULTS AND DISCUSSION

The result and discussion in this chapter are divided into three parts. The first one, section 4.1 is the summary of characterization of Al-TS-1 catalyst. This part consists of the result of the catalyst composition analysis by using XRF technique, the result of the surface area and pore volume analysis 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 section, 4.2, is the solubility of toluene in acidic/salt solutions and the third section, 4.3, is the catalytic activity testing of Al-TS-1 catalyst in the oxidation reaction between toluene and hydrogen peroxide to benzaldehyde.

4.1 Catalyst characterization

4.1.1 Chemical compositions (XRF)

The catalyst composition analysis is carried out on semi-quantitative X-ray fluorescence spectrometry technique using wavelength dispersive X-ray fluorescence Spectrometer (WDXRF) BRUKER AXS, Germany: Model S4 PIONEER. The chemical compositions are reported in Table 4.1.

Table 4.1 Chemical compositions of Al-TS-1.

Catalyst sample	%Si	%Ti	%Al	Si/Ti
Al-TS-1	93.20	1.76	0.68	52.95

4.1.2 Surface area measurement (BET)

Surface area and pore volume analysis of the catalyst, perform using Micremeritrics ASAP 2020 by BET technique, are found to be 366.80 m^2/g and 0.2156 ml/g, respectively.

4.1.3 Fourier transform infrared (FT-IR)

The functional group analysis using FT-IR (Figure 4.1) shows the absorption band around 960 cm^{-1}. This confirms that Ti^{4+} ions have replaced some Si^{4+} of the MFI framework in the tetrahedral group $Ti(SiO)_4$.

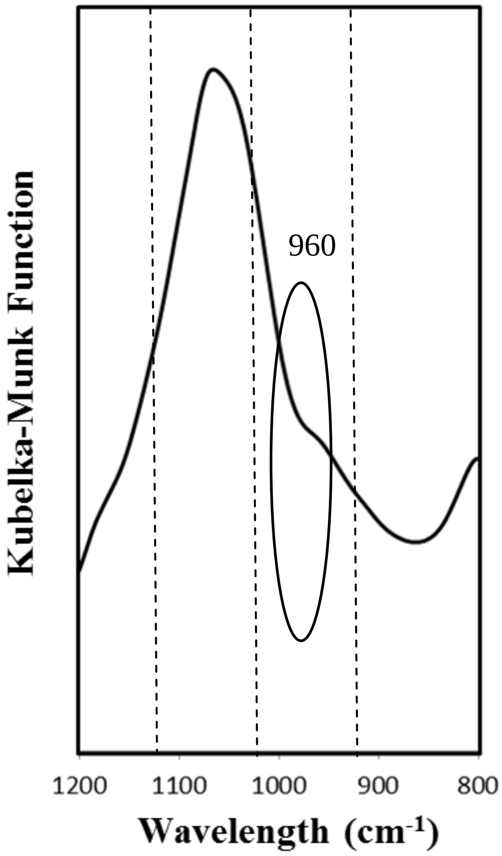


Figure 4.1 The FT-IR pattern of Al-TS-1.

4.1.4 Crystal structure (XRD)

The x-ray diffraction (XRD) patterns showed in Figure 4.2 demonstrates only main typical peaks at 2θ = 8, 8.8, 14.8, 23.1, 24 and 26.7 which belong to MFI structure. Therefore, the structure of TS-1 is not changed when a small portion of aluminium ion presents in the framework.

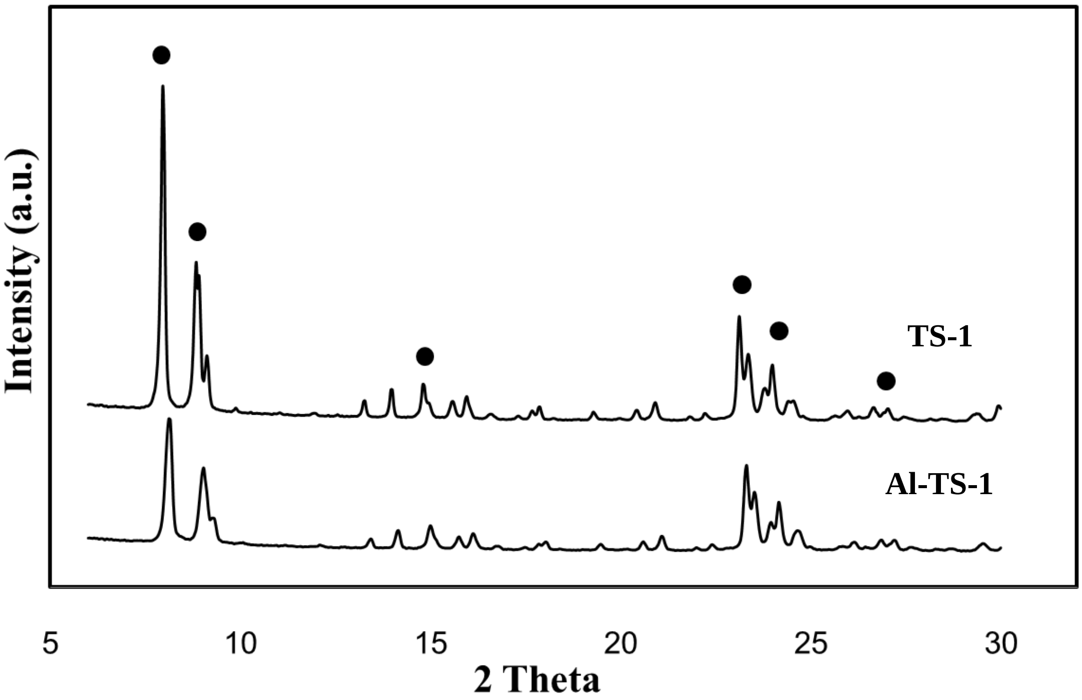


Figure 4.2 The XRD patterns of TS-1 and Al-TS-1.

4.2 The solubility of toluene in the acidic/salt solutions.

The oxidation reaction is performed in a tri-phases system which consists of hydrogen peroxide solution (polar phase), toluene (non-polar phase), and Al-TS-1 (the solid catalyst). The reaction is carried out in a pressurized stirred reactor. The reactor model is schematically presented in Figure 4.3.

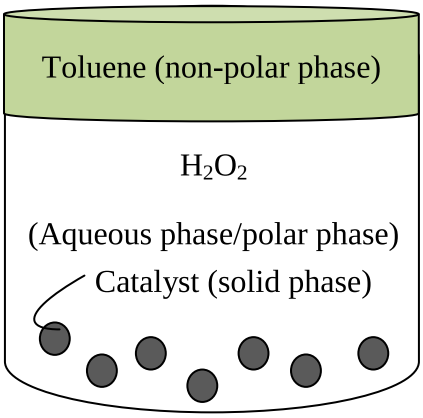


Figure 4.3 System of the oxidation reaction used in this study.

In this system, the catalyst particle is submerged in the aqueous phase. The water is selected to be the reaction medium because hydrogen peroxide is a polar molecule that can dissolve into water. This method can prevent the catalyst from being covered with excessive amount of toluene due to the nature of the catalyst surface which is hydrophobic. In addition, this method also avoid the competitive adsorption of solvent used to homogenize the aqueous and the hydrocarbon phase which hindrances the adsorption of the reactants. This technique, however, leads to too low amount of toluene on the catalyst surface which is limited by the solubility of toluene in the aqueous phase.

The reaction can begin when two reactants (H_2O_2 and toluene) exist on the catalyst surface. However, the limited amount of toluene in the aqueous phase leads to low conversion. The techniques for solving these problems can be

(i) Increases the volume of water as used solvent. This will increase quantity of toluene (quantity = volume of water × toluene concentration in the aqueous phase)

(ii) Increases the reaction temperature. When increasing the reaction temperature, the hydrogen bonding of water will become weaker. Accordingly, the hydrocarbon can easier penetrate into water layer. But too high temperature may result in too fast decomposition of H_2O_2.

(iii) Addition of some the acids/salts. It has been showed previously that the presence of some ions will improve the concentration of toluene in water due to the disruption of the strength of H-bond between H_2O molecules.

In our system, the volume of water used as solvent is increased up to the maximum volume the reactor can handle. In addition, the reaction temperature and pressure are already limited by the structure of the reactor system. Therefore, to increase the amount of hydrocarbon in the aqueous phase, there is only one choice left i.e. the addition of some acids/salts into the aqueous phase.

4.2.1 Effect of ion concentrations on the solubility of toluene in the acidic/salt solutions.

Solubility can be defined as the highest amount of solute (substance A) that can be dissolved in a solvent (substance B) at a specific temperature. The dissolving process involves a consideration of the relative strength of three intermolecular attractive forces. The types of intermolecular attractive forces between molecules of substance A itself and molecules of substance B itself must be considered. The intermolecular attractions must be broken or weaken before the new intermolecular forces of molecule of substance A and B can become effective. The substance A will dissolve in the substance B if the intermolecular attractive forces of substance A and B are great enough to overcome the intermolecular forces of substance A itself and the intermolecular forces of substance B itself. Conversely, the substances will not be soluble in each other if the intermolecular attractive forces of substance A and B are weaker than individual substance A and B intermolecular attractions. An aromatic hydrocarbon is nonpolar substances because it has a weak attraction for one another, known as Van der Waals force. On the other hand, water is a polar substance having hydrogen bond which is a powerful intermolecular force. The attraction between the polar water molecules and the nonpolar toluene molecules is not sufficiently strong enough to form a homogeneous solution having a high concentration of toluene in water. Under normal conditions, only a very small amount of toluene can exist in the aqueous phase.

Several factors can increase the solubility of toluene in water. Temperature is a factor in determining the solubility. Some research has increase temperature in the reaction and the result showed that solubility increasing with raising temperature [8, 16, 19]. This due to strength of hydrogen bonds in water molecules are weakened at high temperature. After that, toluene can easier penetrate into these intermolecular forces. The other factor affects solubility which is the added ions. The presence of some ions can break or weaken the hydrogen bonds between water molecules.

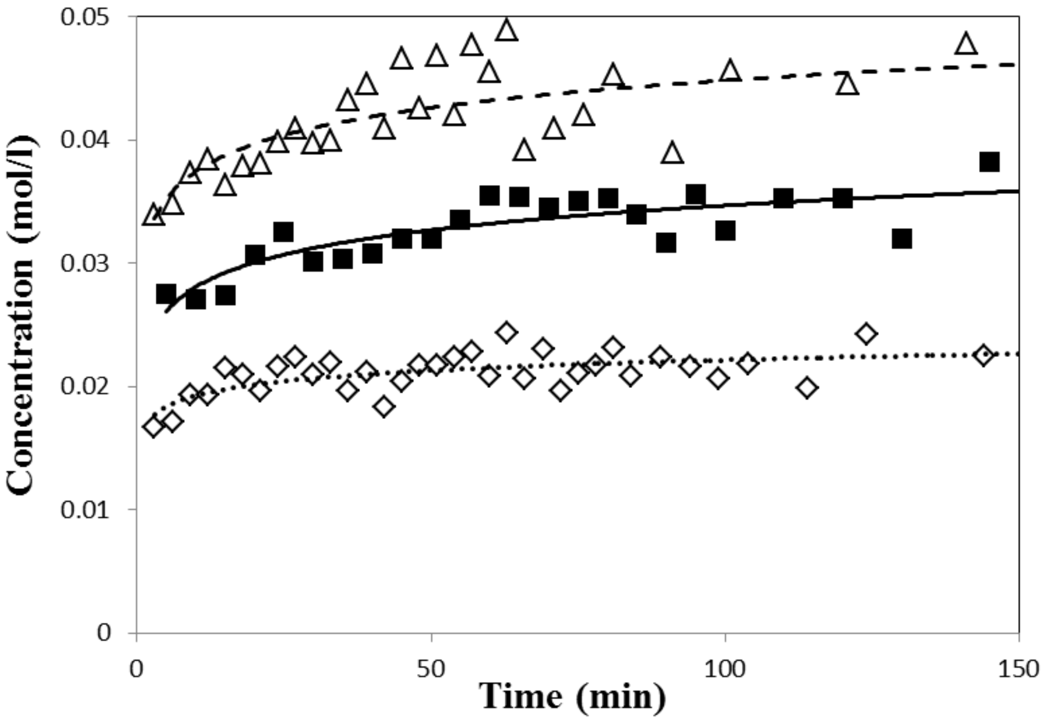


Figure 4.4 The solubility of toluene in the nitric acid solution at different concentrations and room temperature.

Symbol: (◇) 0.05 M, (■) 0.10 M, (△) 0.15 M.

Figure 4.4 compares the concentration profiles of toluene in aqueous solutions having different concentration of nitric acid at room temperature (0.05 M, 0.10M, and 0.15 M). In aqueous solution, nitric acid molecule dissociates into two ions that are H^+ ion and NO_3^- ion. The results clearly show that the solubility of toluene increases with increasing HNO_3 concentration. The equilibrium concentration of toluene in the aqueous solution at different HNO_3 concentrations follows the order: 0.15 M > 0.10 M > 0.05 M.

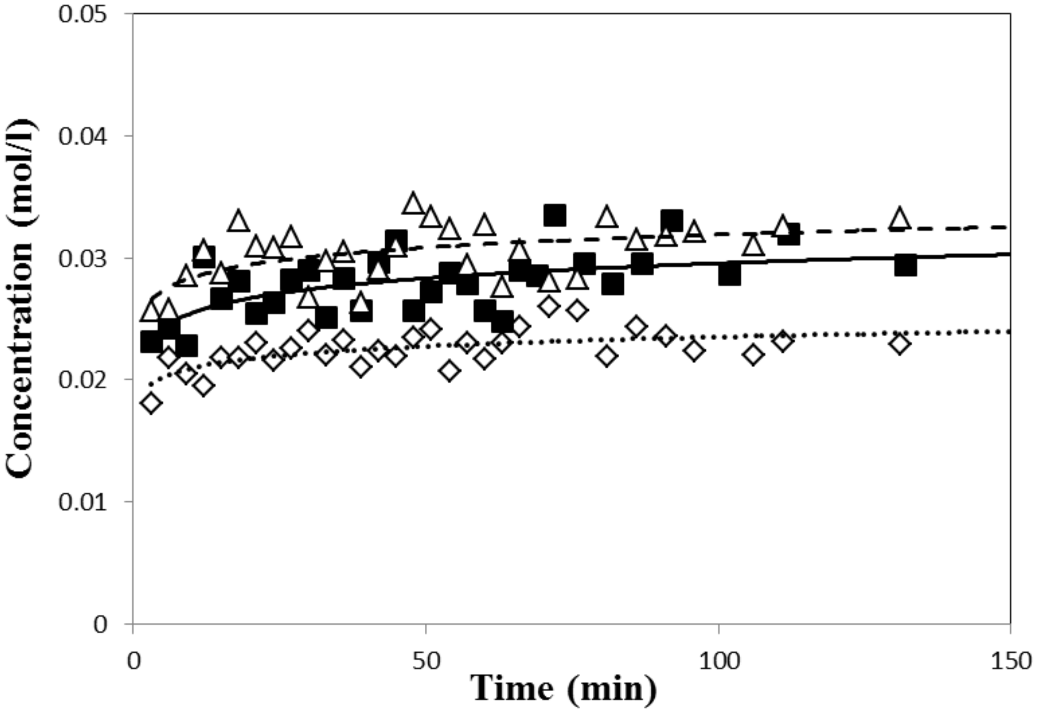


Figure 4.5 The solubility of toluene in ammonium nitrate solution at different concentrations and room temperature.
Symbol: **(◇) 0.05 M, (■) 0.10 M, (△) 0.15 M.**

Figure 4.5 demonstrates the concentration profiles of toluene in aqueous solutions having different concentration of ammonium nitrate at room temperature (0.05 M, 0.10M, and 0.15 M). The ammonium nitrate molecules in aqueous solution have the effect of the two ions that are NH_4^+ ion and NO_3^- ion. Although the distribution of the data is broad, the trend lines of toluene solubility have obviously separated. The results can be seen that the solubility of toluene increases as NH_4NO_3 concentration is raised. The equilibrium concentration of toluene in the aqueous solution at different NH_4NO_3 concentrations follows the order: 0.15 M > 0.10 M > 0.05 M.

From figures 4.4 and 4.5 one can see that at 0.05 M acid/salt concentration, the equilibrium concentrations of toluene in HNO_3 or NH_4NO_3 solutions are about the same, a slightly higher than 0.02 M. At 0.10 M and 0.15 M acid/salt concentrations, the equilibrium concentrations of toluene in HNO_3 solution are higher than in the NH_4NO_3 solution at the same acid/salt concentration. This result shows that H^+ ion, having higher charge density than NH_4^+ ion, has stronger effect on the solubility of toluene in water. The ion having high charge density will form H-bond with water molecule much easier than the ion having low charge density. When water molecules tend to form H-bond with other ions, the strength of H-bond between water molecules will decrease. Therefore, more non-polar molecules, such as toluene in our case, can penetrate into the aqueous phase.

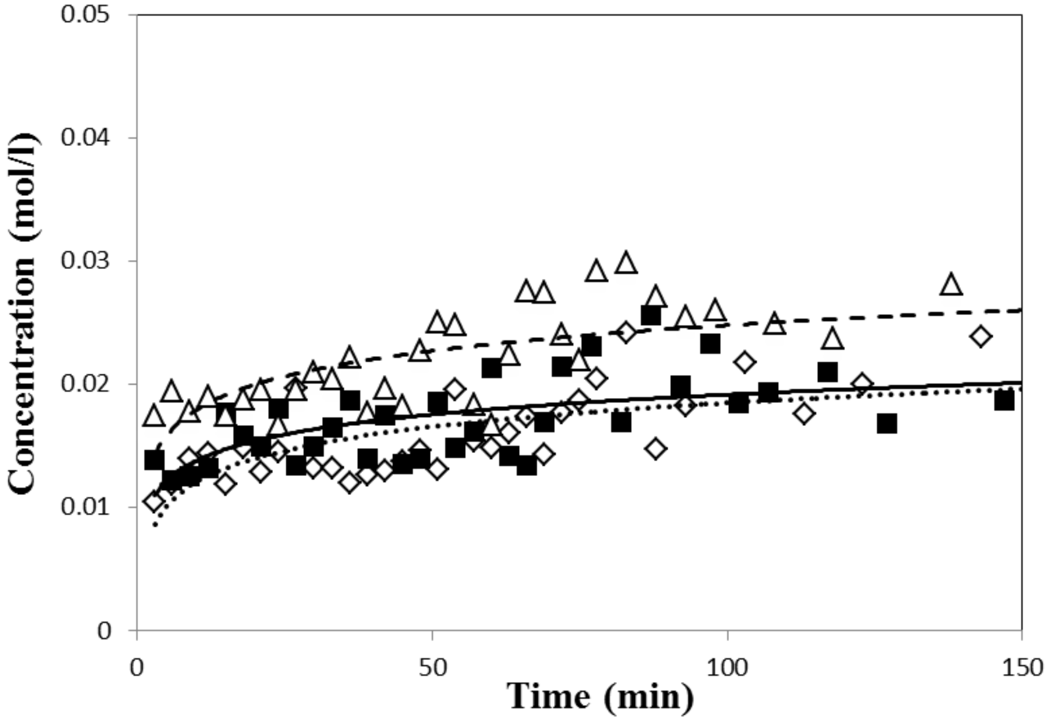


Figure 4.6 The solubility of toluene in ammonium chloride solution at different concentrations and room temperature.
Symbol: (◇) 0.05 M, (■) 0.10 M, (△) 0.15 M.

Figure 4.6 illustrates the concentration profiles of toluene in aqueous solutions having different concentration of ammonium chloride at room temperature (0.05 M, 0.10M, and 0.15 M). The ammonium chloride solution is dissociated into two ions that are NH_4^+ ion and Cl^- ion. The solubility of toluene in the ammonium chloride solution at 0.05 M is slightly lower than that in ammonium chloride solution at 0.10 M and both are considerably lower than that in ammonium chloride solution at 0.15 M.

Here, one can see that the effects of NH_4NO_3 and NH_4Cl on the saturated concentration of toluene in water are about the same. This is due to NO_3^- ion and Cl^- ion has about the same charge density. Because of this reason, the effects of NH_4NO_3 and NH_4Cl on the strength of H-bond between water molecules are about the same.

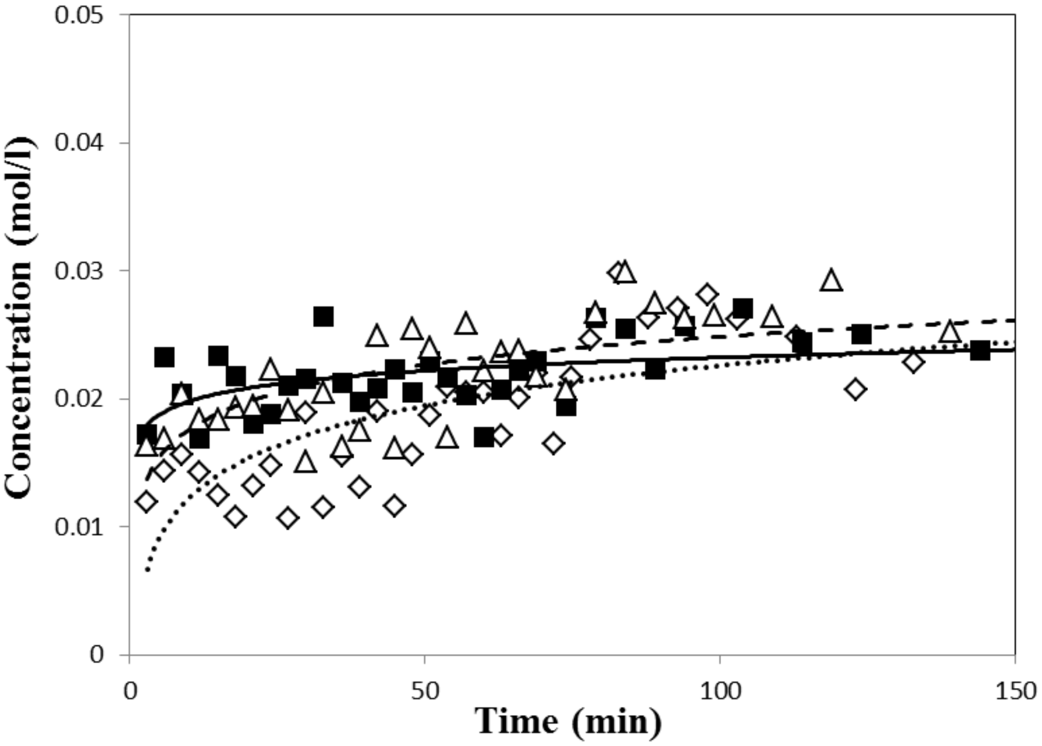


Figure 4.7 The solubility of toluene in sodium chloride solution at different concentrations and room temperature.
Symbol: (◇) 0.05 M, (■) 0.10 M, (△) 0.15 M.

Figure 4.7 demonstrates the concentration profiles of toluene in aqueous solutions at different concentrations of the aqueous phase (0.05 M, 0.10M, and 0.15

M) having by sodium chloride dissolved into. In aqueous solution, sodium chloride molecule dissociates into two ions that are Na^+ ion and Cl^- ion. The results can be seen that the solubility of toluene in the sodium chloride solution at 0.05 M is approximately to the same as sodium chloride solution at 0.10 M and 0.15 M.

From figures 4.6 and 4.7 one can see that the saturated concentrations of toluene in NaCl solutions are lower than in the NH_4Cl solution. This result confirms the effect of charge density on the saturated concentration of toluene in the aqueous phase. Na^+ has lower charge density than NH_4^+ ion. Therefore, the H-bonds between water molecules in NaCl solution are only slightly disturbed, especially for 0.05 M and 0.10 M NaCl solutions.

The solubility of toluene in the aqueous solutions slightly increases after adding acidic/salt solutions can be explained by the effect of ions. The different cations and anions can be divided into two categories that depend on the charge they carry. Ones are the small ions or multiply-charged which have high charge densities. They have stronger interaction with water molecules than the strength of water-water interactions also called “kosmotrope”. For this reason, the amount of toluene can increasingly dissolve in the water molecules. The other kind of ions is the large ions that have low charge densities, called “chaotrope”. It presents weaker interactions with water than water binds itself, therefore, interfering less with the hydrogen bonding of the surrounding water molecules [19].

The comparisons of the four acidic/salt solutions including HNO_3, NH_4NO_3, NH_4Cl, and NaCl at constant concentration are presented in Figures 4.4-4.7. The results show that the equilibrium concentrations in the aqueous solutions of HNO_3 are higher than that in NH_4NO_3 solutions, and the saturated concentrations of toluene in NH_4Cl solutions are higher than in the NaCl solution. It clears that the effect of cations follows the order of the charge density i.e. $H^+ > NH_4^+ > Na^+$. According to the definition, the proton ion is kosmotrope due to small ion and high charge density. The size and the density charge of the ion are an important characteristic of the ion. The charge density depends on the radius and the total charge of the ion. Moreover, it affects the strength and the number of hydrogen bonds in water. From figures 4.5-4.6, compare the equilibrium concentration of toluene in two different anion solutions consist of NH_4NO_3 and NH_4Cl, it is found that the presence of NO_3^- ion has more effect than the presence of Cl^- ion. In this case, NO_3^- and Cl^- are chaotrope and the typical ordering of the anion series were $NO_3^- > Cl^-$.

4.3 Effects on the progress of reaction

In this part, we study the effect of ion concentrations on the oxidation reaction between toluene and hydrogen peroxide using Al-TS-1 catalyst. Four aqueous solutions are used in this research, nitric acid, ammonium nitrate, ammonium chloride and sodium chloride solutions. The reaction is carried out at 120°C unless otherwise stated. It is found that the reaction in the four aqueous solutions produces only benzaldehyde as organic product. The results of the experiment are reported in terms of conversion of H_2O_2 to organic product or the percentage of H_2O_2 conversion.

The percentage of H_2O_2 conversion

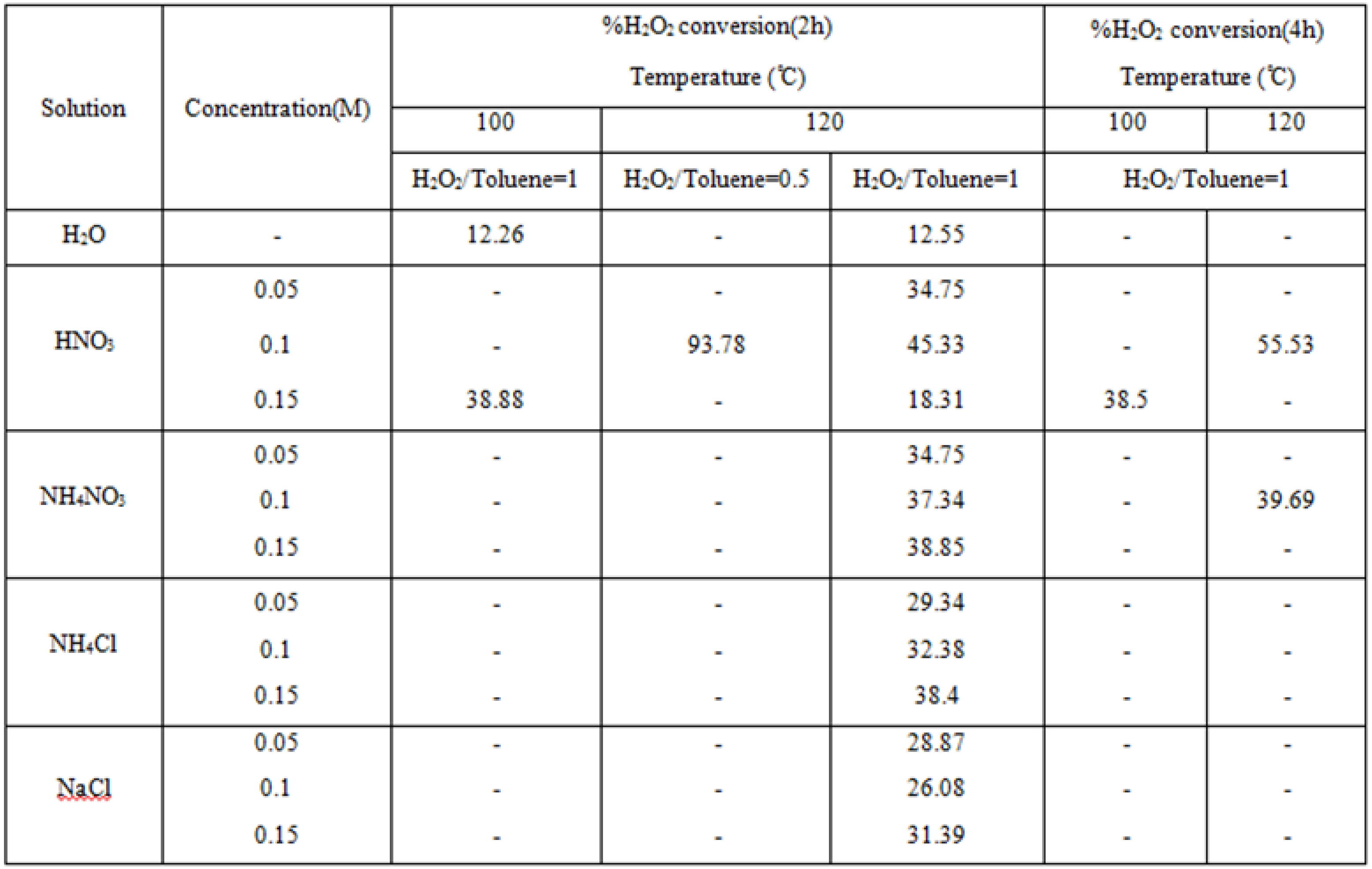
$$\text{The } \%H_2O_2 \text{ converts to product} = \frac{2xN_B}{N_{H_2O_2}} \qquad (4.1)$$

Where;

N_B = the overall mole of benzaldehyde formed

$N_{H_2O_2}$ = the overall mole of H_2O_2 introduced

Table 4.2 Percentage of hydrogen peroxide conversion in the oxidation reaction with various conditions.



Solution	Concentration(M)	%H_2O_2 conversion(2h) Temperature (℃)			%H_2O_2 conversion(4h) Temperature (℃)	
		100	120		100	120
		H_2O_2/Toluene=1	H_2O_2/Toluene=0.5	H_2O_2/Toluene=1	H_2O_2/Toluene=1	
H_2O	-	12.26	-	12.55	-	-
HNO_3	0.05	-	-	34.75	-	-
	0.1	-	93.78	45.33	-	55.53
	0.15	38.88	-	18.31	38.5	-
NH_4NO_3	0.05	-	-	34.75	-	-
	0.1	-	-	37.34	-	39.69
	0.15	-	-	38.85	-	-
NH_4Cl	0.05	-	-	29.34	-	-
	0.1	-	-	32.38	-	-
	0.15	-	-	38.4	-	-
NaCl	0.05	-	-	28.87	-	-
	0.1	-	-	26.08	-	-
	0.15	-	-	31.39	-	-

4.3.1 Effect of ion concentrations on the oxidation reaction

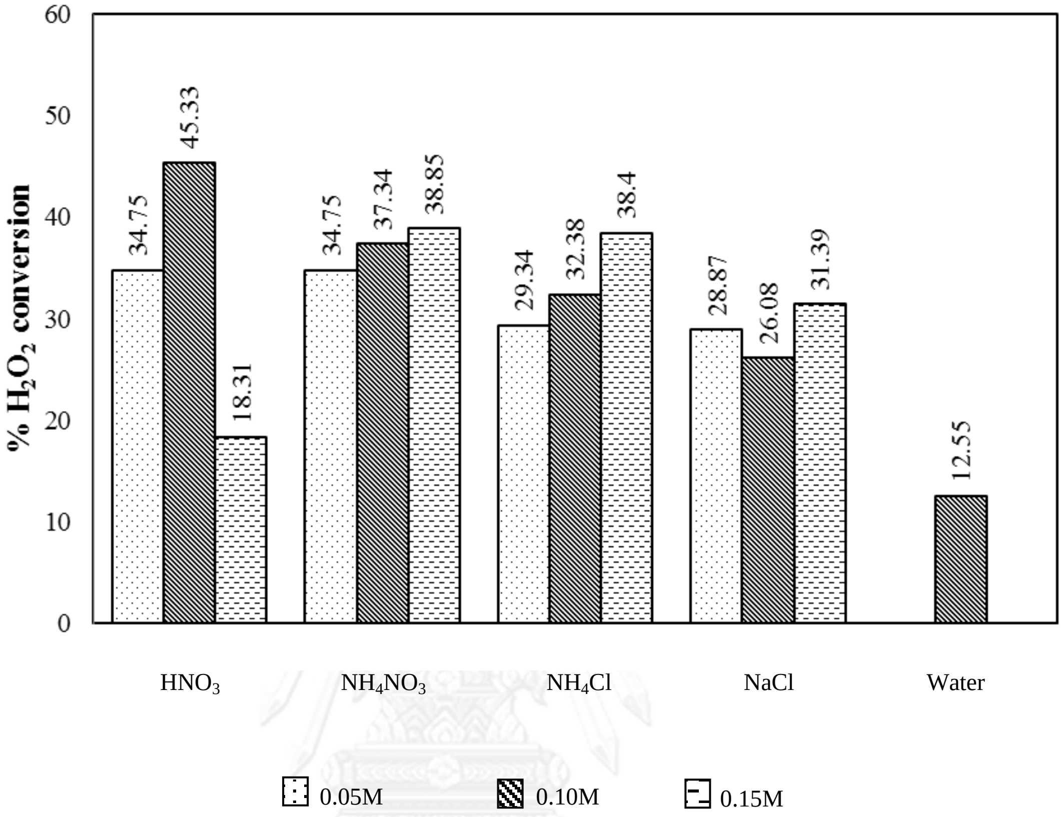


Figure 4.8 Percentage of H_2O_2 convert to product at 120°C.

Figure 4.8 illustrates the effects of ion concentrations on the oxidation reaction between toluene and H_2O_2 conversion. This bar graph compares the percentage of hydrogen peroxide involves in the organic product formation at 120 °C and 2 h reaction time in four different acidic/salt solutions and three concentrations.

If deionized water is used as solvent, the catalyst surface will be mostly covered with H_2O_2 molecules. Only a small amount of toluene presents on the catalyst surface. Thus, the conversion of H_2O_2 to benzaldehyde is very low (approx. 12%). If the saturated concentration of benzaldehyde and/or the rate of dissolution can be increased, the conversion of H_2O_2 to benzaldehyde is expected to increase also. The experimental results using solutions contain 0.05 M of HNO_3, NH_4NO_3,

NH_4Cl, or NaCl confirm what is expected. In these solutions, the conversions of H_2O_2 to benzaldehyde increase 2-3 times higher than in deionized water.

From previous topic, the results exhibit that the adding some ions can improve the solubility of toluene in acidic/salt solutions. The amount of toluene is controlled by a tri-phases system. In addition, the character of the TS-1 catalyst surface is the hydrophobic. Therefore, the catalyst surface likes to absorb hydrophobic molecules (toluene) rather than the water molecules. If toluene abundantly dissolved in the aqueous phase, the dissolved toluene will cover most of the surface of TS-1 catalyst. This will decrease the reaction rate because for the reaction to occur, both reactants (toluene and hydrogen peroxide) must be equally absorbed on the catalyst surface to achieve the highest reaction rate.

This reaction phenomenon follows the mechanism of a Langmuir-Hinshelwood (LH) surface reaction. The mechanism of a Langmuir-Hinshelwood (LH) surface reaction is represented in Figure 4.9.

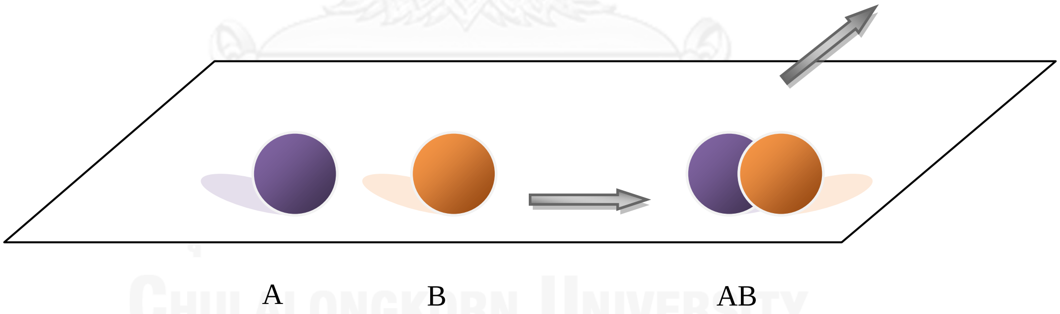


Figure 4.9 The mechanism of a Langmuir-Hinshelwood surface reaction. A and B reactants may stand for toluene and hydrogen peroxide. Moreover, AB product may stand for benzaldehyde.

For a reaction to occur, the both reactants are firstly absorbed on the Al-TS-1 surface. Then, they can meet together and combine on the catalyst surface. Then, the formed product will desorb from the catalyst surface. In an aqueous phase having no ion, the amount of toluene is very low on the catalyst surface due to its low solubility. Hence, if the solubility of toluene in an aqueous phase is increased by the presence of some ions, more amount of toluene can further dissolve into the acidic/salt solution and can improve the reaction rate. However, the concentration of toluene on the Al-TS-1 surface must be appropriately controlled to achieve the highest reaction rate. Due to the nature of the surface of catalyst which likes to absorb hydrophobic molecules more than the hydrogen peroxide molecules, if most of the catalyst surface is covered by toluene, the amount of hydrogen peroxide exists on the catalyst surface will become very low. This will lead to decreasing of the reaction rate. The equal mole ratio of toluene and H_2O_2 can produce the highest reaction rate from the theory.

Figure 4.8 shows that there is an optimal conversion point for HNO_3 solution. When HNO_3 concentration is increase from 0.05 M to 0.10 M, the conversion of H_2O_2 to benzaldehyde increases significantly. Further HNO_3 concentration increase to 0.15 M, however, leads to a negative result. The H_2O_2 conversion in 0.15 M HNO_3 solution is much lower than in 0.10 M and 0.05 M HNO_3 solutions though the saturated concentration of toluene in 0.15 M HNO_3 concentration is the highest. This phenomena follow the Langmuir-Hinshelwood model described above. Too excessive toluene in aqueous will inhibit the adsorption of H_2O_2 on the catalyst surface because the nature of the catalyst surface that prefers non-polar molecule to polar molecule. Hence, the conversion of H_2O_2 obviously decreases, using 0.15M HNO_3, when the amount of toluene dissolves excessively in aqueous phase.

To confirm that the observed decrease of H_2O_2 conversion when using 0.15 M HNO_3 solution is due to too high equilibrium concentration of toluene in the aqueous phase, not due to the effect of HNO_3, an additional experiment is carried out by decreasing the reaction temperature from 120°C to 100°C while maintain HNO_3 concentration at 0.15 M. The experimental result shows that H_2O_2 convert to product can be increased from 18.31% at reaction temperature 120°C to 38.88% when the reaction temperature is decreased to 100°C (see data in Table 4.2). The solubility of toluene in an aqueous phase at 100°C is lower than the solubility of toluene at 120°C, thus preventing the catalyst surface from being excessively covered by toluene molecule. Therefore, it confirms that too excessive toluene in aqueous is a problem according to the theory of Langmuir-Hinshelwood (LH) mechanism which leads to low conversion.

In case of NH_4NO_3 solution, increasing the concentration of NH_4NO_3 in the aqueous solution increases the saturated concentration of toluene in the aqueous solution. But the saturated concentration of toluene does not increase rapidly as in the case of HNO_3 solution. In this case the catalyst surface is not excessively covered with toluene molecules; therefore, no drop of H_2O_2 conversion is observed when the concentration of NH_4NO_3 is increased from 0.05 M to 0.15 M.

A different explanation is required for NH_4Cl and NaCl solutions. It should be noted here that the conversion of H_2O_2 to organic product depends on the initial concentration of toluene in the aqueous phase and the concentration of toluene during the progress of reaction. The concentration of toluene during the progress of reaction depends on (i) the consumption rate which depends on the reaction and (ii) the replacement rate which depends on the solubility rate. Increasing the concentration of NH_4Cl or NaCl only marginally increases the saturated concentration of toluene in the aqueous phase. The observed increase of the H_2O_2 conversion, therefore, can not be explained using only the higher saturated concentration of toluene in the aqueous phase. The factor plays a significant role in NH_4Cl and NaCl solutions is the increase in the solubility rate of toluene into the aqueous phase. Previous study [8] showed that the presence of NH_4Cl or NaCl slightly increases the saturated concentration of toluene, but significantly increases the solubility rate of toluene into the aqueous phase. The observed increase of H_2O_2 conversion is due to the ability of liquid toluene to rapidly replace the dissolved toluene consumed by the reaction.

4.3.2 Effect of reaction time

In practice, unreacted H_2O_2 is considered as an unrecoverable reactant. Total H_2O_2 consumption in the reaction, hence, will be an advantage. In our study, an attempt to increase the consumption of H_2O_2 has been made by expanding the reaction time from 2 hours to 4 hours. Three conditions from section 4.3.1 are selected in this study. Those conditions are

(i) 0.10 M HNO_3 120°C
(ii) 0.10 M NH_4NO_3 120°C and
(iii) 0.15 M HNO_3 100°C

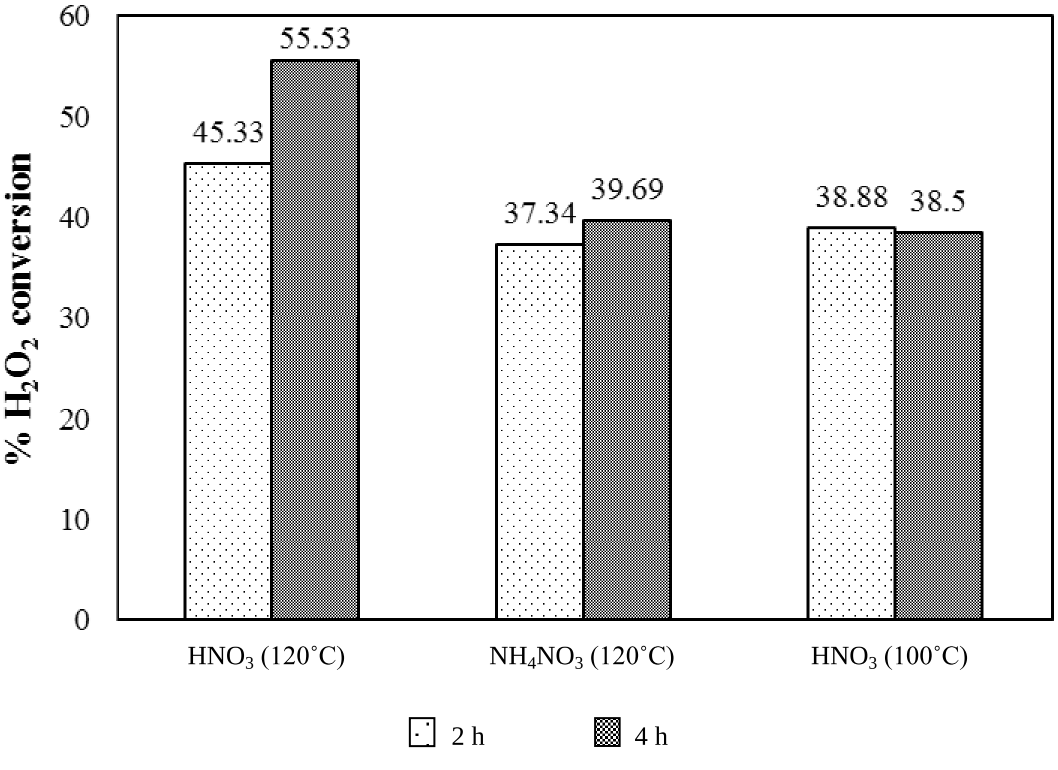


Figure 4.10 Percentage of H_2O_2 conversion in the 0.10M HNO_3 solution at 120°C, the 0.10M NH_4NO_3 solution at 120°C, and the 0.15M HNO_3 solution at 100°C for reaction time 2 hours and 4 hours.

The reason why these solutions are selected because the 0.10M HNO_3 solution at 120°C that is the highest conversion of H_2O_2. Moreover, the 0.10M NH_4NO_3 solution at 120°C and the 0.15M HNO_3 solution at 100°C are the largest H_2O_2 conversion next to the 0.10M HNO_3 solution at 120°C. The experimental results shown in Figure 4.10 reveal that expanding the reaction time from 2 hours to 4 hours does not largely increase the conversion of H_2O_2 as expected. H_2O_2 conversions increase for only 10% for condition (i), marginally increase for condition (ii), and about the same for condition (iii).

There are 2 hypotheses which can explain the above results. The first one is H_2O_2 also self decomposes co-currently with the oxidation reaction. Only a fraction of H_2O_2 can react with toluene while the rest decomposes to H_2O and O_2 molecule. The second one is benzaldehyde may further react with H_2O_2 to other organic products deposit on the catalyst surface which can not be extracted by ethanol.

To test the above hypotheses, an additional experiment is carried out using condition (i) but decreasing the mole ratio of H_2O_2 used from H_2O_2: toluene 1:1 to 0.5:1. In this latter case it is found that the conversion of H_2O_2 is 93.78%. It should be mentioned here that the higher H_2O_2 conversion observed in the latter case is due to the lower amount of H_2O_2 used (only half). Comparison the amount of H_2O_2 converted to benzaldehyde in both case (1:1 and 0.5:1) reveals that the amount of H_2O_2 converted to benzaldehyde is about the same. Therefore, the self-decomposition of H_2O_2 is not likely the reason that prevents the total consumption of H_2O_2.

To test the second hypothesis, the used catalyst sample is characterized by FT-IR to determine whether there are some organic compounds which can not be extracted by ethanol deposit on the catalyst surface. The FT-IR results show that the functional group of other organic product is not detected. Because of this, the catalyst is probably deactivated by another mechanism which should be determined in future work.

CHAPTER 5

CONCLUSIONS

The present work investigates effect of ion types and ion concentrations on the oxidation reaction of toluene to benzaldehyde over Al-TS-1 catalyst. The conclusions are presented in section 5.1.

5.1 Conclusions

1. The oxidation reaction between toluene and hydrogen peroxide in some acidic/salt solutions can produce bezaldehyde as the only major product.

2. Increasing ion concentrations can increase the solubility of toluene in an aqueous phase and the conversion of H_2O_2 which depend on the type of ions.

3. Amount of toluene dissolves excessively in aqueous phase leads to low H_2O_2 conversion.

4. The conversion of H_2O_2 does not depend on the increasing of reaction time.

5. Decreasing mole ratio of H_2O_2 per toluene 1:1 to 0.5:1 does not increase the amount of H_2O_2 converted to benzaldehyde.

5.2 Suggestion for future work.

The catalyst should be determined in future work in order to test the hypothesis that the catalyst is probably deactivated by another mechanism.

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APPENDIX

APPENDIX A
CALCULATION FOR CATALYST PREPARATION

The calculation in catalyst preparation is based on weight of sodium silicalite ($Na_2O{\cdot}SiO_2{\cdot}H_2O$) in B1 and B2 solutions in Table 3.2.

Molecular Weight of Si = 28.0855

Molecular Weight of SiO_2 = 60.0843

Weight percent of SiO_2 in sodium Silicate = 28.5

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

$$\text{Mole of Si is used} = \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W.of Si})}{(\text{M.W.of SiO}_2)} \times \frac{(1\,\text{mole})}{(\text{M.W.of Si})}$$

$$= 69 \times (28.5/100) \times (1/60.0843)$$

$$= 0.3273$$

For instance, Si/Ti atomic ratio of 50 is prepared by using $Ti[O(CH_2)_3CH_3]_4$ for titanium source.

Molecular weight of Ti = 47.88

Molecular weight of $Ti[O(CH_2)_3CH_3]_4$ = 340.36

Weight % purities of $Ti[O(CH_2)_3CH_3]_4$ = 97

Si/Ti atomic ratio = 50

Mole of $Ti[O(CH_2)_3CH_3]_4$ required = 0.3273/50

= 6.546×10^{-3} mole

The amount of $Ti[O(CH_2)_3CH_3]_4$ = $(6.546 \times 10^{-3}) \times (340.36) \times (100/97)$

= 2.2970 g

For example, Si/Al atomic ratio of 150 is prepared by using $Al(NO_3)_3{\cdot}9H_2O$ for cobalt source.

Molecular weight of Al = 26.98

Molecular weight of $Al(NO_3)_3 \cdot 9H_2O$ = 375.13

Si/Al atomic ratio = 150

Mole of $Al(NO_3)_3 \cdot 9H_2O$ required = 0.3273/150

= 2.18×10^{-3} mole

The amount of $Al(NO_3)_3 \cdot 9H_2O$ = $(2.18 \times 10^{-3}) \times (375.13)$

This is used in A1 and A2 solutions. = 0.82 g

APPENDIX B
CALIBRATION CURVES

This part shows the calibration curves in order to calculate the concentration of dissolve toluene in aqueous phase and benzaldehyde formed in the oxidation reaction between toluene and hydrogen peroxide.

The samples are analyzed by a gas chromatograph (Shimadzu GC8A) equipped with FID and a GP 10% SP-2100 packed column to determine the concentration of toluene and benzaldehyde of the oxidation reaction.

The concentration of toluene in y-axis and area reported by gas chromatograph in x-axis are presented in the curves. The calibration curve of toluene is illustrated in the Figure B1 and B2 respectively.

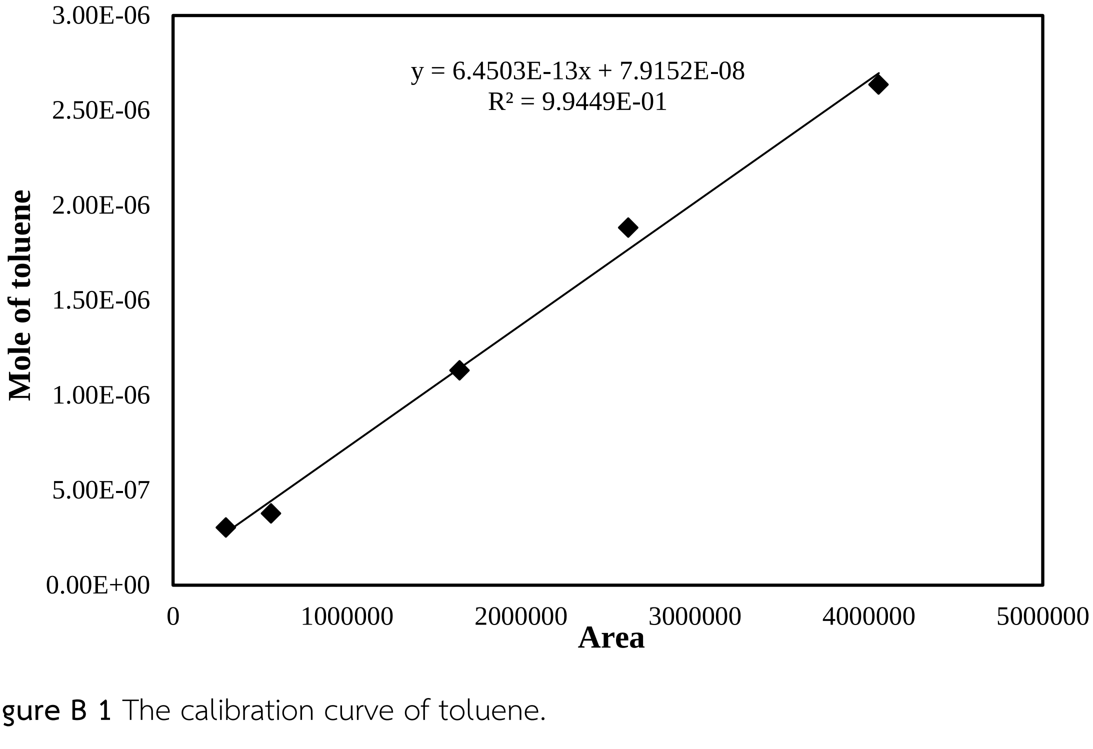

Figure B 1 The calibration curve of toluene.

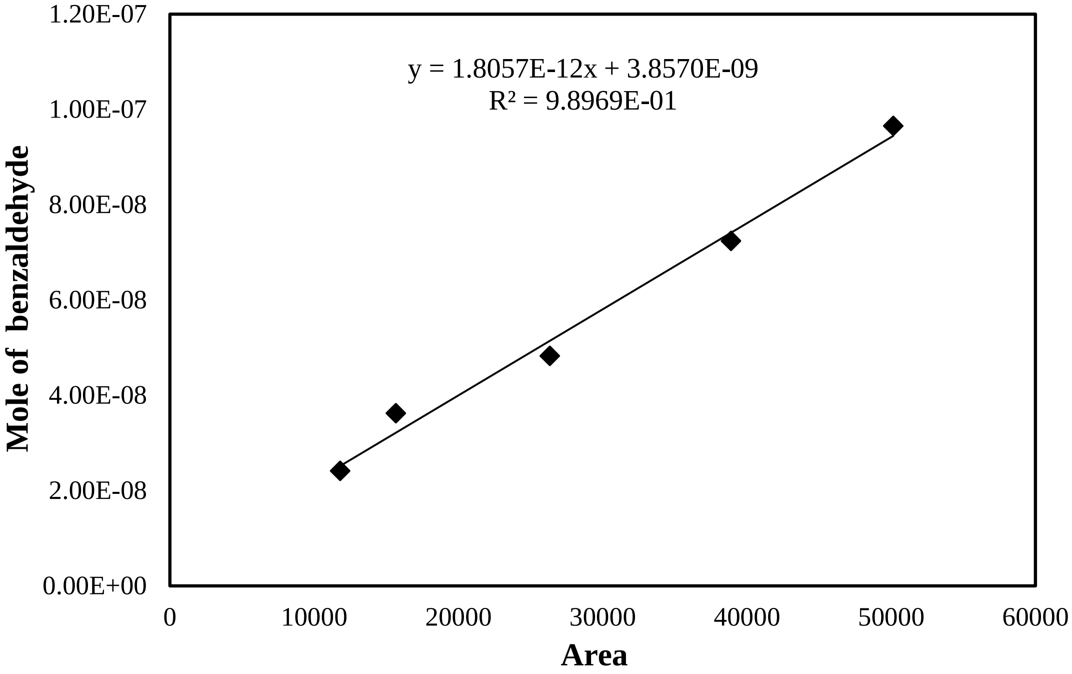

Figure B 2 The calibration curve of benzaldehyde.

APPENDIX C
CALCULATION OF CONVERSION

The overall mole of H_2O_2 can be calculated as follows:

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

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

In addition, the overall mole of benzaldehyde in the reaction can be calculated as follows:

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

Where;

N_i = the overall mole of product in the solution
i = benzaldehyde
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 μl)

Mole of benzaldehyde can be calculated from the calibration curves in Figure B2 reported previously in Appendix B as follows:

$$\text{Mole of benzaldehyde } (n_B) = [(1.8057\times10^{-14})\times Area]+(3.8570\times10^{-9}) \qquad \text{(C3)}$$

Total volume of solution in this system can be calculated as following:

Total volume of solution (V_{all}) = vol. of acidic/salt solution + vol. of toluene + vol. of H_2O_2 + vol. of water + vol. of ethanol

= 120 ml + 1.1 ml +1 ml + 1 ml + 80 ml

= 203.1 ml of solution

Therefore, the overall mole of product in the solution

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

APPENDIX D
DATA OF EXPERIMENTS

Table D 1 Data of toluene concentration in HNO_3 solution (as show in Figure 4.4).

Time(min)	Toluene concentration (mol/l)		
	0.05 M	**0.10 M**	**0.15 M**
3	0.0167	0.0275	0.0339
6	0.0172	0.0271	0.0349
9	0.0193	0.0274	0.0373
12	0.0193	0.0307	0.0384
15	0.0216	0.0325	0.0364
18	0.0210	0.0302	0.0379
21	0.0196	0.0304	0.0381
24	0.0215	0.0308	0.0398
27	0.0224	0.0319	0.0409
30	0.0210	0.0320	0.0397
33	0.0220	0.0335	0.0399
36	0.0196	0.0355	0.0433
39	0.0212	0.0354	0.0445
42	0.0184	0.0345	0.0410
45	0.0204	0.0351	0.0467
48	0.0218	0.0353	0.0427
51	0.0217	0.0339	0.0468
54	0.0224	0.0317	0.0420
57	0.0229	0.0356	0.0477
60	0.0209	0.0326	0.0455
63	0.0243	0.0347	0.0490
66	0.0207	0.0353	0.0392
71	0.0231	0.0351	0.0410
76	0.0215	0.0339	0.0421
81	0.0219	0.0357	0.0453
86	0.0210	0.0365	0.0390
91	0.0217	0.0375	0.0457
96	0.0232	0.0382	0.0446
106	0.0232	0.0362	0.0479
111	0.0208	0.0361	0.0425
131	0.0224	0.0354	0.0465
151	0.0242	0.0373	0.0433

Table D 2 Data of toluene concentration in NH_4NO_3 solution (as show in Figure 4.5).

Time(min)	Toluene concentration (mol/l)		
	0.05 M	**0.10 M**	**0.15 M**
3	0.0181	0.0232	0.0256
6	0.0218	0.0242	0.0258
9	0.0205	0.0228	0.0286
12	0.0195	0.0301	0.0307
15	0.0218	0.0266	0.0287
18	0.0219	0.0281	0.0330
21	0.0231	0.0254	0.0310
24	0.0216	0.0263	0.0309
27	0.0226	0.0282	0.0317
30	0.0240	0.0289	0.0267
33	0.0221	0.0251	0.0298
36	0.0232	0.0283	0.0305
39	0.0211	0.0256	0.0263
42	0.0223	0.0296	0.0291
45	0.0219	0.0314	0.0310
48	0.0234	0.0257	0.0345
51	0.0241	0.0272	0.0334
54	0.0207	0.0288	0.0324
57	0.0230	0.0279	0.0295
60	0.0217	0.0257	0.0327
63	0.0231	0.0247	0.0277
66	0.0244	0.0289	0.0306
71	0.0260	0.0285	0.0281
76	0.0256	0.0335	0.0283
81	0.0219	0.0295	0.0334
86	0.0244	0.0279	0.0315
91	0.0235	0.0295	0.0319
96	0.0223	0.0330	0.0322
106	0.0220	0.0287	0.0311
111	0.0231	0.0319	0.0326
131	0.0230	0.0294	0.0333
151	0.0233	0.0293	0.0344

Table D 3 Data of toluene concentration in NH_4Cl solution (as show in Figure 4.6).

Time(min)	Toluene concentration (mol/l)		
	0.05 M	**0.10 M**	**0.15 M**
3	0.0104	0.0138	0.174
6	0.0119	0.0122	0.0194
9	0.0140	0.0125	0.0178
12	0.0144	0.0132	0.0191
15	0.0118	0.0177	0.0175
18	0.0148	0.0158	0.0188
21	0.0129	0.0150	0.0196
24	0.0145	0.0180	0.0167
27	0.0197	0.0134	0.0195
30	0.0132	0.150	0.0209
33	0.0132	0.0165	0.0204
36	0.0120	0.0187	0.0222
39	0.0127	0.0140	0.0177
42	0.0129	0.0175	0.0197
45	0.0137	0.0135	0.0182
48	0.0146	0.0140	0.0228
51	0.0131	0.0186	0.0251
54	0.0195	0.0148	0.0248
57	0.0154	0.0161	0.0183
60	0.0149	0.0213	0.0167
63	0.0161	0.014	0.0224
66	0.0173	0.0134	0.0276
71	0.0143	0.0169	0.0275
76	0.0177	0.0215	0.0241
81	0.0186	0.0231	0.0220
86	0.0204	0.0169	0.0292
91	0.0241	0.0256	0.0298
96	0.0148	0.0199	0.0271
106	0.0183	0.0233	0.0255
111	0.0217	0.0184	0.0261
131	0.0200	0.0193	0.0250
151	0.0239	0.0210	0.0237

Table D 4 Data of toluene concentration in NaCl solution (as show in Figure 4.7).

Time(min)	Toluene concentration (mol/l)		
	0.05 M	**0.10 M**	**0.15 M**
3	0.0119	0.0172	0.0164
6	0.0144	0.0232	0.0169
9	0.0156	0.0204	0.0204
12	0.0143	0.0169	0.0184
15	0.0125	0.0234	0.0184
18	0.0108	0.0218	0.0193
21	0.0132	0.0181	0.0194
24	0.0148	0.0187	0.0223
27	0.0106	0.0210	0.0191
30	0.0189	0.0215	0.0151
33	0.0115	0.0264	0.0205
36	0.0156	0.0212	0.0163
39	0.0131	0.0198	0.0176
42	0.0191	0.0208	0.0249
45	0.0116	0.0223	0.0162
48	0.0156	0.0205	0.0255
51	0.0187	0.0229	0.0240
54	0.0209	0.0216	0.0170
57	0.0205	0.0202	0.0259
60	0.0205	0.0170	0.0222
63	0.0171	0.0207	0.0237
66	0.0201	0.0222	0.0237
71	0.0219	0.0230	0.0217
76	0.0165	0.0195	0.0207
81	0.0217	0.0263	0.0267
86	0.0247	0.0255	0.0299
91	0.0298	0.0223	0.0275
96	0.0263	0.0257	0.0263
106	0.0270	0.0271	0.0265
111	0.0281	0.0244	0.0264
131	0.0262	0.0250	0.0293
151	0.0267	0.0237	0.0252

APPENDIX E
MATERIAL SAFETY DATA SHEET

Material safety data sheet of chemical substance is shown in Appendix E. The chemical substance is used in the experiment such as toluene, hydrogen peroxide, nitric acid, ammonium chloride, ammonium nitrate, and sodium nitrate. The origin of the document: http://www.fishersci.com

I. Toluene

General

Synonyms : Methylbenzene; Toluol; Phenylmethane
Molecular formula : $C_6H_5CH_3$

Physical data

Physical State : Liquid
Appearance : Colorless
Odor : aromatic
Vapor Pressure : 29 mbar @ 20 ℃
Vapor Density : 3.1 (Air = 1.0)
Viscosity : 0.6 mPa.s @ 20 ℃
Boiling Point/Range : 111℃ / 231.8°F@ 760 mmHg
Melting Point/Range : -95℃ / -139°F
Flash Point : 4℃ / 39.2°F
Evaporation Rate : 2.4 (Butyl acetate = 1.0)
Specific Gravity : 0.866
Solubility : Insoluble in water
Molecular Weight : 92.14

Stability and reactivity

Stability : Stable under normal conditions.

Conditions to Avoid : Incompatible products. Excess heat. Keep away from open flames, hot surfaces and sources of ignition.

Incompatible Materials : Strong oxidizing agents, Strong acids

Hazardous Decomposition Products : Carbon monoxide (CO), Carbon dioxide (CO_2)

Hazards identification

Flammable liquid and vapor. Causes eye, skin, and respiratory tract irritation. Vapors may cause drowsiness and dizziness. Aspiration hazard if swallowed - can enter lungs and cause damage. Danger of serious damage to health by prolonged exposure. Possible risk of harm to the unborn child. May cause adverse kidney effects. May cause adverse liver effects.

First aid measures

Eye Contact : Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Immediate medical attention is required.

Skin Contact : Wash off immediately with plenty of water for at least 15 minutes. Immediate medical attention is required.

Inhalation : Move to fresh air. If breathing is difficult, give oxygen.
Do not use mouth-to-mouth resuscitation if victim ingested or inhaled the substance; induce artificial respiration with a respiratory medical device. Immediate medical attention is required. Aspiration into lungs can produce severe lung damage.

Ingestion :Clean mouth with water and drink afterwards plenty of water. Do not induce vomiting. Call a physician or Poison Control Center immediately. If vomiting occurs, lean victim forward to reduce the risk of aspiration.

II. Hydrogen Peroxide 30%

General

Synonyms : No information available.
Molecular formula : H_2O_2

Physical data

Physical State : Liquid
Appearance : Colorless
Odor : slight
pH : 3.3
Vapor Pressure : 23 mmHg @ 30°C
Vapor Density : 1.10
Boiling Point/Range : 108°C / 226.4°F@ 760 mmHg
Melting Point/Range : -33°C / -27.4°F
Decomposition temperature : > 125°C
Evaporation Rate : >1.0 (Butyl Acetate = 1.0)
Specific Gravity : 1.110
Solubility : Miscible with water

Stability and reactivity

Stability : Stable under normal conditions. Light sensitive.

Conditions to Avoid : Combustible material. Incompatible products. Excess heat. Exposure to light. Avoid shock and friction.

Incompatible Materials : Strong oxidizing agents, Metals, Reducing agents, Alcohols, Ammonia, copper, Copper alloys, lead oxides, Cyanides, Sulfides, lead, Acetone

Hazardous Decomposition Products : Hydrogen, oxygen

Hazards identification

Causes severe eye irritation and possible burns. Irritating to skin. Harmful if swallowed.

First aid measures

Eye Contact : Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Immediate medical attention is required.

Skin Contact : Wash off immediately with plenty of water for at least 15 minutes. Get medical attention immediately if symptoms occur.

Inhalation : Move to fresh air. If breathing is difficult, give oxygen. Get medical attention immediately if symptoms occur.

Ingestion : Do not induce vomiting. Call a physician or Poison Control Center immediately

III. Nitric acid

General

Synonyms : Azotic acid; Engraver's acid; Aqua fortis

Molecular formula : HNO_3

Physical data

Physical State : Liquid

Appearance : Clear Colorless, Light yellow

Odor : strong Acrid

pH : 1.0 (0.1M)

Vapor Pressure : 0.94 kPa (20°C)

Boiling Point/Range : 120.5°C / 248.9°F

Melting Point/Range : -41°C / -41.8°F

Specific Gravity : 1.40

Molecular Weight : 63.02

Stability and reactivity

Stability : Oxidizer; Contact with combustible/organic material may cause fire.

Conditions to Avoid : Incompatible products. Combustible material. Excess heat.

Incompatible Materials : Strong bases, Reducing agents, Organic materials, Aldehydes, Alcohols, Cyanides, Metals, Powdered metals, Ammonia

Hazardous Decomposition Products : Nitrogen oxides (NO_x) Toxicology

Hazards identification

Oxidizer: Contact with combustible/organic material may cause fire. Causes severe burns by all exposure routes. May cause pulmonary edema.

First aid measures

Eye Contact : Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Immediate medical attention is required.

Skin Contact : Wash off immediately with plenty of water for at least 15 minutes. Immediate medical attention is required.

Inhalation : Move to fresh air. If breathing is difficult, give oxygen. Do not use mouth-to-mouth resuscitation if victim ingested or inhaled the substance; induce artificial respiration with a respiratory medical device. Immediate medical attention is required.

Ingestion : Do not induce vomiting. Call a physician or Poison Control Center immediately.

IV. Ammonium nitrate

General

Synonyms : Nitric acid, ammonium salt; Norway saltpeter.
Molecular formula : NH_4NO_3

Physical data

Physical State : Solid
Appearance : White
Odor : odorless
pH : 4.5-6.0 5% aq.sol.
Boiling Point/Range : 210°C
Melting Point/Range : 169°C / 336.2°F
Specific Gravity : 1.720
Molecular Weight : 80.04

Stability and reactivity

Stability : Oxidizer; Contact with combustible/organic material may cause fire. Hygroscopic.

Conditions to Avoid : Incompatible products. Excess heat. Combustible material. Avoid dust formation. Exposure to moist air or water.

Incompatible Materials : Strong oxidizing agents, Strong reducing agents, Strong acids, Powdered metals.

Hazardous Decomposition Products : Carbon monoxide (CO), Carbon dioxide (CO_2), Nitrogen oxides (NO_x), Ammonia.

Hazards identification

Oxidizer: Contact with combustible/organic material may cause fire. Explosive when mixed with combustible material. Irritating to eyes, respiratory system and skin. Hygroscopic.

First aid measures

Eye Contact : Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Obtain medical attention.

Skin Contact : Wash off immediately with plenty of water for at least 15 minutes. Obtain medical attention.

Inhalation : Move to fresh air. If breathing is difficult, give oxygen. Obtain medical attention.

Ingestion : Do not induce vomiting. Obtain medical attention.

V. Ammonium chloride

General

Synonyms : Ammonium Chloratum; Ammonium Chloridum; Ammonium Muriate

Molecular formula : NH_4Cl

Physical data

Physical State : Solid

Appearance : White

Odor : Odorless

pH : 5.0 (@ 25) 10% aq.sol.(25°C)

Vapor Pressure : 1.3 mbar @ 160 °C

Melting Point/Range : 340°C / 644°F

Decomposition temperature : 350 °C

Solubility : Partly soluble in water

Molecular Weight : 53.49

Stability and reactivity

Stability : Hygroscopic.

Conditions to Avoid : Incompatible products. Excess heat. Avoid dust formation. Exposure to moist air or water.

Incompatible Materials : Strong oxidizing agents

Hazardous Decomposition Products : Carbon monoxide (CO), Carbon dioxide (CO_2)

Hazards identification

Harmful if swallowed. Irritating to eyes. May cause skin and respiratory tract irritation. Hygroscopic.

First aid measures

Eye Contact : Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Obtain medical attention.

Skin Contact : Wash off immediately with plenty of water for at least 15 minutes. Get medical attention immediately if symptoms occur.

Inhalation : Move to fresh air. If breathing is difficult, give oxygen. Do not use mouth-to-mouth resuscitation if victim ingested or inhaled the substance; induce artificial respiration with a respiratory medical device. Get medical attention immediately if symptoms occur.

Ingestion **:** Do not induce vomiting. Call a physician or Poison Control Center immediately.

VI. Sodium chloride

General

Synonyms : Salt

Molecular formula : $NaCl$

Physical data

Physical State : Solid

Appearance : White

Odor : odorless

ph : 5.0-8.0@ 20°C ; 5% aq.sol.

Vapor Pressure : 1 mmHg @ 865 °C

Boiling Point/Range : 1461°C / 2661.8°F@ 760 mmHg

Melting Point/Range : 801°C / 1473.8°F

Specific Gravity : 2.165

Solubility : Partly soluble in water

Molecular Weight : 58.44

Stability and reactivity

Stability : Hygroscopic.

Conditions to Avoid : Incompatible products. Excess heat. Avoid dust formation. Exposure to moist air or water

Incompatible Materials : Strong oxidizing agents, Metals, Strong acids

Hazardous Decomposition Products : Hydrogen chloride gas, Sodium oxides.

Hazards identification

Irritating to eyes. The toxicological properties have not been fully investigated. Hygroscopic.

First aid measures

Eye Contact : Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Obtain medical attention.

Skin Contact : Wash off immediately with plenty of water for at least 15 minutes. Get medical attention immediately if symptoms occur.

Inhalation : Move to fresh air. If breathing is difficult, give oxygen. Get medical attention immediately if symptoms occur.

Ingestion : Do not induce vomiting. Obtain medical attention

VITA

Miss Parichat Pongjira was born on November 7th, 1989 in Suphanburi, Thailand. She finished high school from Satriwatrakhang School in 2007, and received the bachelor’s degree of Chemical Technology from Chulalongkorn University in 2012. She continued her master’s study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University on June, 2014. She participated in the 23th Thailand Chemical Engineering and Applied Chemistry Conference (TIChE) in the topic “Effects of HCl and HNO3 on the oxidation reaction of toluene to benzaldehyde by H2O2 over TS-1 modified with Al in aqueous phase” on October, 17-18, 2013 at Khan Kaen, Thailand.